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was born in Držkov 1938 and obtained an education in ceramics (1962) and solid-state physics (1968) together with a worldwide experience in Sweden (1969) and USA (1970). He devoted his scientific proficiency to experimental and theoretical studies related to the thermodynamics of materials, particularly to non-equilibrated systems such as glasses. He authored and edited 12 books and monographs (such as „Kinetic Phase Diagrams“ 1991 or „Special Technologies and Advanced Materials“ 1993) and published almost 300 scientific papers that have received over 2000 citations. He is member of various editorial (J. Thermal Analysis, Thermochim. Acta or J. Mining and Metallurgy) and scientific boards. He gave over 150 invited and plenary lectures. He was presented with various scientific awards and medals such as NATAS, USA 1974; Kurnakov, USSR 1985; Bodenheimer, Izrael 1988; ICTAC, England 1992; Hanuš (Czech Chem. Soc.) and Heyrovský (Czech Acad. Sci.) both in Prague 1998 and 2000. He is a renowned teacher and mentor who have tried to introduce many new methods of interdisciplinary learning (Charles University and Institute of Chemical Technology in Prague, Czech Regional Universities of Pardubice, Liberec and Pilzen, University of New York in Prague and Kyoto University in Japan). He is also a recognized photographer (more than 20 photoexhibitions home and abroad); some of his art photos are presented in the book as the chapter's frontispieces.

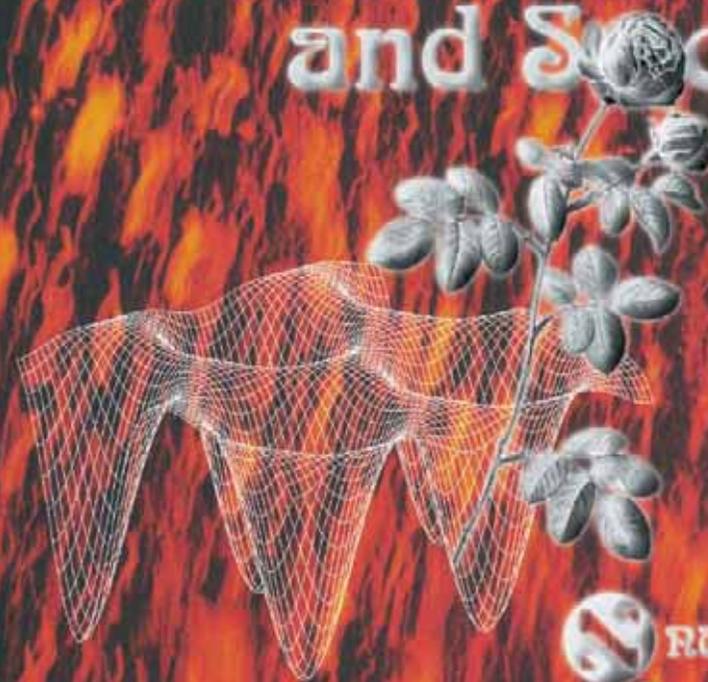
The size of this book is A4 (210 x 297mm); it comprises 400 pages with 169 illustrations, 23 tables and includes about 1000 bibliographical references, index data and 360 short characteristics of some great scientists as well as 56 photos. The text endeavors to elucidate wide spectrum of scientific and philosophical problems from classical to quantum thermodynamics, from energy science to informatics or from Euclidian to fractal geometry including the general impact of power laws. The book emphasizes the study of properties of various interfaces not only in physics but also in learning and cultural frontiers. Text requires minimum effort on reader's mathematics and is thus recommendable to students and interested public readers as well as to the advanced scientific community. The book has already received very positive review responses from both the humanistic and scientific sources appreciating its innovative, cross-disciplinary and wide-ranging approach, which is presented in an instructive and nontraditional manner worth reading. The book is printed black on the coated (scratchboard) paper and is hardbound.

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Jaroslav Šesták

Heat, Thermal Analysis and Society



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CONTENTS

Volume one

Aspects of history and links to modern science – development of understanding

1) What makes thermal science beneficial?

- a) Searching nature and the scale dimensions
- b) Thermal feeling (fuzzy versus deliberated)
- c) Databases in thermal material sciences
- d) Horizons of knowledge
- e) Appraisal of the Internet

2) Roots of Western civilization

- a) Heat as a manufacturing tool
- b) Mechanical motion and heat transfer
- c) Ways to better understanding of our universe
- d) Miracle of commencement – rising new ideas
- e) Growth of modern theories and hypothesis

3) Fire as a philosophical archetype

- a) Sources and effects of fire
- b) Early Greek philosophical views
- c) Concept of four elements (fire, air, water, earth)
- d) Impact of alchemy (Hermetic philosophy)

4) Renaissance and the New Age

- a) Emerging new ideas (alchemy versus chemistry)
- b) Phlogiston and caloric (dilatation explained)
- c) Heat and energy (latent heat and temperature)
- d) Atomists and matter (periodicity)
- e) Underpinning of thermodynamics

Volume two

Appreciation of heat and thermal physics

5) Heat, temperature and gradients

- a) Development of the concept of temperature
- b) Heat transfer – analogy of Fick and Ohm Laws
- c) Non-stationary heat diffusion and the Schrödinger equation – common characteristics of transfer
- d) Practical aspects of heat flow – contact resistance and periodical outcome (thermal noise)
- e) Warm-cool feeling (such as the touch of clothes)
- f) Turbulent boundary layers
- g) Special aspects of non-equilibrium heat transfer

6) Thermodynamic principles

- a) Aspects of chemical thermodynamics
- b) Effect of the rate of heating
- c) Thermal properties and measurable quantities
- d) Chemical reactions (affinity, activity, enthalpy)
- e) Estimation and simulation of thermodynamic data for some inorganic compounds (data tabulation)
- f) Heterogeneous systems and the effect of surface energy (formation of a critical radius)
- g) Effect of perturbations and features of a rational approach (nonequilibrium state, entropy query)

7) Equilibrium and kinetic phase diagrams, nucleation and growth, glasses

- a) Equilibria and generalized Clapeyron equations
- b) Ideal and real solid solutions, phase diagrams
- c) Nucleation phenomena and phase transitions
- d) Kinetic phase diagrams (extent of metastability)
- e) Aspects of invariant and variant processes
- f) Thermodynamics of non-equilibrium glass transition (vitrification, relaxation, fictitiousity)
- g) Use of temperature diagrams for a better understanding of transition processes in glasses

8) Thermal physics of processes dynamics

- a) Phase transitions and their order
- b) Broadened phase transformations
- c) Equilibrium background and kinetic degree of a phase transition (isothermal and nonisothermal)
- d) Constitutive equations applied in chemical kinetics (concentration - interface geometry)
- e) Modeling used in the description of reaction mechanism (spherical models, activation energy)
- f) T-T and C-T phase diagrams

Volume three

Thermal treatment and the methods of thermal analysis

9) Thermophysical examinations and temperature control

- a) Measurements and modes of assessment
- b) Treatment of the output signal
- c) Characterization of experimental curves
- d) Purpose of the measurement – exemplifying thermogravimetry and its practical execution
- e) Origins of modern thermal analysis

10) Thermal study of materials and substances

- a) Temperature control
- b) Temperature detection
- c) Extreme temperature changes and the sample preparation methods – principles of quenching
- d) Surface treatment by lasers
- e) Controversial character of bulk and spot observations (DTA/DSC versus SEM)
- f) Particularity of temperature modulation

11) Thermal analysis and calorimetry

- a) Systematic of calorimetry
- b) Classification of thermoanalytical methods – heat balance and their analytical description
- c) DTA and DSC as quantitative instruments
- d) DTA calibration and the use of defined electrical pulses (what parts compose a DTA peak)
- f) Practical cases of applications – Cp data
- g) Temperature modulated modes

CONTENTS

12) Non-isothermal kinetics by thermal analysis

- a) Fundamental aspects of kinetic data evaluation
- b) Formal kinetic models and the role of an accommodation function (activation energy)
- c) Peculiarities of non-isothermal models
- d) Optimal evaluation procedures
- e) Oscillation-controlled-rate modes of thermal analysis (CRTA methods)
- f) Kinetic compensation effect

Volume four

Thermal dynamics and non-equilibrium phenomena – state progression

13) Power laws, fractals, chaos and information; or how nature is smart

- a) Stimulation responses, power and logarithmic dependencies – sensation and perception
- b) Significance of limits and self-similarity
- c) Sierpinski gaskets and fractal dimensions
- d) Deterministic chaos, periodic points and logistic functions – Faigenbaum universality constant
- e) Order, entropy and information (joule versus bit)
- f) Information and organization

14) Oscillation modes and modern theories of state

- a) Pendulum and related theory of ordered and chaotic motions
- b) Particles and their energies
- c) Vibration structures in condensed state and the description of vacancies creation
- d) Mathematical treatment of strong non-linearity above T_g transition
- e) Micro-model of solid-liquid transition: two types of vibration units
- f) Source of diffusion movements: nondeterministic elements

15) Advanced evaluation of processes – disequilibria and dendritic growth

- a) Classical kinetics and non-equilibrium thermodynamics – how to make evaluation
- b) Accounting on multiple fluxes
- c) Stereology aspects – sectioning by random probe
- d) Dissipative structures (bifurcations)
- e) Interface stability, perturbation and oscillatory modes – growth of perturbed grains
- f) Chaotic-like case of dendritic growth

16) The principle of least action and selforganization of chemical reactions

- a) How to evaluate unusual experiments
- b) Regular patterns provided by living organisms
- c) Repetitious order in some inorganic reactions
- d) Bénard convective rolls (instabilities)

- e) Principle of least action – Liesegang rings
- f) Diffusion action of Brownian particles
- g) Oscillatory regime of the Belousov-Zhabotinsky reactions – diffusivity, impact of Planck constant
- h) Quantum criterion and speed of diffusion

Volume five

Society, science and ecology – progress against survival

17) Energy science and society – environmental dilemma, its present state and future potentials

- a) Heat as a motive power – Otto and Diesel engines
- b) Alternative energy sources perspective to replace intermediary heat production, wind and fuel cells
- c) Resources of energy – how long they would last
- d) Heat production as a source of unwanted emission – problem of ‘clean energy’
- e) Non-equilibrium thermodynamics of fluid systems and our ‘cosmological engine’

18) Thermodynamics and civilization – laws versus feelings – phase diagrams applied to society

- a) Application of thermodynamic laws to society behavior – functions versus dispositions
- b) Some extended thermodynamic thoughts in economics – Carnot customized cycle
- c) Rules of behavior: strategy for survival and evolution – theory of games

19) Modern materials and society

- a) Intelligent processing and manufacturing of advanced materials – foreseeing the future
- b) Metallic glasses
- c) Ceramic high-temperature superconductors
- d) Bio-compatible glass-ceramics as mimetic materials for the bone tissue implantations

20) Advanced trends in understanding our Universe – mesoscopic thermodynamics

- a) Bartoli’s thermal engine and the zero-point radiation (spectral distribution)
- b) Energy in vacuum and Casimir forces
- c) Hypothetical Bartoli’s engine working with zeropoint electromagnetic radiation (quantum face of the second law applicability)
- d) Quantum impact on the study of low dimensional systems (quantum-wire patchcord)
- e) Quantum information processing (bit versus qubit, teleportation)
- f) Solar microwave background radiation

Heat, Thermal Analysis and Society

by

Jaroslav Šesták



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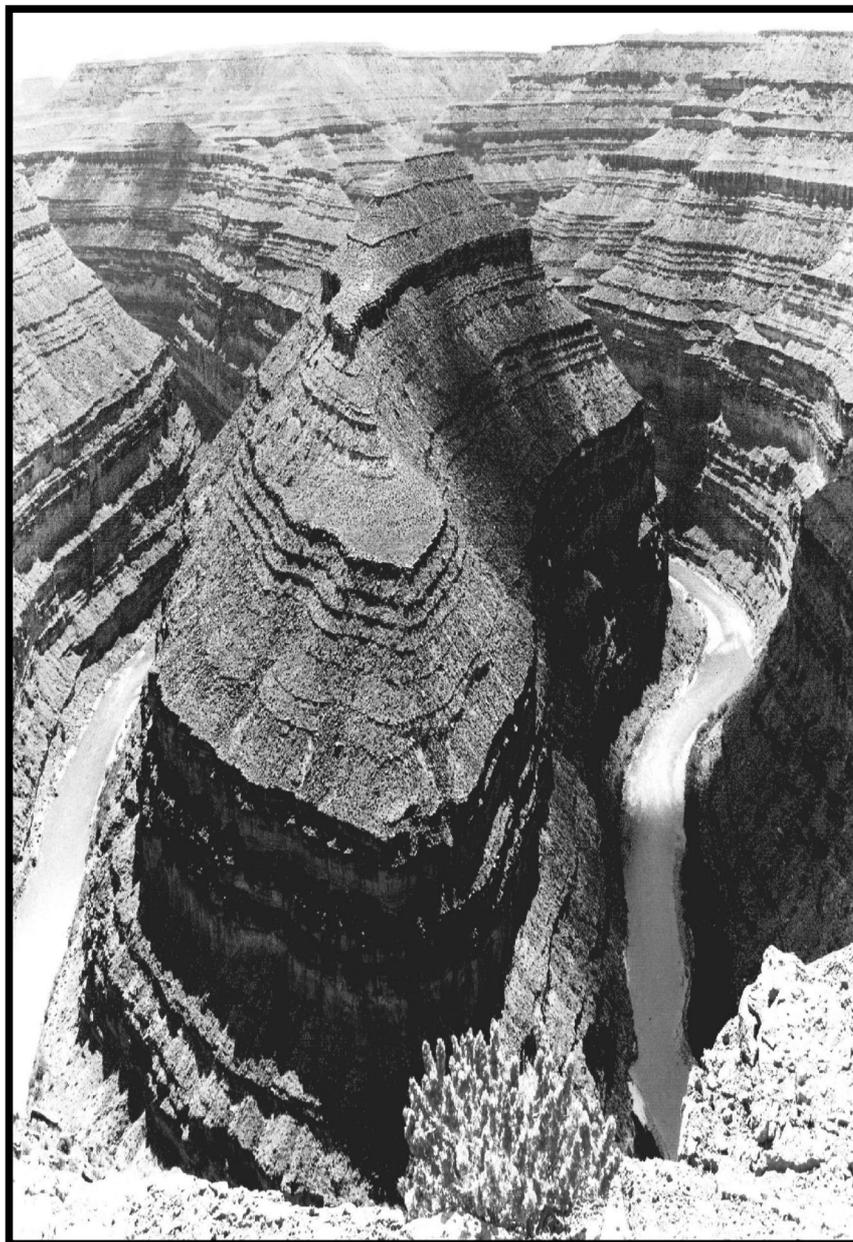
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MOTTO "The hills melted like wax at the presence of the Lord"
[PSALM 97:5]



The miraculous spectacles of natural formations
(Goose Neck National Monument, Utah 1994)



Dedicated to my family



Věra

Alžběta

Pavel

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of the 50th anniversary
of the Institute of Physics
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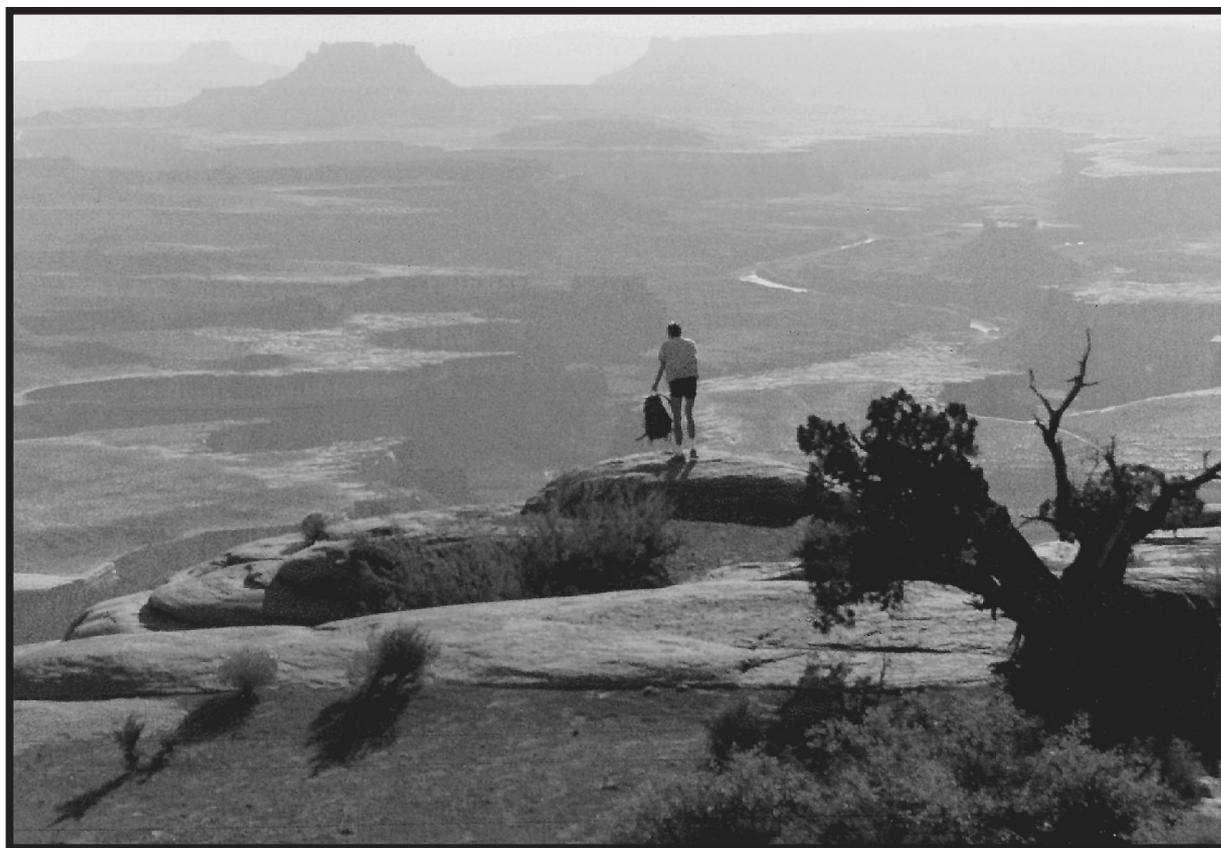
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CONTENTS



Preface	12
Introduction to thermal science	20
<i>Volume one</i>	
Aspects of history and links to modern science	29
1) What makes thermal science beneficial?	32
a) Searching nature and the scale dimensions	32
b) Thermal feeling	34
c) Databases in thermal material sciences	35
d) Horizons of knowledge	38
e) Appraisal of the Internet	41
2) Roots of Western civilization	46
a) Heat as a manufacturing tool	46
b) Mechanical motion and heat transfer	48

CONTENTS

c) Understanding our universe	52
d) Miracle of commencement.....	56
e) Growth of modern theories	58
3) Fire as a philosophical archetype.....	66
a) Sources and effects of fire,.....	66
b) Early Greek philosophical views	68
c) Concept of four elements	70
d) Impact of alchemy.....	72
4) Renaissance and the New Age.....	80
a) Emerging new ideas	80
b) Phlogiston and caloric.....	82
c) Heat and energy	83
d) Atomists and matter	86
e) Underpinning of thermodynamics	89
Literature.....	93
<i>Volume two</i>	
Appreciation of heat and thermal physics.....	97
5) Heat, temperature and gradients.....	100
a) Development of the concept of temperature.....	100
b) Heat transfer.....	102
c) Non-stationary heat diffusion and the Schrödinger equation	105
d) Practical aspects of heat flow – contact resistance and periodical outcome	105
e) Warm-cool feeling.....	107
f) Turbulent boundary layers	108
g) Special aspects of non-equilibrium heat transfer.....	108
6) Thermodynamic principles.....	112
a) Aspects of chemical thermodynamics.....	112
b) Effect of the rate of heating	114
c) Thermal properties and measurable quantities.....	114
d) Chemical reactions	115
e) Estimation and simulation of thermodynamic data for some inorganic compounds	116
f) Heterogeneous systems and the effect of surface energy	119
g) Effect of perturbations and features of a rational approach	122
7) Equilibrium and kinetic phase diagrams, nucleation and growth, glasses.....	126
a) Equilibria and generalized Clapeyron equations	126
b) Ideal and real solid solutions, phase diagrams	127
c) Nucleation phenomena and phase transitions	129
d) Kinetic phase diagrams	132
e) Aspects of invariant and variant processes	135
f) Thermodynamics of non-equilibrium glass transition	135
g) Use of temperature diagrams for a better understanding of transition processes in glasses.....	138
8) Thermal physics of processes dynamics.....	142
a) Phase transitions and their order.....	142
b) Broadened phase transformations	143

CONTENTS

c) Equilibrium background and kinetic degree of a phase transition	144
d) Constitutive equations applied in chemical kinetics.....	144
e) Modeling used in the description of reaction mechanism.....	147
f) T-T-T and C-T phase diagrams	149

Literature	151
-------------------------	-----

Volume three

Thermal treatment and the methods of thermal analysis	155
--	-----

9) Thermophysical examinations and temperature control	158
a) Measurements and modes of assessment.....	158
b) Treatment of the output signal	161
c) Characterization of experimental curves	164
d) Purpose of the measurement – exemplifying thermogravimetry.....	166
e) Origins of modern thermal analysis.....	169

10) Thermal study of materials and substances	174
a) Temperature control	174
b) Temperature detection	177
c) Extreme temperature changes and the sample preparation methods.....	178
d) Surface treatment by lasers	182
e) Controversial character of bulk and spot observations.....	185
f) Particularity of temperature modulation	187

11) Thermal analysis and calorimetry	190
a) Systematic of calorimetry	190
b) Classification of thermoanalytical methods – heat balance.....	191
c) DTA and DSC as quantitative instruments	192
e) DTA calibration and the use of defined electrical pulses	194
f) Practical cases of applications	196
g) Temperature modulated modes	198

12) Non-isothermal kinetics by thermal analysis	204
a) Fundamental aspects of kinetic data evaluation	204
b) Formal kinetic models and the role of an accommodation function.....	206
c) Peculiarities of non-isothermal models.....	208
d) Optimal evaluation procedures	211
e) Oscillation-controlled-rate modes of thermal analysis,	212
f) Kinetic compensation effect.....	213

Literature	215
-------------------------	-----

Volume four

Thermal dynamics and non-equilibrium phenomena	219
---	-----

13) Power laws, fractals, chaos and information; or how nature is smart	222
a) Stimulation responses and logarithmic dependences.....	222
b) Significance of limits and self-similarity.....	224
c) Sierpinski gaskets and fractal dimensions	227
d) Deterministic chaos, periodic points and logistic functions	230

CONTENTS

e) Order, entropy and information	232
f) Information and organization	235
14) Oscillation modes and modern theories of state	242
a) Pendulum and related theory of ordered and chaotic motions	242
b) Particles and their energies	243
c) Vibration structures in condensed state and the description of vacancies creation	245
d) Mathematical treatment of strong non-linearity above T_g transition	245
e) Micro-model of solid-liquid transition: two types of vibration units	246
f) Source of diffusion movements: non-deterministic elements	247
15) Advanced evaluation of processes – disequilibria and dendritic growth	250
a) Classical kinetics and non-equilibrium thermodynamics	250
b) Accounting on multiple fluxes	252
c) Stereology aspects	253
d) Dissipative structures	254
e) Interface stability, perturbation and oscillatory modes	255
f) Chaotic-like case of dendritic growth	257
16) The principle of least action and self-organization of chemical reactions	260
a) How to evaluate unusual experiments	260
b) Regular patterns provided by living organisms	261
c) Repetitious order in some inorganic reactions	262
d) Bénard convective rolls	264
e) Principle of least action	266
f) Diffusion action of Brownian particles	267
g) Oscillatory regime of the Belousov- Zhabotinsky reactions	268
h) Quantum criterion and speed of diffusion	270
Literature	273
<i>Volume five</i>	
Society, science and ecology – progress against survival	277
17) Energy science and society – environmental dilemma	280
a) Heat as a motive power – engines	280
b) Alternative energy sources perspective to replace intermediary heat production	282
c) Resources of energy – how long they would last	285
d) Heat production as a source of unwanted emission – problem of ‘clean energy’	288
e) Non-equilibrium thermodynamics of fluid systems and our ‘cosmological engine’	291
18) Thermodynamics and society – laws versus feelings	298
a) Application of thermodynamic laws to society behavior	298
b) Some extended thermodynamic thoughts in economics	300
c) Rules of behavior: strategy for survival and evolution	302
19) Modern materials and society	306
a) Intelligent processing and manufacturing of advanced materials	306
b) Metallic glasses	308
c) Ceramic high-temperature superconductors	311
d) Bio-compatible glass-ceramics as mimetic materials for the bone tissue implantations	318

CONTENTS

20) Advanced trends in understanding our Universe	326
a) Bartoli's thermal engine and the zero-point radiation	326
b) Energy in vacuum and Casimir forces	327
c) Hypothetical Bartoli's engine working with zero-point electromagnetic radiation	328
d) Quantum impact on the study of low dimensional systems	331
e) Quantum information processing.....	332
f) Solar microwave background radiation	333
Literature	339
Conclusions	344
Acknowledgement	349
Personalities	352
Index	361
Layout of the art photos	371
Informercial	373

Motto "Ordered by number and by weight of every one"

[EZRA. 8:38]



Telling a tale to teach a moral
(village Manang 3600 m, Annapurna region of Himalaya, 1982)

PREFACE

Preface

Gradually by the turn of the 80th, I accomplished my long-lasting target to publish an extended treatise [1] dealing with the theoretical aspects of thermal analysis in relation to the general subject of thermophysical properties of solids. Somewhat unnecessarily it was crowded by detailed mathematical derivations and formulae, which made the text demanding to read. The pioneering Czech version appeared first in 1982, successively followed by the English (1984) and Russian (1988) translations. I am fulfilled to remark that the Russian version became a bestseller on the 1988 USSR market and 2000 books were sold out within one week (see Fig. 1). The other versions also disappeared from the bookshops in few years leaving behind a rather pleasing index of abundant citation responses (350 out of my total record of

associated thermal treatment to the better understanding of the science of *heat* or, if you like, *thermal physics*. It can be seen to consist of the two main areas of generalized interest: the *force fields* (that is, particularly, the *temperature* expressing the motional state of consisting particles) and the *arrangement deformations* (that is *entropy*, which is specific for ordering the constituent particles and the associated ‘information’ worth). This lead me to see supplementary links to neighboring subjects that are, so far, not common in the yet specialized books dealing with the classically understood field of thermal analysis.

It, certainly, needed a gradual development. In 1991, I co-edited another theoretical book [3] attentive to inquisitive problems of non-equilibrium phase transitions dealing with the non-stationary processes of nucleation and crystal growth and their impact on modern technologies [4], later applied to glasses [5]. Consequently I also became involved in some related areas of humanities and their oversight of the civilization progress, which was heavily influenced under the wide-spreading use of new man-made materials manufactured by the controlled impact of irreplaceable fire. I have become occupied in an extensive lecturing, beside the short courses mostly read on thermodynamics and thermal analysis (among others, in Italy, USA, Norway, India, Germany, Argentina, Chili or Taiwan), I enjoyed complete full-term courses given at the Czech University of Pardubice (1988–1999, Modern materials), University of Kyoto (1996, Energy science), Charles University in Prague (1997–2001, Thermodynamics and society as well On the borderland of science and philosophy of nature), and University of New York in Prague (1999–, Scientific world). I was also proud to be given the challenge of supervising the constitution of a novel, Czech educational domain on interdisciplinary studies (West Bohemian University in Pilsen) and an associated cooperation project with the University of Kyoto (Japan). It gave me space to be in contact with enquiring students and made it easier for me to think about thermal science within a wider contest of history, philosophy, ecology, sociology, environmental anthropology, informatics and energetics. It helped me to included the completely new allocations to this new addition, e.g., the influence of the Greek philosophical views, understanding heat as a manufacturing tool and the early development of concepts of heat and temperature, extension of non-equilibrium thermodynamic chart, natural impact of logarithmic scale, genera-

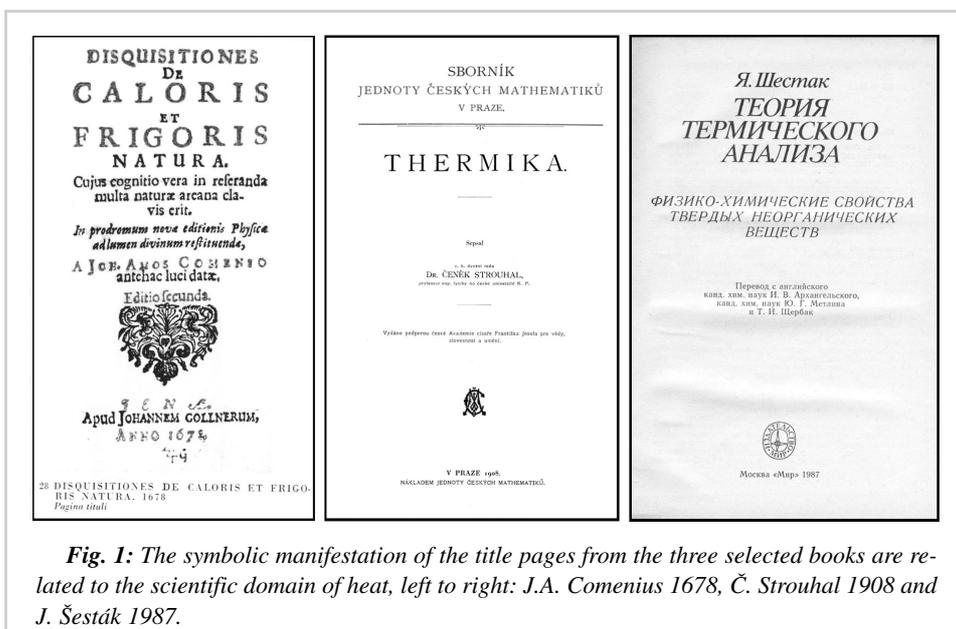


Fig. 1: The symbolic manifestation of the title pages from the three selected books are related to the scientific domain of heat, left to right: J.A. Comenius 1678, Č. Strouhal 1908 and J. Šesták 1987.

2000). Compilation and writing the manuscript requested my effort lasting almost five years, and its completion required hard work, although, I had certain experience resulting from the similarly aimed compendium, which was completed as early as in 1973 [2].

Recently I was asked to think over the preparation of an English re-addition of my book. With a twenty years delay I, therefore, carefully read the book again and I was satisfied to realize that the text could be more and less repeated identically as before with the need for only a few corrections and some updating. The content did not lose its contemporary value, innovative approach, mathematical impact and can still be considered as being in contest with the similarly aimed books published even much later on. I am happy to allow myself to boast about my initial achievement in such an early-day presentation of theoretical basis based on thermodynamics in its creative way adequate to the true thermal-dynamics exploited in thermal analysis.

In the mean time, however, I have devoted myself to a more general comprehension of *thermal analysis* and

PREFACE

lized authority of power laws, overview of fractal geometry and, last but not least, the importance of energy science and its influence to societal life.

Accordingly, the most important area of interest became the study of properties of various *interfaces*, which are understood as a continuity defect or disorder emergence created at the boundary between two entities regardless if it is physics (body surface, phase interfaces), fields of learning (thoughts, science and humanities) or people behavior (minds, physical and cultural frontier). It entirely affects the extent of our awareness beyond which starts our confusion or misapprehension, or for the want of a better word, *chaos*. It brings in play another correlation that is the interface between the traditional language of visible forms of the familiar Euclidean geometry and the new language used to describe complex forms often met in nature and called *fractals*. The allied and most general model functions is the *power law* (leading to the limiting logarithmic function), which provides not only a spontaneous linkage between the mathematics of fractal geometry of nature and that of human's inherent sensation of external stimuli, but also penetrates almost all correlations (information dimension, fractal dimension). The key for this attitude is the recognition that many random structures obey a self-affinity symmetry, which is as striking as that obeyed by regularly symmetrical patterns taught in the classical Euclidean pedagogy.

However, it requested the text be written not in the usual sense of a conservative thermoanalytical textbook but under a more popular scientific style with the surcharge of atypical chapters (see, e.g., the Volumes 4 and 5), where I tried to elaborate some novel, yet unfamiliar ideas (developed in cooperation with my colleagues) such as a more general impact of the *Planck* constant in self-organization of some macroscopic events (Chapter 16) or indicating not yet familiar zero-point energy fluctuation as the ground and resource state of vacuum (Chapter 20). I also endeavored to give basic ideas about the mathematical rules self-installed by nature (Chapter 13). Similarly in the last Volume 5 (progress in society, science and ecology) I have attempted to bring some unusual eyesight to energy science and civilization, applicability of thermodynamic laws to society behavior or even the futuristic perception about the relevance of the second law of thermodynamics in quantum systems.

The interface turned also out as a focal point of modern material science assuming the two traditional limiting cases of crystalline order (long-range arrangement) and disorder (short-range arrangement), which has recently been added by the intermediate state of middle arrangement (mesoscopic nano-crystallites). It became important for many tailored materials such as fine-metals (subcritical magnetic domains), modulated structures (quasicrystals in metallic glasses or even in liquid water), low-dimension (quantum dots and wells) and many others spheres (cryopreservation, biological pathways, therapeutic dietary supply, etc.). Further it involves the interface creation often connected with the process of new phase formation, i.e., *nucleation* affecting rather divergent fields, besides

traditional advanced materials (examples, see Chapter 19), it is ecology (formation of smog, rain), biology (critical size of viruses), medicine (growth of critical embryos such as cancer), pharmacology, nuclear energy (wall cracks formation due to the irradiation), and even touches some aspects of cosmology.

I also tried to highlight the flux approach (Chapter 15) where I benefited from my early attempts to make a rational thermodynamic approach for studying processes by thermal analysis published as early as in the beginning of seventies [6], which latter stretched out to our volume treaties [3,7] and resulted in the introduction of a new discipline that we coined as "*kinetic phase diagrams*". I also appreciated the attention of the public, and am particularly thankful for the attentiveness of my friends and co-workers as my writing was widely enhanced when a compendium [8] was prepared in my honor. I again have to be grateful for the contributors who bothered themselves to be supportive towards my long-lasting curiosity-filled dreams bestowed to thermal science.

My rather extended experience in the laboratory research and university education helped me to finish this book's manuscript within an unexpectedly short period of two years. It was once again, a hard, non-paid and time-consuming job. While writing it, my motivating force was the vision for making some new and imaginative dimensions for a wider family of thermoanalysts, so as to encompass their view of thermal analysis from a much broader spectacle. At the same time, I have attempted to assist the expert public to spiritualize thermal analysis as a broad-spectrum science on heat. This was the reason why I undertook the challenge to write this book from a new, yet untraditional outlook to include both aspects of natural and humanity sciences, i.e., thermal physics [9] and society consequential operation-ability. Thus, I have tried to get a credit with having popularized the role of heat from the micro- up to the macro- world, and have endeavored to explain that the processes are almost the same – only differing in the scale dimension of inherent heat fluxes. I, certainly, did not forget my thermoanalytical background [1,2] (see the Volume 3 aimed to the thermal treatment and the methods of thermal analysis) although I intentionally tried to restrict my favorite mathematics to a minimum. A pattern of books popularizing the science of physics through the freely available understandability (e.g., by *Prigogine* [10], *Feynman* [11], *Barrow* [12] and many others), served me here as unattainable examples.

I am hopeful (and curious too) if this book will be accepted as positively as my previous, more methodological and narrow-faced publications where I merely concentrated on theoretical aspects of thermal analysis, its methods and instrumentation. However, this new presentation, which you now have in your hands and which I regard as a somehow more inventive and across-the-board approach to the science of heat, did not leave much space to work out a thorough description of any theoretical background. The interested readers are regrettably referred to the more detailed mathematics presented in

PREFACE

my original books [1–7] and review articles cited in the forthcoming text. It is understandable that I based the book's new content mostly on the papers that I have published during the past twenty years. I also intentionally reduced the number of citations to minimum so that, for a more detailed list of references, the readers are kindly advised to find the original literature or yet turn their attention to my previously published books [1–7] or my papers (the survey of which was published in ref. [8]).

I am aware of the books evident setbacks (whereupon it may appear, due to my rather 'impulsive' trace of scientific growth, that there is a certain scientific restlessness), which are manifested here in somewhat heterogeneous idea and chapter assortment. Therefore, I have tried to make the contents more compact, enveloping, at least, the text of five volumes (subordinated parts) though forced to respect the necessitated boundary of an acceptably readable book – not exceeding 400 pages. In terms of my written English in this version of my book, its thorough understandability may be questionable but excusable as it is written by an author whose mother tongue is fundamentally and grammatically very different – the Slavic language of the Czechs. Moreover some readers may become negatively excited by my 'extempore' trips to the deeper recess of nature as sheltered in the Chapters 2 (Roots of Western Civilization) and/or 20 (Advanced Trends in the Understanding of our Universe). I kindly ask all those who are experts in these fields not to get irritated or aggravated when reading some of these inherently indistinct ideas, or better, to skip these chapters altogether from their attention in advance.

Undoubtedly, my educational and scientific background has the Czech roots and, thus, it is easy imagin-

able that I was proud of and stimulated by the history of sciences based in the territory of the present day Czech Republic (particularly noting early thermal analysis and thermodynamics [13]). It can be traced as far back to the year 1348 when the first middle European university was founded by the *Charles IV* in Prague. Some milestones, associated with exploitation of heat, can be mentioned such as the foundation in 1378 of the first brewery in the South-West Bohemian town of 'Domažlice', and the later-allied but yet earliest treatise on the beer-making '*De cerevisia*' published by the Czech alchemists *Hajek* in 1585. It is also worth noting that the first printed book emerged in the Bohemia soon after the *Gutenberg's* discovery of typography and was already printed in the Czech language in Pilzen 1468. Another triumph was the establishment of the glassworks; the most famous one was opened in the North Bohemia town of 'Chřibská' in 1414 (inquisitively operating without interruption even today).

In the middle of 17th century the high-spirited Czech thinker and famous Bohemian world teacher *Jan Amos Comenius (Komenský)* published important educational books, among others the treaty on "*The nature of heat and cold, whose true knowledge will be a key to open many secrets of nature*" [14] (1678, see Fig. 1). There he stated the almost modern definition of thermal analysis "*to observe clearly the effect of heat and cold, a visible object should be subjected to heating and subsequent cooling, the sensible changes made by heat and cold will then be visible to the eye*".

Nationally, the modern use of thermoanalytical methods began with the studies of *Matějka* (1913) who, by using an instrument of his own construction, published

a paper on changes observed in kaolin during its firing. In 1932, Latter *Škrumovský* invented the 'statmograph', which was, at that time, a very advanced concept for thermogravimetry [15] and in 1950, *Bárta* introduced the modern concept of DTA instrumentation. A number of Czecho-Slovak scientists also participated in the discovery of specialized techniques, such as dielectric (*Bergstein*), emanation (*Balek*), hydrothermal (*Šatava*), periodic (*Proks*), photometric (*Chromý*) or permeability (*Komrská*) methods of thermal analysis. The book entitled "*Thermika*" (Science of heat, see Fig. 1) is worth of mentioning [16] as it was an original and outstanding treatise on early thermodynamic concepts, published by *Strouhal* as early as in 1905, dealing in detail with wide aspects of heat and temperature. It served for me as a good quality precedent as well as providing the tradition of an excellent school of physical-chemistry of thermodynamics, developed in Czecho-Slovakia by *Wald*,

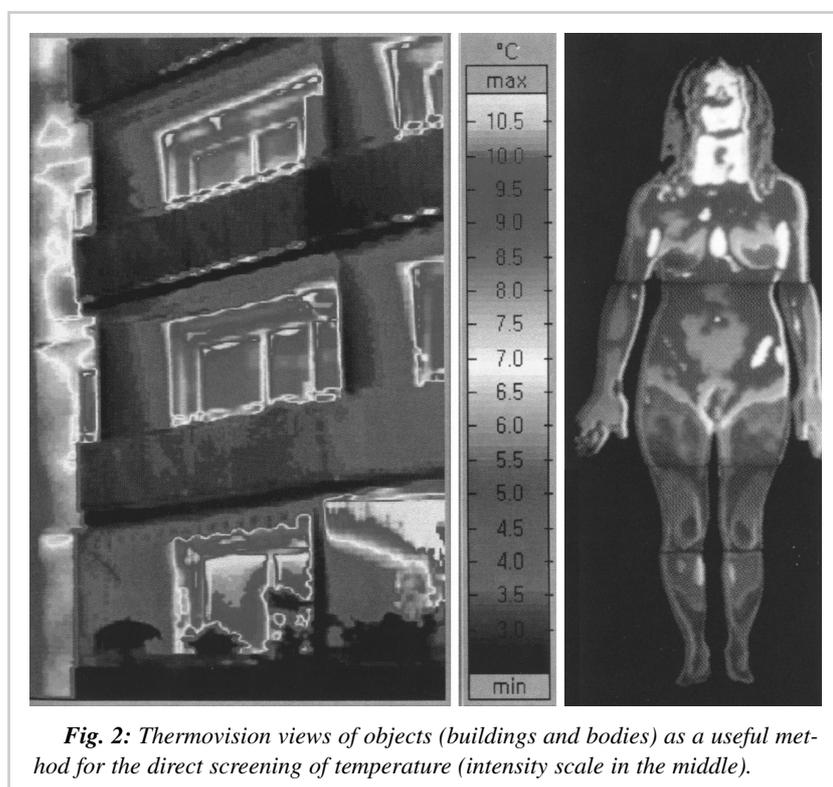


Fig. 2: Thermovision views of objects (buildings and bodies) as a useful method for the direct screening of temperature (intensity scale in the middle).

PREFACE

Strouhal, Závíška, Quadrat, Brdička, Regner, Hála, Boublík, Reiser, Kvasnica, Malinovský, Šatava, Černý, Samohýl, Maršík and many others, not forgetting experimental and theoretical basis of thermal analysis and calorimetry (Kallauner, Matějka, Škramovský, Šatava, Proks, Velíšek, Velich, Brandštetr, Pekárek, Blažek, Holba, Jesenák, Vaniš, Nevřiva, Balek, Málek, etc.). The importance of some other nationally acclaimed and early published books by *Nachtigal* (Technical physics [17]), *Horák* (Practical physics [18]), *Závíška* (Thermodynamics [19]), *Brož* (Magnetic measurements [20]), *Eliášek, Štovič, Zahradník* (DTA [21]), *Brdička* (Continuum mechanics [22]) or *Šatava* (Physical chemistry of silicates [23]) should also be stressed out as they have greatly influenced the advancement of the Czech school of thermo-physical measurements.

Such a fruitful past requested of me an avid obligation for my quality accomplishment – to write a respectable book. Therefore, I shall be satisfied to contribute to the already rich understanding, and to do so within my limited capacity and within my certain insight, progressively. I don't, however, feel competent enough to make a better and more detailed historical survey about the roots of thermodynamics and thermal analysis as has already been accomplished by my friends *Robert C. Mackenzie* [24] and *Ivo Proks* (introductory chapter in ref. [3]). Similarly I could not present a more detailed analysis of advanced theories (mathematics of dynamic modes of oscillations or truly non-linear thermodynamics [10]) or to go into deeper thoughts about theoretical physics [9,11]. I can only try to present my synopsis, affected by long-lasting scientific experience and idea overlapping, in a manner that shows thermal analysis in the wider perspective of thermal science, touching almost all domains of human activity.

It, therefore, should be rendered noticeable that the sphere of *thermal analysis* spans over a wide intellectual landscape, and the following examples can illustrate the possible extend of its applicability. The notion of thermal analysis has been always used in wider sense, even in describing the generalized heating features in construction or technological processing [25]. In the greater scale of things we can see the generalized idea of thermal analysis in studying temperature differences on the Earth due to the incoming solar radiation and the related thermal flows that govern our weather. There is also a clear association with the adjacent technical fields of hydro-thermal-dynamics. As another consequence, the building thermal characteristics are often characterized by thermal vision (see Fig. 2) and are revealed in the associated field of *thermography*, which was an early synonym for thermal analysis, itself. Though the use of this term was not allowed by the ICTAC nomenclature committee it is yet employed in thermoanalytical circles within Russia. It follows that the idiom 'thermal analysis' factually includes broad aspects of thermal phenomena inherent in the man's exploitation and knowledge of heat and, in this survey, it is dealt with in the forthcoming text, alienated in the five liberally related volumes. Each volume can



stand on its own and can be read independently from the others.

But let's restrict ourselves to the narrowed meaning of thermal analysis as a method (mostly comprehended in the volumes two and three), the development of which, together with the appropriate understanding of the role of temperature in all type of measurements, would not be possible without an increased international cooperation. Among others, let me mention the first international conference on thermal analysis held in the Northern Polytechnic in London, 1965 which paved the way to the foundation of the International Confederation on Thermal Analysis

PREFACE



Fig. 4: Illustrative photo of the founding members (and the first executive committee) of the Czech Working Group on Thermal Analysis, upper row, from the left, Karel Tobola, Karel Habersberger, Miloš Nevřiva, late Jaroslav Rosický, lower row: Pavel Holba, Milan Beránek, Vladimír Balek and Jaroslav Šesták.

(ICTA) a few months latter. I am proud that I could assist in that time the great pioneers of thermal analysts (*MacKenzie, Garn, Wendlant, Redfern, Erdey, Dollimore, Murphy, Bárta, Berg, Lombardi, Paulik, Berggren*, etc.), cf. Fig. 3, in their effort to establish such a constructive scientific forum cooperative for all thermoanalysts. An international platform of thermal sciences thence began in earnest when ICTAC was established in Aberdeen, 1965, which has productively kept going until now. It was supported by the foundation of the international journal of *Thermochemica Acta* in the year 1970 by Elsevier and, for a long time, edited by *Wesley W. Wendlandt*, with the help of a wide-ranging international board (such as *Flynn, Ozawa, Reich, Šesták*, etc.). It was just one year before when another specialized *Journal of Thermal Analysis* was founded by *Judit Simon* (who has been serving as the editor-in-chief even today) and launched under the supervision of *Academia Kiadó* in Budapest (*Erdey, Paulik brothers, Liptay*, etc.) to aid preferably the worthwhile East European science suffering then behind the egregious ‘iron curtain’. The Czech working group on thermal analysis was founded soon after in 1971, (see Fig. 4.), and helped me to enjoy the state-of-art of thermal science (coming up with such enthusiasm to even make a cabaret performances showing the virtual foundation of thermal analysis through the experiments on frostiness by a facetious person *Kopřiva*).

This account would not be completed without mentioning some internationally acknowledged books, some of which are often referred to as thermoanalytical ‘bibles’. Among others, the most useful is a thorough description of thermoanalytical instrumentation by *Wendlandt* [26] or the early treatise of already advanced thermoanalytical kinetics by *Garn* [27] or particularized attention to polymers by *Wunderlich* [28]. Worth mentioning is also the extensive gallery of books aimed to the basis of thermal analysis [26–33], DTA [21,34–38], TG [39–41], calorimetry [42–45], ETA [46], curve databases [47] up to the

current survey of modern instrumentation means [48]. There, certainly, are books covering a more extended analysis dealing with thermodynamics [16,49–51] and thermal physics [9,16,22], which served for me as an comprehensive sources of information and helped to bring about my wished treaties aimed to complete my broader ‘thermal’ vision. By no means should I forget to mention the various sources of complementary humanistic viewpoints of the nature – also the appreciated resource of finances, which made it possible to publish this book.

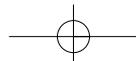
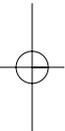
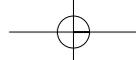
I would like to precede my herewith discourse on heat by accentuating that the complete realization of an absolute zero is impossible by any finite processes of supercooling. In such an unachievable and unique ‘nil’ state, all motion of atoms would cease and ever presented fluctuations (‘errors’), as an internal driving force for any change, would fade away. The system would attain the distinctly perfect state, which is deficient in any defects. We know that such a perfect state is impossible as, e.g., no practical crystal can truthfully exist without the disordering effect of admixtures, impurities, vacancies, dislocations, tensions or so. This is an objective reason to verbalize that even no manuscript could ever be written faultlessly. In this context, any idea presentation, items specification, mathematical description, citation evidence, etc., are always associated with unprompted mistakes. As mentioned in the forthcoming text, any errors (i.e., a standard state of fluctuations) can play the most important roles in any positive development of the state of matter and/or society itself, and without such ‘faults’ there would be nor evolution neither life and even no fun in any scientific progress. Therefore, please, regard any misprints, errors and concept distortion, you will surely find in many places of my book, in a more courteous way of ‘incontrovertibly enhanced proficiency’. Do not criticize without appreciating how much labor and time has been involved in completing this somewhat inquisitive but excessively wide-ranging and, thus, unavoidably dispersed idea-mixing approach, and think rather in what way it could be improved and accomplished or where it may be further applied or made serviceable.

In conclusion let me disclose my complaisance: when I was asked what is my specialization I always queried who made the question, if a physicists, I answered that I was a chemists and vice versa, if asked by a chemists, I replayed to be a physicists. The worst case, however, happened when I was quizzed by a physical-chemist. Then I had to pretend that I was an artist! Accordingly I feel now obliged to provide a certain apology to those of you who have already heard this anecdote, and allow me to present some modest evidence that it was not so big a fiction and kindly accept this book in such a design where some of my art photos, that were exhibited in more than twenty photo-exhibits at home [52] and abroad, are used as the frontispieces of each chapter. It may also refresh the comeliness of the book in your hands. Thank you.

Jaroslav Šesták
December 2003

PREFACE

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Motto "Fire shall try every man's work"

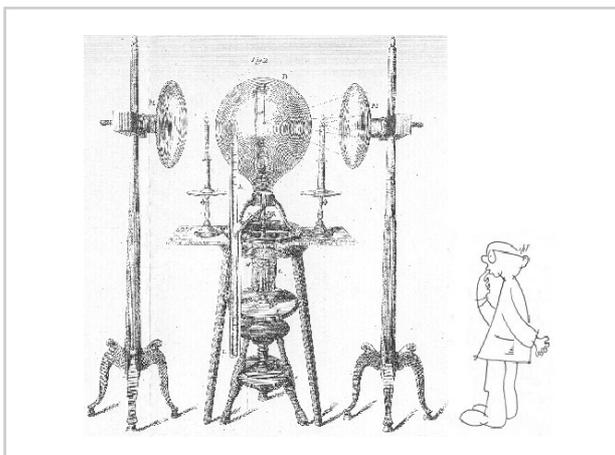
[CORINTH. 3:13]



*In hope of a better future
(Czech 'velvet' revolution, Wenceslas' Square, Prague 1989)*

Introduction to thermal science

Roughly speaking, it is probably true to say that the modern science of thermal physics and the interrelated field of thermal analysis started to develop in the seventeenth century following the invention of thermometric instruments that enabled quantitative studies of thermal phenomena. However, this statement should not be interpreted quite speciously, or in such a way that there was no scientific theory dealing with heat effects before this date. Equally wrong would also be to believe a more widely shared understanding that after the thermometer became a recognized instrument then scholars had a clear idea of what temperature (and heat) was, and that by making experiments with thermometers they were aware of what they were actually doing. Initially, *Rumford's* conception of heat included the belief that there is a cold "frigoric" radiation (consisting of cold particles called 'frigoids') existing side by side with the heat radiation¹, see next Fig.



It is clear that early science dealt predominantly with easily describable phenomena, such as motion. It, however, may be found quite surprising that the requisite part of ancient natural philosophy consisted just of what we now call thermal physics and that the theories and hypotheses suggested by old philosophers were, more than one and a half centuries after the invention of thermometer, still active. How was it possible to build up the predicative theory of thermal phenomena ignoring such a quantity as temperature? To give an answer to this question it is worth to say a few words about these, for us as modern scientists, quite strange theories. In the beginning, only two opposing forces were unintentionally experienced:

(i) One *aiming down* to the rest and now associated with gravity, recently characterized by the universal gravitational constant, g ($= 6.672059 \cdot 10^{-11}$ [N m² kg⁻² or m³ kg⁻¹ s⁻²]), as a natural part of the basic unit called the *Planck length* (of the magnitude of $10^{-34} = \sqrt{(gh/c^3)}$, where h { $= 6.6260755 \cdot 10^{-34}$ [J Hz⁻¹] }, and c { $= 299\,792\,458$ [m s⁻¹] } are respectively the *Planck* constant and the speed of light in vacuum}. The other

(ii) one *tending upwards* to swell (symbolized by fire), which is currently represented by the thermal kinetic energy of particles, $mv^2/2 = kT$, where k ($= 1.380\,658 \cdot 10^{-23}$

[J K⁻¹]) is the *Boltzmann* constant and T [K] is temperature (as a natural part of the basic unit called the *thermal length*, $h/\sqrt{(m k T)}$).

The forms of *potency* (*energy* in our contemporary terminology derived from Greek 'ergon' – action and 'energia' – activity), generally known to ancient people, numbering only two again, were explicitly mechanical and thermal (the knowledge of electric energy documented, e.g., in the Bible should be considered as extraordinarily exclusive). From the corresponding physical disciplines, however, only mechanics and optics were available for clear mathematical description. The rest dealing with the structure of matter and including thermal, meteorological, chemical or physiological phenomena were treated only by means of verbal arguments and logical constructions. The most representative theory of this type had been formulated by *Aristotle* already in the fourth Century BC and survived from ancient to middle age. It was based on the famous doctrine of the four Rudiments (or Elements), and its everlasting inference even into modern views of physics, act as a joining feature in the forthcoming text.

By measuring temperature it becomes clear that we do not live in a thermostatic equilibrium². Instead we actually reside in an obvious disequilibrium. This can be also witnessed in a series of a self-organized patterns and processes lying evidently outside the traditional concept of equilibrium. It links with a delicate interplay between *chance* and *necessity*, *order* and *chaos* as well as amid *fluctuation* and *deterministic laws* and it is always under subtle interactions between *mass flows* and *heat flows*.

The idea of equilibrium is also reflected in our gradual development of the understanding of our Universe, which has progressed from a static view up to the present complex world of novelty and diversity, the description of which is also a modest aim of this book.

We, mankind, would like to live in thermostable environments, but the Earth's ecosystem, sometimes simplified as a sort of a Carnot super-engine (or better myriads of tiny motors working as a team), is not stable and pleasant everywhere. The systems used by mankind to obtain what it wants is usually done so in a dissipative way by heating and cooling, and with machines when manipulating these disequilibria in micro- (reactions), ordinary- (machinery, experiments) and macro- (ecosystem) levels. Disequilibria can thus be a source of desired work but also grounds for thermo-stabilizing as well as destabilizing power. Disequilibria are also a global datum of Nature as it derives from the cosmological history of the present Universe (cosmic microwave background). On a smaller scale, the Earth (atmosphere, biosphere, etc.) experiences a non-equilibrium due to the constant influx of heat delivered from the Sun. On an even smaller scale, we have everyday experience of the variety of non-equilibrium processes visualized in the formation of, e.g., snowflakes or living cells and we can also encounter it during laboratory experiments. However, all dissipative processes take place with a time arrow. They belong to a world in which exist the past and the future, memories, culture and discoveries, including the recent invention of the laws of thermodynamics and irreversibility themselves.

Through the process of better understanding of the notions 'light-fire-heat-energy-entropy' it was recognized that although energy is conserved in physical processes, it is degraded into less ordered and less useful forms as is habitually observed in a closed system that tends to become more and more disordered. Whenever entropy, literally, prevails over energy, the resulting structure is dominated by randomness (and fractal and chaos) rather than by our familiarity of a traditional 'Euclidean orderliness'. This is not a law like gravity but, instead, a principle having a statistical nature and thus turns out to be very important for consideration of what is technologically possible and practically attainable. Yet latter succession was found in the interconnection between the notions of entropy and information and their gain or loss. It follows that information can be seen as a commodity and it takes effort to acquire it. So that it is possible to classify all technological enterprises in terms of the amount of information that is needed to specify the structure completely and the rate at which the information needs to be changed in order for the system to improve or arrange or organize. It needs lot of efforts, understanding and willingness to get across the boundary of narrow minds and special considerations. There is no reason to think that the Universe was constructed for our convenience.

Deeper thought about the nature and its knowability was particularized by *Majmonides* already at the turn of thirteenth century in his book '*More mevuchim*' ("Handbook for scatterbrained afloaters") where he attempted to categorize the knowledge to that, which is *known, knowable but yet unknown* and *unknowable*. In his view God is unknowable and whether one can have faith in God or not, both are unverifiable and its testimony is up to one's conviction and it can be relocated on many other subjects of thinking. His famous example was a person who tries to move an ocean by poring it out by a pail, one by one. Clearly it is not feasible but it is also not (theoretically) unachievable! He said that it is always more difficult to answer the question '*why*' (philosophy, e.g., why a stone is moving, life began surfacing) then to reply to the question of '*how*' (sciences, e.g., how is the stone moving in its current trajectory? How did life begin?). This became reflected in the modern way of the presentation of basic questions about nature as those, which are *answerable, yet unanswerable, ultimately unanswerable* and *senseless to ever ask*. Here we should remember *Cantor* who said that '*the art of asking the right question in mathematics is more important than the art of solving them*' as well as the *Einstein's* phrase '*any physical theory cannot be fully testified but just disproved – we are often blind trying to understand our nature*'.

The level of conscionable knowledge depends on the databases of all kinds (minds, experience, libraries) and they are continuously enlarging at a tremendous rate. It brings, at the same time, its positive and negative effects as reflected on the society life (smart exploration vs. brainless browsing). It is obvious that knowledge can be both the endowment and the adversity, or even a weapon. Similarly, the understanding of ecological intercommunity has developed and can be viewed to follow a tradi-

tional spiral-like evolution. It took centuries to cultivate science to the present day's level of sophistication. It is obvious that a long chain of educational years are needed before a science student is equipped to start understanding what is going on at one of the frontiers of natural sciences. It then usually takes two or more years before they are able to make unaided contribution to science. This educational path is not optimized for science research and engineering applications as it must accommodate all sorts of people. As our knowledge deepens and widens, it will require longer time in order to reach any new frontiers – this situation can be combated only by increased specialization so that an even progressively smaller part of the frontier is targeted; yet more fragmenting of our understanding of the Universe. Very serious is the possibility that the early creative period of a scientists' life will be passed by the time of mere digesting what is known, even despite the new discoveries that can make knowledge available to a global audience almost instantaneously. The globalization of education, which allows many more people to be taught by one person, has many obvious benefits but also its downsides. We also learned that a coordination of different specialists' outputs from



their individual contributions is more than the sum of the parts involved. We have to admit an important role of intuitive deduction and experienced path of proofs and errors. We may wonder whether a consideration of scientific limits is within the activity of elder advisor scientists as all young scientists need to be consumed by the desire to solve problems and make new contributions, while very specialized individuals are of little help in managing a progress as a whole. Here we also need a type of '*philosophers*' in their original Pythagoreans meaning of comprehensive understanding of Nature that is possible only by parallel survival of a wider-angle education, i.e., building bridges between various fields. It has been emerging and is becoming widespread as an unavoidable annexation of cross-disciplinarity (inter-disciplinary education mostly touching the spheres of humanities) where the role of fire/heat/energy plays its incommutable role.

The differential equations have become the language in which the modern science encodes the laws of nature. Although the topic of differential equations is, at least, three centuries old and the results have filled libraries, nobody would have thought that it is possible that they could behave chaotically. By the end of the nineteenth's century, there were available two different mathematical tools to model natural phenomena: exact, deterministic equations of motion and the equations used in thermal physics based on statistical analysis of average quantities. Whenever any non-linearity appeared, it was put in linear regimes. Those which made double cause produced double effect, the solution of which was always linearity as quoted by classical laws of thermodynamics. Small changes produce small effects and large effects are due either to large changes or to a sum of many small changes. On the other hand, in non-linear systems small changes may have dramatic effects because they may be amplified repeatedly by a self-reinforcing feedback mechanism, and are thus the basis of both the instability and the sudden emergence of new forms of orders, characteristic for *self-organization*. Such a drastic move away from a standard configuration can lead to states displaying spatial or temporal order and such states created dissipative structures that can only exist in conjunction with their environment. If constraints are relaxed the system returns (equilibrates) to a standard static (equilibrium) state and the entire long-range molecular organization collapses tending to re-create a standard (static) short-range set up.

The 'linear' perception of world was reflected in the construction of man's traditional assemblages. The earth's based and man's assembled machines such as the engine, motor, clockwork or other automaton, can be regarded as *information transducers* that actually does not change their self during their work-producing thermodynamic processes, except in cases of abrasion or deterioration due to their wearing out. It implies that for producing useful work, it is necessary to apply energy but also know-how, i.e., cognition in the sense of today's information. It was derived from the Greek '*in-formare*' in the meaning of '*ether*' as internal shape joining thus the four early-thought elements of *earth, water, air and fire*. It is evident that any applied energy must include information within itself (such as the alternation of electric current) to ease the interaction with some transducer (alternator as a motor) proportionally less complex with the increasing information content received. For that reason, instead of constructing an even a more and more sophisticated combustion engine, we need only to employ an alternative mechanism (such as the combustion cell) where the information-vacant heat is transformed or substituted by another form of information-richer energy, which contains certain implementation of potentiality within itself.

Besides the man's oversights, a particular uncertainty of different levels and weights is always inherent in any of the assemblages arising from kind of its set-up and inherent physical properties. Quantum mechanics states the principle of microscopic uncertainty as the simultaneous determination of position (x) and momentum (p), $\Delta x \Delta p = h$ and/or time (t) and energy (E), which is written

as $\Delta t \Delta E = h$. It puts on view a *specific limit* (identified, e.g., by the quantum volume of a particle/fermions, $\Delta x^3 = N (h / 2\pi)^3 / \Delta p^3$) abridge as a specific span, which cannot be overtaken by any finite process leading either to equilibrium ($\Delta t \rightarrow 0$, attaining the static state of classical crystal structure, $E = \text{constant}$) or to disequilibrium (providing the dynamically static state of 'lively equilibrium' under continuing t and supplying E) often exemplified by self-organized processes. Typical are the *Zhabotinsky-Belousov* reactions carried out exclusively under a continuous input and self-catalyzing feedback curiously constrained by the *Planck* constant through both the *principle of least action* and the effect of thermal length, $h/\sqrt{(m k T)}$, (cf. Chapter 16.). Factually, most of the macroscopically accounted diffusion-scaled processes are drawn near the dimensions appropriate to the micro-world following the *Schrödinger* wave equation when many such processes possess the matching mathematical formulae. It appears that the quantum world in solids is



in the hands of electrons while protons realize that for aqueous environments. In addition, it also shows that the micro-space possess a fractal structure (*Nottole*), i.e., $v \sim (v_1 + v_2) / (1 + v_1 v_2 / c^2) \sim \ln(\Delta x_1 / \Delta x_2)$. It is not unreliable that even the synchronized staying power of heat (Q) and temperature (T) may have certain, similar limits, such as the product of $\Delta T \Delta Q$ obeying a certain limiting constant. It can encompass such a meaning that we cannot determine the temperature precisely enough for large heat flows and vice versa.

We may witness other limits such as that encountered in the transmission of entropy in the sense of its statistical interpretation related to the information content and linked to the number, n , of different arrangements that can be taken up by a given collection of particles (states) with the same likelihood (probability or average basic uncertainty of one binary digit = bit)⁴. There we would face such an involvedness as is the quality of information, algorithmic complexity (possibly identifiable with minimum number of bits necessary to solve given task), logic depth and likely to be missing a qualified definition of what is information itself. Next we have to examine the cost which we have to pay for the information lost when deteriorated to heat. If applied to computer memory there

is the puzzle when this dissipation credit is payable, usually it is assumed to happen during the memory erasing. This may even be extrapolated to a more fantastical example focusing on such a curiosity when asking what might happen with information when swallowed by a 'black hole'. It extends to the neighbored subject of information flux, possibly to see it proportional to the strength of question and to the gradient between the questions and answers (envisaged as information fields).

From the thermodynamic and causality considerations of what is the general upper bond on the rate at which information can be transferred in terms of the message energy, it can be theoretically inferred to the avoidance of thermal self-destruction (*Bekenstein*). It may be seen as parallel to the self-protection role of the power law established by *Weber* and *Fechner* for the interrelation between an organism and its perception of information due to a stimulus, which protects an organism from being overwhelmed by a 'yet to be paid for in full' sensation of excruciating overload. It involves problems of issuing and transferring information from micro- to macro- world and it well demonstrates the involvedness of thermal physics and its capacity to comprise the systems under study within various scales, from diminutive to gigantic, as well as its intricacy, from extremely simple to very complex.

History of thermal physics illustrates the everlasting dilemma of how to distinguish between the overlapping notions of heat and temperature. Though this puzzle has brought up devious but fruitful ideas about immaterial fluids of '*phlogiston*' and '*caloricum*', which, in fact, enabled a better understanding of early view to different transformations. Scientists often challenge the dilemma of which understanding is more efficient. In this example, *Black* was already aware of the incorrectness of the material theory of caloricum but, at the same time, he also realized that such a fluid representation is more convenient for the phenomenal cognoscibility and associated mathematical description. We may even face the similar situation today when dealing with new but yet unobservable notions of dark matter and dark energy, which is helping us to solve the analogous mystery of gravity and anti-gravity forces in the Universe. *Black's* great intuitive invention was the introduction of measurable quantities such as heat capacity and latent heat. There were long-lasting struggles between famous scientists of different scientific school backing and opposing caloricum, like *Laplas*, *Fourier* against *Bernouli*, etc.

Newton was one of the greatest scientists to live. He gave to us, amongst other things, the deterministic description of our physical world whilst always aware that it could be a part of a superior universe (extending from the very small to the extremely large). He intuitively associated heat conduction with temperature gradients called '*gradus caloricum*' (whereupon gradient is derived from Greek '*gradus*' which means felicitous, congenial). *Newton* even tried to make some quantitative observations by heating one end of a metallic bar and observing heat propagation by detecting the progress of melting of various substances (wax) at different distances. It helped him to formulate the law of cooling without knowing what heat

actually was. At the turn of eighteenth century, *Buffon* applied *Newton's* cooling law in an effort to estimate the age of the Earth based upon an approximation of cooling rates of various substances. He arrived to the value of 75 000 years. The scientist *Kelvin* later tried to make a more accurate attempt at estimating the age of the Earth, arriving to the value of 100 000 000 years, which was based on the amount and rate of energy lost radiation to the Earth's surrounds from the time when it was formed from contracting interstellar dust. The most important invention of *Kelvin*, however, was to abandon the standards necessary for correct temperature measurements so that he defined temperature on the basis of the efficiency of thermal work whilst putting faith into the idea of caloricum. In fact, even the current definition of temperature is somehow awkward due to the fact that the absolute zero temperature is a limiting state which cannot be achieved by any finite process. It would have been more convenient to define such a 'nil' point as an untouchable infinity (logarithmic proposal by *Thomson*) even under the penalty of a different structuring to thermodynamics.

Hess enunciated an important law, which is now associated with his name, that the amount of heat evolved in a reaction is the same irrespective of whether the reaction occurs in one stage or in several steps. It, however, became indispensable to make thermal observations more accessible, which turned out to be feasible by *Seebeck's* investigations who, in 1821, observed that an electric current was generated when one junction of two dissimilar metals in contact was heated, even if only by the hand. The current became easy detectable by using a magnetic needle in a spiral coil termed a galvanometer by *Ampere*, who based his work on the observation of *Oersted*. This system grew to be popular when applied to high temperatures in 1826 by *Becquerel* who used the junction of platinum and palladium. The increase in conductivity on lowering temperatures was first observed by *Davy* and latter confirmed by *Ohm* during his investigation in 1826 that established the law that bears his name.

Actual thermodynamic thoughts became necessary, if not irreplaceable, when the determination of thermo-physical properties became needful and significant. It was initiated as early as in the middle of seventeenth century by *Boyle* and *Mariott* who related the pressure and volume of air, and by *Hooke*, who determined the simple relation between the deformation and stress. A century latter it was supplemented by *Gay-Lussac's* detection that the heat expansivity of all gases is the same, which lead to the famous state equation of gases. It strongly affected the conception of heat to be associated with the internal motion and collision of molecules, first connected with their linear movement by *Kroening* in 1856. From the balance of impulses it followed that the pressure is proportional to the medium kinetic energy of molecules and is equal to $3/2kT$ where T is the absolute temperature and k is the *Boltzmann* constant. It acted in accordance with the *Petit* and *Dulong* observations on heat capacities showing that the medium kinetic energy of a fixed atom in the crystal network is equal to $3kT$. It proved that, for each degree of freedom, for an atom to move it required a mean energy of $kT/2$.

Important roles in early thermal physics were played by statistics and the *Boltzmann* relation between the ratio of heat over temperature (entropy). These, as well as the probability of the arrangement of atoms, were used by Planck to show that the *Wien* radiation law for low frequencies and the *Rayleigh-Jeans* radiation law for high frequencies could be explained by individual atoms that emit discrete frequencies. *Planck's work* allowed him to derive his radiation law on the basis of the thermodynamic equilibrium between emitted photons and the absolutely black surroundings encountered on the condition of maximum entropy and thus providing a bridge between the micro- and macro- world of very small and very large collections. Recently these principles have been used to analyze the background structure of the entire universe,



i.e., the arguable *vacuum*, previously known as the 'ether', which is now understood to be bursting with unidirectional zero-point radiation (seen as the ocean resource of energy which is borrowed on account of the creation of asymmetry and returned back on the energy re-execution, cf. Chapter 20).

Altogether the above mentioned ideas assisted the formulation of a new and rather productive field of thermodynamics, which became a definite physical domain based on general laws of energy conservation and transformation, and where its consequences have been deduced to serve for practical applications. It studies real bodies that consist of many integrating parts. The basic assumptions for such real mixtures are the same as those that are also fulfilled by pure components, but rather that all the properties of mixtures are the consequence of the constitution of the components, although, however, are not a simple summation of components as various interactions between components must be taken in account. One of the most important laws is the second law of thermodynamics, which, in common words, says that any spontaneous process must be only such that any resulting state is more easily accessible than the state of any previous (competing) process. We can see that thermodynamics can also provide an idea of a global (non-material) driving force showing that the process always follows the circumfluent contour lines of the straightforward access to all intermediate states on its reaction path. This, in fact, is very similar to the objective of our curved universe,

where the easiest path is controlled by gravity lines of force or, in everyday experience, by the uniplanar contour line of comfort walking.

Every thermodynamic process is associated with a certain dissipation of energy, as well as an associated degree of entropy production, which is also the measure of the irreversibility of time. Inherent thermal processes are sensitive to the criterion (or, perhaps, our point-of-view) of what is stability, metastability and instability. There can exist equilibria characterized by special solutions of complex mathematical equations, whose stability is straightforward, however, the comprehensively developed field of *thermal physics* primarily deals with equilibrium states that are unable to fully provide general principles for all arbitrarily wide, fully open systems, which would encompass every unsteady or somehow re-stabilized disequilibrium. It, however, can promote the unlocking of important scientific insights, which lead to a better understanding of chaos and are an inquisitive source for the evolution of systems (such as life).

Any thermodynamic system bears its own clear definition criteria, i.e., a real material body has its volume and is circumscribed by its surface, which, in fact, means the defect on the exterior otherwise homogeneously defined body. A system can be any macroscopic entity, biological being or even ecological formation. A system can be imagined to be composed from certain material points or sites, which we may call subsystems, where each point, or any other fraction of a whole, cannot be merely an atom or a molecule but any elementary part of a body that is understood as a continuum. Thanks to the body's interactions with its surroundings, there are certain primitive characteristics, representing the behavior of the system, as each constituent point can move and can change its temperature. There, certainly, are other important quantities that play crucial roles in the general laws of balances, i.e., mass, momentum, energy and/or entropy. Energy in the space, however, is directionless, which is why we often use the help of an auxiliary parameter: the directional vector of momentum across a surface. A system's interaction can be identified with any type of reciprocation of balances. The number of parameters is often greater than the number of balance laws, so it is necessary to have other axioms and interconnections. Among the most important are causality, determinism, equipresence, objectivity, material's invariance, time irreversibility, and decisive effect of nearest neighbors, and nearby history.

When the thermodynamic parameters of a process are changing so slowly that their relaxation time is longer than the time of observation these processes are called quasistatic and they have important technical consequentiality. This, in fact, means that these processes are in states of both the equilibria and disequilibria at the same time. Without this simplification, however, we would not be able to study most of nature's processes because only a negligible fraction of them are time independent. Generally we assume *equilibration* during which any well-isolated system achieves, within a long enough time, its stable, well balanced and further noticeably unchanging ground state (i.e., death, which is the stabilization of original 'fluctuation').

An important quantity is heat, which is understood as the energy absorbed or evolved by a system as a result of a change in temperature and, thus, heat is a form of the energy transfer. However, the most basic and also unlocking quantities in thermodynamics are *temperature* and *entropy*, where the latter is an artificially introduced phenomenological parameter expressed as the ratio of heat and temperature. Temperature and entropy characterize collective behavior of the studied corpus of constituent species. Temperature is a measurable quantity and represents the degree of the mean energy, which is inter-exchanged by species (atoms) that constitute the system. On the other hand entropy is not a directly measurable parameter, similarly to heat; we can observe only associated changes. From a standard phenomenological viewpoint, we can also treat entropy as the normalized heat in the sense that the higher the temperature the higher the 'quality' of heat.

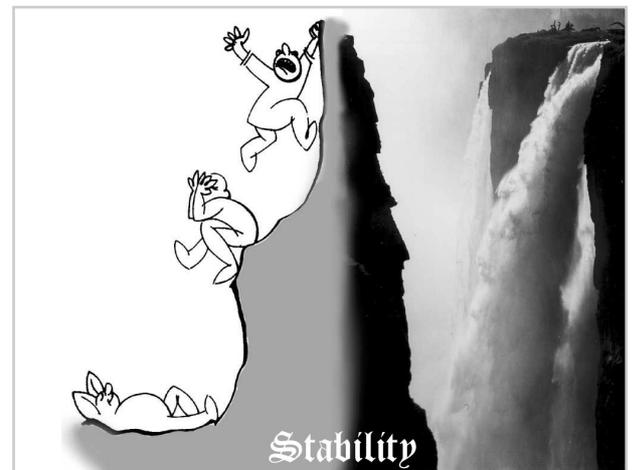
Entropy has accoutered various connotations, corresponding to the system's make up, i.e., incidentalness of the internal evolution of the arrangement of system constituents, which can be definite species or logical thoughts. It has also initiated a perception of chaos that is excessively original within habitual mathematical descriptions but has opened-up new perspectives on disorder as a vital part of our universe where we employ only practicable solutions (e.g., acceptable ever-presented vibration of aircraft wings to assure safe flying against their anomalous quivering indicative of danger).

The theory of thermal science is important for our practical applications as it teaches us that the best yields can be only obtained from infinitesimal changes, which are associated with reversible processes where all adjustments are close to zero, i.e., motion damps out and concretization would last exceptionally long. However, if some action is due to a real execution it must possess a finite driving force, even if it is negligibly small. We have always to decide whether to employ high driving forces with lower work efficiency or make it more energetically economic upon decreasing gradients but paying time for its prolonged realization. For getting an easy profit the thermodynamic laws are somehow cruel and impossible to circumambulate (even by any persuasive ecological arguing). We can humorously make our mind up with an aphorism that, in the heat-to-conversion game, the first law of thermodynamics says that one cannot win; at the best we can only break even. The second law reveals that we can break even only at the absolute zero and the third law adds that we can never reach the desired zero temperature.

As all other living things do, we 'Homo sapiens' – a most significant form of life, demand and would require thermal energy in the form of food and heat. The man-made haste in the mining of energy may be seen by the Nature hazardous as an activity rather close to wrongdoing. The Nature may wish to have a control over human activity like the goddess 'Venus' liked to visit the God 'Volcano' as to keep graceful control of his dubious behavior in his underground dwellings. We wordlessly witness accumulation of ash from the combustion of fossil-fuels,

radioactive wastes and other manmade litters, without pushing natural recycling by the ecosystem, which is vulnerable to events it has never witnessed before. The ancient Greeks saw the ecosystem as 'Nature of the Earth' to be something agitated by divine vitality and even now we should keep remindful of its beauty. It is clear that naturally enough smart 'Goddess Earth' is beginning to show her first signs of suffering.

Therefore, we cannot exclude a brief examination of the types of energy in concluding this introduction for the book dealing with heat, which we use to employ to live and to assure us a desirably comfortable life. It is fair to say that one of the most embarrassing question to ponder is how much we exploit energy and what is the availability and sustainability of its reservoirs. The energy resources can be divided into two broad categories: *energy capital sources*, i.e., those sources of energy which, once used, cannot be replaced on any time scale less than millions of years and *income energy sources*, which are more and less continuously refreshed by nature (or even by man assisting nature). For large scales we often utilize

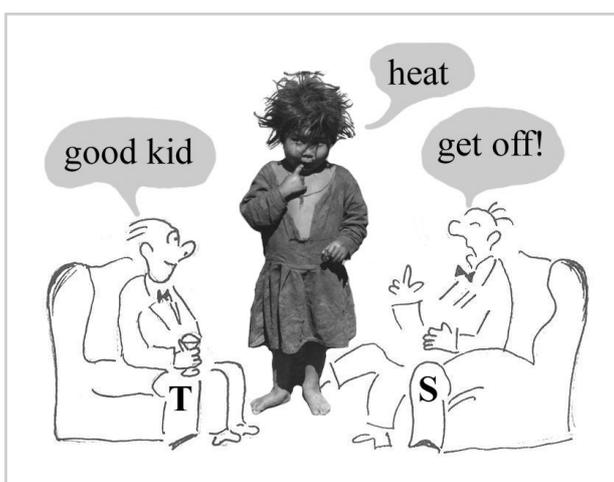


a more easily imaginable unit, coined as Q , which equals to 3×10^{14} kWh, roughly representing the amount of energy required to bring the US Lake Michigan to boil (about $5\,000\text{ km}^3$ of water). Over the past two millennia, the total world energy consumption has been approximately 22 Q corresponding to an average annual use of about one hundredth of Q . Recently the annual energy consumption has terrifically increased to lie close to 0.5 Q , and roughly its 20% is used by the US alone. The important question is how efficient is our use of energy? Since the sixties the average energy-efficiency increased by a few percent to about 32% , but most power stations are machine-based and use heat engines and the efficiencies are limited to no more than the limit given by the *Carnot* (ideal) thermodynamic cycle, which implies a realistic upper bound limit of about 40% .

In our research into thermal physics we could, certainly, can manage to exploit even small efficiencies and small thermal gradients if we have time enough to carry out it and sufficient technical means to manage it. For example, if an electric generating system would be driven

by the temperature difference between the surface and the depth temperatures of the ocean, the maximum efficiency obtainable is about 3.5 %, which would reduce down to an operating efficiency of mere 2 %. If approximately 1700 Q of the solar energy, which falls upon the ocean annually, were utilized by this OTEC (Ocean Energy Thermal Energy Conversion) it would provide tremendous 35 Q; even a portion of this amount would be a nice prospect for a very high-tech future hungry for energy. Certainly it does not account for possible ecological disasters due to be ensuing, and assumingly robust changes in weather including changing sweeping streams and deep-sea whirls.

Even nuclear fission is not limitless. The reserves for light-water reactors technology is close to 10 Q and per-



haps 600 Q for a scenario involving the use of breeder reactor technology, which may last not more than couple hundreds years only, nothing in the distant-time-view of future civilizations. Dependent on the capital source of energy, which will eventually become exhausted, the world inhabitants will need to undergo a drastic downward shift in the human population. It will happen due to the radical change of the energy lifestyle, unless, of course, a radically *new system of energy conversion will be revealed in order to span our traditional business governed by a low-efficient thermal engine.*

Over a normal year, however, the earth receives over five thousand Q, and about half becomes available for such purposes as powering photosynthesis, warming the earth surface and also providing available energy for mankind – this is about ten thousand times the current energy requirements of the human race. Recently, we can practically account on hydropower (<0.05 Q), biological sources (trees, waste materials, <0.03 Q), temperature differences (wind, waves, <0.09 Q) and solar-thermal-electrics (provision of heat for direct heating and variety of techniques for converting sunlight to electrical energy, difficult to estimate but merely yet in tenth of percent). We can imagine that covering just one percent of desert would satisfy the present world energy thirst. If the surface of US highways were made from solar sells it would exceed four times the US need of energy. All is always

only 'if', because we must accustom new materials and further 'spacious' requirements, except that the sun does not shine 24 hours a day, acknowledge that the light density varies, highways surface deteriorate, dirt must be cleaned up and sweeper labour employed, cells would fade and corrode, electricity circulated far away, etc..

Existing conversion units and energy production units are high-priced and the typical efficiency of commercially manufactured solar sells do not exceeds more than 25 % even in the laboratory scale where it stays close to theoretical values. We can expect progress on amorphous ($\eta=13$ %) and crystalline silicon (24%), CuInSe_2 (18 %) and composed semiconductors (GaInP/GaAs/Ge at 32 %), the latter representing a danger due to poisonous nature of arsenic on its consequent disposal. On the other hand, silicon would have no dangerous wastes and is about 10^4 more plentiful on the earth than arsenic, gallium or indium but still needs a lot of energy for its manufacturing. If solar energies are to be more widely used it must become economically competitive – the consuming price is still above 5 US cents per kWh, at best, while conventional electric power plant can still deliver it ten times cheaper. In order to get a real progress, the photovoltaic energy production must obtain a strong economic impulse (earnest background and supporting bounteous finances) as well as a suitable profit like that which is still thriving in the coal or oil business. We have still to wait and, in the mean time, not to be disloyal to nuclear sourced energy sticking to often very naive argumentation about the hazard of nuclear wastes, which is relatively much less dangerous to the environment than the huge amounts of gaseous exhausts, pollutant ashes and other by-products (due to neutralization) produced by the classically fed power-plants.

In our widespread approach to theoretical treaties on thermodynamics we owe to it, last but not least, to guide its eclectic application into penetrating other fields, such as sociology or economy, as already preceded by one of the fathers of thermodynamics, *Lewis*, who wrote in the year 1923 a paper on plans for the economic stability process. Recently another attempt to apply thermodynamic rules to societal behaviour was introduced by *Mimkes*, who reasoned that notion of 'work' has the same meaning in physics as well as in economics. In fact, the economic work is calculated by costs in US\$ and in physics it is assessed in kWh. Both these values are linked through the outlay of energy. Work can be done by both, people or machines so that the efficiency may be calculated by the laws of works under the application of generalized thermodynamics cycle, which were once upon a time invented by *Carnot* (cf. Fig. 18.4.). Such thermodynamic examples of brief trips to the nature of sociology could give us certain ideas to improve the art of both the natural and humanistic sciences whose interconnections were more native until the past millennium when the notion of heat became the driving force for civilization progress and was analyzed to become the natural roots of thermal science.

Lastly, let us mention that it has been made known that even an artificial life⁵ can be shaped just on an 'inorganic' basis, even originated on a certain assembly of coding or

commands within the synthetic neuron structure (today often represented by an automaton-computer) or on their broader network (already possessing the launch of elaborate web, as represented by Internet). In order to accomplish any vital progress through the self-expansion (or even self-ordering), all systems need to compete for more working space developing various strategies to stay alive. Its logical complexity may even simulate the physical creation of biological life through very complex interactions within a continuous processes of self-organization.

Within this book we shall intentionally restrict our attention to the inorganic (lifeless) world, trying to emphasize some of its curious self-orderliness, which matches to the author's researching experience intimate to various inorganic materials, such as oxide magnetics and superconductors or metallic glasses and single-crystal semiconductors. Obviously, such an intentionally limited approach to thermal material's science has required the omission of the tremendously rich forte of organic and related biological materials but yet enables us to be logically guided to the world of natural fractality, often innate to life, which, besides the unavoidable mathematics, leads us in so far as to trace such subjects as reactions and methodic, energy resources and advanced processing, etc., which all have ever been the driving force in modern civilization and has led to master special heat-rooted technologies in order to produce the distinctively tailored belongings.

In order to facilitate the comprehension of generalized thermal analysis, in its broader view, covering various thermal-related phenomena and aspects of the impact of heat on societal maturity, we ventured to divide the text into five parts – interconnected volumes. Each of these contains four chapters to cover the distinct areas with the aim to provide a more general perception of the given sphere of interest. Among others, we sketched some humanity links trying to interlink the historical background with modern thoughts and advancement, showing basic aspects of thermodynamics and underlying thermal

analysis applicability to steady conditions adjacent to routine and feasible equilibrium. We want to briefly enter (not yet fully accepted and appreciated) the field of non-equilibrium treatments, to cope with some aspects of fractal geometry and chaotic behavior and, last but not least, to discuss some problems of environmental science with respect to the most appreciable item: the heat in terms of energy, its consumption and conservation policy necessary to furnish, with certainty, mankind's survival.

In every subject matter we, understandably, have to restrict our viewpoint which may still, however, be differently comprehended. Some might see it too immature in its professional inquisitiveness, such as the part dealing with engines (but important in our everyday life and habitual need for the fuel appraisal by combustion calorimetry). For others, some parts might be too complex for ready comprehension such as the discussion related to the concept of fractals or vacuum (the latter may, however, appear as the crucial point in the future portrayal of energetically accessibility). As in the other reports, the success of this written message would, certainly, become dependent on the authors' own laboratory experience, which is hopefully ensued by tackling not only generalized thermophysical measurements but also the special cases of advanced inorganic materials showing the role of vitrification upon quenching (glassy metals), the impact of synthesis technology to assure required non-stoichiometry and structure (superconductors) and the function of manufactured morphology to tolerate biocompatibility (ceramics tuned to cultivate osteoblasts). The examples were chosen from many appropriate materials, hopefully representative enough, similarly to other demonstrations shown in this book, where we just got the hang of other least potential examples, such as the fuel cells and wind as an incomplete demonstration of alternative energies. In spite of the fact that there are five volumes, this book should not be judged as separated in parts but rather comprehended as an all-encompassing text that aims to provide a more all-inclusive and interconnected vision of what thermal science is and what it can incorporate.

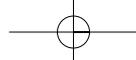
¹ This is the reproduction of the original drawing made by *Poincare* showing his experiment to distinguish that heat carrier particles. [M.-A. Poincare, *Essais de physique*, Manget 1790]. The instrument consisted of two opposite parabolic mirrors aligned in a precisely collateral position, common focal point equipped by a socket to keep a thermometer for measuring temperature changes while the other focal seated replaceable holders to operate variously worm substances. In the case of a candle insertion, the increasing temperature in the opposite focus documented that there was a heat flow between the mirrors in the direction from candle towards the thermometer. On contrary, when the candle was replaced by a piece of ice the thermometer displayed a definite temperature decrease which was explained by the opposite flow of particles of cold from the ice towards the thermometer. Why? – Try to solve it yourself?

² Equilibrium is the final state of time evolution at which all capacity for a system's change is spent. A system is a part of the Universe under study and separated from its surroundings by a real or imaginary boundary. Environment is the nonliving part of our ecosystem surroundings (including the water, soil and atmosphere). Mechanics is the branch of science that deals with motion of objects (material systems) and the forces that act on them. The momentum [$N \cdot s = m \cdot kg/s$] of an object of mass, m , and velocity, v , is defined as the product ($m \cdot v$). The impulse of a force on an object over a time interval equals to the object's change of momentum and can be seen as a sudden driving forward, push or impetus or the effect caused by impelling force. The force [in Newtons = $m \cdot kg/s^2$] is the influence on a body, which causes it to accelerate (a vector equal to the body's time rate of change of momentum) and work [in Joules = $kg \cdot m^2/s^2$] is the force that is exerted over times the distance over which it is exerted. The power [in Watts = $kg \cdot m^2/s^3$] is the measure of the amount of work done [J/s] or energy expended. Secularly, it has been found infeasible to give a generally strict definition to energy (as witnessed from *Poincare* to *Feynman*). What is sure that there is the principle of the conservation of energy, which simply signifies that there is something that remains constant. Nonetheless, energy is comprehended as the capacity for doing the work and work is thus the transference of energy [J/s] that occurs when a force is applied to a body that is doing some

Introduction to thermal science

action, such as moving, changing its state (of temperature, stress, etc.). Even more complicated is the connotation of the term entropy [J/K], which is the quantity that determines a systems capacity to evolve irreversibly in time. Its ascendant meaning follows from thermodynamics where it is understood as the function of state whose change in differential irreversible processes is equal to the heat absorbed by the system from its surroundings (Q) divided by the absolute temperature (T) of the system. In statistical mechanics it is the measure of complexion determined by logarithmic law, $S = k \log W$, where W of the number of possible arrangements of microscopic states involved in the system set-up and k is the *Boltzmann* constant. In mathematical context it expresses the amounts of disorder inherent or produced. In communication it is rented as a measure of the absence of information about a situation, or videlicet, the uncertainty associated with the nature of situation. Finally let us define two connotation of *Planck* constant either in [J s] as \hbar or in [J Hz⁻¹] as $h (= 2\pi \hbar)$.

- ³ Allow me to mention my youthful experience from the past Soviet Union, which I visited in the seventies and where, on one occasion, I went to a grocery to buy meat. A rawish cow was slashed piece by piece and given to persons waiting in queue without any chance to select the piece. On my turn I was ordered to get the newspaper at a neighboring news-stand to get the piece wrapped. It was a curiosity in view of modern services in the West, where meat was covered by plastic and at the pay-counter packed in another plastic sack again (as a product of ongoing scientific discoveries). A decade latter I went shopping for meat in a modern US hypermarket and at the pay-counter I was asked, do you have your own paper bag, you can get a discount – it is easier to eliminate wastes from paper (known already by Egyptians) than from plastics (introduced recently). We have to learn not only how to make progress with new materials but also how to make them easier for disposal by nature itself. (It well illustrates the spiral-like progress of entropy, as shown in the last part, cf. Fig. 17.6).
- ⁴ Accounting for the two limiting conditions of 0 and 1 (minus or plus) of the binary source, that the receiver accepts 0 with a probability of 9/10, and 1 with 1/10, so that the uncertainty of the source conditioned at the receiver is seen as $\{9/10 \ln_2 10/9 + 1/10 \ln_2 10/1\} = 0.47$ bit. Accordingly we can even account the construction of a single digit heat engine (*Szilard*, cf. Chapter 13, where $W = kT \ln 2$ and $\Delta S = k \ln 2 = 1$ bit), which would show the importance of the engine memory ‘cleanup’ (erasure of information data) as well as the capability to distinguish between the position or motion (up or down, right and left or minus and plus). Similarly, there can be presented a computer definition of algorithmic information without depicting any ensemble. It is defined as the length of the shortest processor encode (program usually in bits), fully specifying the state of a system, which is minimal when the string of morsels (bits) is entirely random. Although there is no known way to systematically approximate information, the average algorithmic entropy for an ensemble of similar systems can be well estimated using the *Gibbs-Boltzmann* entropy obtained via statistical mechanics. Likewise we can derive an optimal strategy for the investigator to formulate the question, and the information is thus a measure of how successful this strategy is. Namely, the information can be seen as the average number of questions asked until the right knowledge box is discovered. Clearly, as the box size, s, decreases the information must increase and its plot versus the logarithmic inverse scale reveal the traditional power law, $I_s \approx I_0 + D_1 \log_2 (1/s)$, where I_0 is a constant and the fractal D_1 characterizes the information growth (cf. Chapter 13.). Factually it can be seen as the additional amount of information obtained when doubling the resolution and is often called the information dimension ($1.21 < D_1 < 1.24$).
- ⁵ Natural life is analogically constructed and developed organic systems build upon the complex, carbon-based structures exhibiting rivalry for evolution, food and other forms of energy supplies, compulsory for them to survive at the given environmental conditions and competition from other species. They progress in time and space by tuning into the optimization of their self-reproduction. On the other hand, the computer is a digitally constructed inorganic system based on the logical machine instructions furnished by given hardware and software that may be even developed to contest each other for possessing enough space in memory and for acquiring sufficient processing time in order to prolong its functioning. However, certain population of digital codes may turn out to represent specific behavioral aspects of artificial life.



Volume one
ASPECTS OF HISTORY AND LINKS TO MODERN SCIENCE

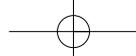
What makes thermal science beneficial?

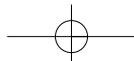
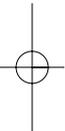
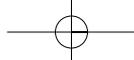
Roots of Western civilization

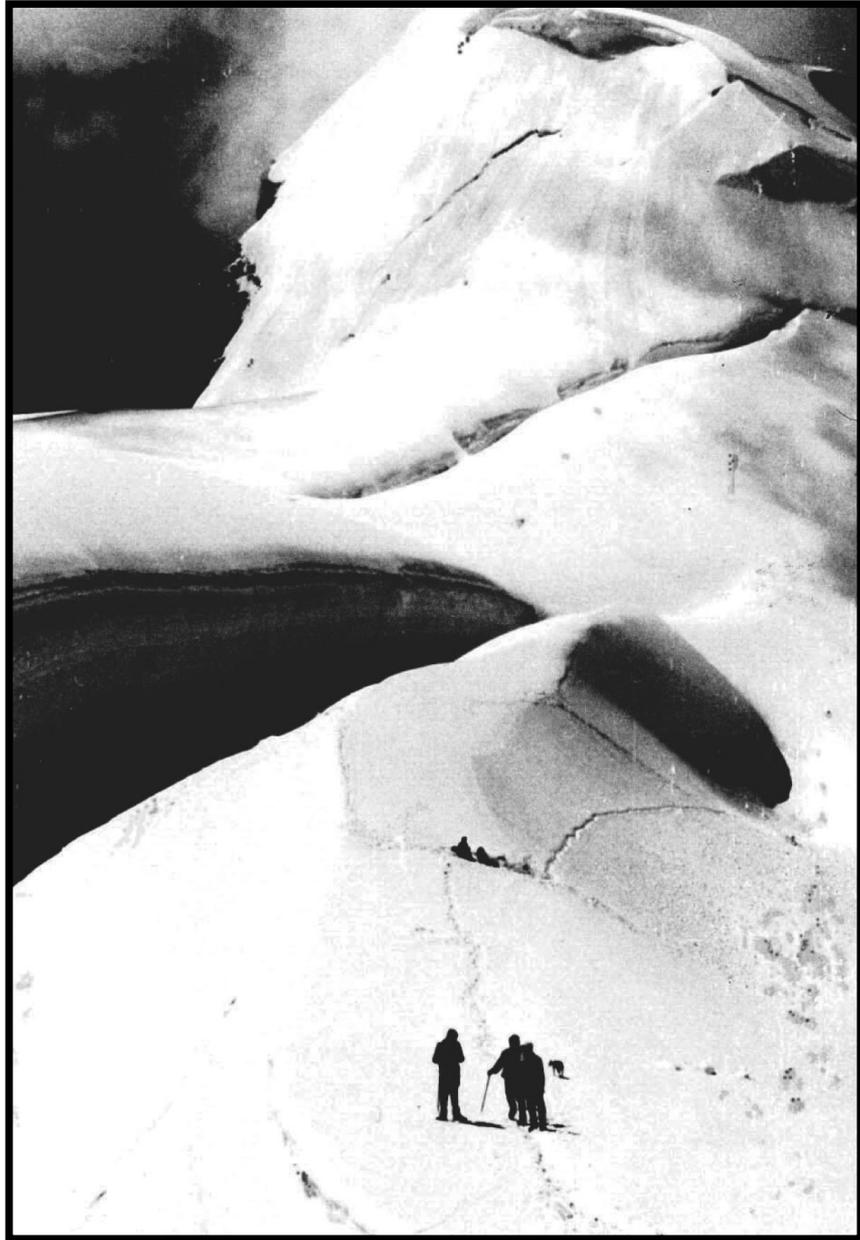
Fire as a philosophical archetype

Renaissance and the New Age

Literature







CHAPTER ONE

1. What makes thermal science beneficial

a) Searching nature and the scale dimensions

The understanding of nature and the pattern of its description are not given a priori but they have been developed according to how they were gradually encountered during, and assimilated into man's existing practices. It has been conditioned by the development of perceiving sensors and their interconnecting cobweb matured under the effect of mankind's manufacturing and conceptual activities. Evaluation of sensations required the definition of measuring values, i.e., the discretion of what is available (experience, awareness, inheritance). The sensation must be classed according to the given state of the organism, i.e., connected to the environment in which the evaluation is made. It has incorporated every-day occurrences and resulted in the outgrowth of so called state custom. It, however, is somehow subjective because for more objective proportions we must develop measures independent of individual sensation, i.e., scales for identifying the conceptual dimensions of our surroundings (territorial and/or force-field parameters such as remoteness (distance) or warmness (temperature), mutually having quite irreconcilable characteristics).

Our educational experience causes most of us to feel like inhabitants of a certain geographical (three-dimensional) continuum in which our actual position, or location, is not necessarily indispensable. A similar view may be also applied to the other areas such as knowledge, lastingness, warmness etc. If we were, for example, to traverse an arbitrary (assumingly 2-D) landscape we would realize that some areas are more relevant than others. Indeed, the relative significance of acknowledged objects depends on their separated distance – that can be described as their 'nearness' [1]. It can be visualized as a function, the value of which proportionally decreases with distance it is away from us, ultimately diminishing entirely at the 'horizon' (and the space beyond). The horizon, as a limit, exists in many of our attributes (knowledge, experience, capability).

When the wanderer strolls from place to place, his 'here', 'there', his horizon as well as his field of relevance gradually shifts whilst the implicit form of nearness remains unchanged. If the various past fields of relevance are superimposed a new field of relevance emerges, no longer containing a central position of 'here'. This new field may be called the cognitive map, as coined by *Havel* [1] for our positional terrain (as well as for our knowledge

extent). Individual cognitive maps are shaped more by memories (experience, learning) of the past than by immediate visual or kinesthetic encounters.

It is not difficult to imagine a multitude of cognitive maps of some aggregates to form, e.g., a collective cognition map of community, field, etc., thus available for wider public use. However, to match up individual maps we need to be sure of the application of adequately rational levels, called scales. Returning to the above geographical illustrations we may see it as the superimposition of large-scale maps on top of another smaller-scale maps, which, together, yields a more generalized dimension, called the 'spatial-scale axis'. A movement in the upward direction along this scale axis resembles zooming out using a camera (objects shrink and patterns become denser) while the opposite downward movement is similar to zooming in (objects are magnified and patterns become dispersed or even lost). Somewhere in the region center of this region (about the direct proportions one-to-one) exists our perception of the world, a world that, to us, is readily understandable.

Our moving up and down in the scale is usually conditioned by artificial instruments (telescopes, microscopes) that are often tools of scientific research. Even when we look through a microscope we use our natural vision. We do not get closer to the observed but we take the observed closer to us enabling new horizons to emerge and employ our imagination and experience. We may say that we import objects, from that other reality, closer to us. Only gradually, have physical sciences, on the basis of laborious experimental and theoretical investigations, extended our habitant picture of nature to such neighboring scales.

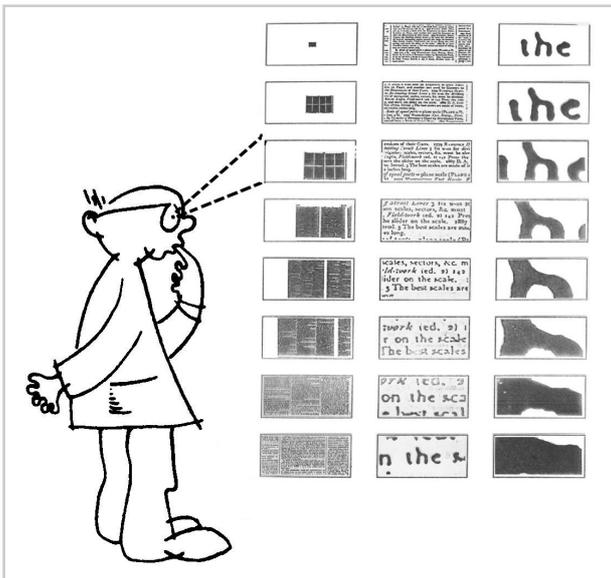
Let us consider the simplest concept of shape. The most common are squares or circles easily recognizable at a glance – such objects can be called 'scale-thin'. Certainly there are objects with more complex shapes such as the recently popular self-similar objects of fractals that can utilize the concept of the scale dimension quite naturally because they represent a recursive scale order. At its limit, some 'conclusive' fractal structures use to penetrate through arbitrary small scales, as its scale relevance function does not diminish as one zooms up and down along the exercise. It reflects a decision by modern physics to give up the assumption of the scale invariance (e.g., different behavior of quantum and macroscopic particles).

The role of mathematics in this translation is important and it is not clear to what extent mathematical and other scientific concepts are really independent of our human scale location and the scale of locality. *Vopěnka* [2] in 1989 proposed a simplifying program of naturalization of certain parts of mathematics: „we should not be able to gain any insight about the classical (geometrical) world since it is impossible to see this world at all. We see a world bordered on a horizon, which enables us to gain an insight, and these lead us to obtain nontrivial results. However, we are not seeing the classical, but the natural (geometrical) world differing in the classification of its infinity as the form of natural infinity“ (alternative theory of semi-sets that are countable but infinite beyond the horizon).



One consequence is the way we fragment real-world entities into several categories [1]: things, events and processes. By things, we typically mean those entities which are separable, with identifiable shapes and size, and which persist in time. Events, on the other hand, have a relatively short duration and are composed of the interactions of several things of various sizes. Processes are, in this last property, similar to events but, like things, have a relatively long duration. However, many other entities may have a transient character such as vortices, flames, clouds, sounds, ceremonies, etc.. There is an obvious difference between generic categories and particular entities because a category may be scale-thin in two different ways: generically (atoms, birds, etc.) or individually (geometrical concepts, etc.).

There is an interesting asymmetry with respect to the scale axes [3]; we have a different attitude towards examining events that occur inside things than what we consider exists on their outside. Moreover there are only a few relevant scales for a given object, occasionally separated by gaps. When considering, for example, a steam engine



the most important scale is that of macroscopic machinery while the second relevant scale is set much lower, on a smaller scale, and involves the inspection of molecules whose behavior supports the thermodynamic cycle. Whatever the scale spectrum in the designer's perspective is, there is always one and only one relevant 'scale-here' range where the meaning of the object or process is located as meaningful.

In the case of complex objects, there is a close relationship between their distribution over scales and a hierarchy of their structural, functional and describable levels. We tend to assign objects of our concern into the structural levels and events as well as processes into the functional levels. Obvious differences of individual levels yield different descriptions, different terminology (languages) and eventually different disciplines. Two types of difficulty, however, emerge, one caused by our limited understanding of whether and how distinct levels of a system

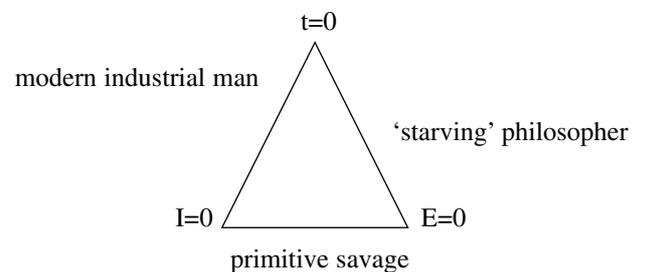
can directly interact and, the other, related to the communication (language) barriers developed over decades of specialization of scientific disciplines (providing the urgent need for cross-disciplinarity).

One of the first mathematical theories in science that dealt with inter-level interactions was the *Boltzmann* statistical physics, which are related to thermodynamics and the study of collective phenomena. It succeeded in eliminating the lower (microscopic) level from the macroscopic laws by decomposing the phase space to what is considered macroscopically relevant subsets and by introducing new concepts, such as the mannered entropy principle. It requested to widely adopt the function of logarithm that was already and perpetually accustomed by nature alone (physiology, psychology). In comparison, another scaled sphere of a natural process can be mentioned here where the gradual evolution of living parts has been matured and completed in the *log vs. log* relations, called the allometric dependence.

Another relevant area is the study of order/disorder phenomena acknowledging that microscopically tiny fluctuations can be somewhat 'immediately' amplified to a macroscopic scale. What seems to be a purely random event on one level can appear to be deterministically lawful behavior on some other level. Quantum mechanics may serve as another example where the question of measurement is actually the eminent question of interpreting macroscopic images of the quantum-scale events. Factually we use to construct 'things' on basis of information.

Humanities, particularly economics, are further fascinating spheres for analysis. However, its evaluation can become more complicated as individual scale-levels may be mutually and intermediately interacting with each other. Namely any forecasting is disconcerted assuming that any weather prediction (chaos) cannot change the weather itself while the economic activity displays the inevitable dependence of what is being evaluated or forecasted.

Yet another sphere of multilevel interactions is the concept of active information – another reference area worthy mentioning. Beside reciprocal interrelation to 'entropical' disorder we can also mention the growth of a civilization's ability to store and process information, which encompasses at least two different scales. On one hand, there is the need for a growing ability to deal with entities that become composite and more complicated. On the other hand, there is necessity to compress information storage into smaller and smaller volumes of space. The man's progress in its elaborateness is hinted at by the triangle [4] of his rivalry scales: time, *t*, information, *I*, and energy, *E*.



Weinberg is worth noting, who said, „time is likely to become, increasingly, our most important resource. The value of energy and information is, ultimately, that it gives us more freedom to allocate our time“. If we have lots of time we do not need much information because we can indulge in a haphazard of slow trial-and-error search. But if time becomes expensive, then we need to know the fastest way to do things and that requires lots of information and time organization. The above treated spatial ‘here’ suggests an obvious analogue in the temporal ‘now’ (temporal field relevance).

Thermal processes requires another, often forgotten, scale-dependent criterion that decide whether or not any (thermally) stable state is stable and in what scale, dimensionally viewing, maintains yet its stability. When the approached stability is of a simple natural scale this problem is more elementary but when equilibrium exists in the face of more complicated couplings between the different competing influences (forces) then the state definition of what is stability becomes rather more complicated. There can exist equilibria, characterized by special solutions of complex mathematical equations, whose stability is not obvious. Although the comprehensively developed field of thermal physics deals with equilibrium states it cannot fully provide a general law for all arbitrary "open" systems of stabilized disequilibria but, for example, it can help to unlock an important scientific insight for a better understanding of chaos as a curious but entire source for systems evolution.

b) Thermal feeling

One of the most decisive processes of men’s sensation is to understand *warmness* – the combined effect of *heat* and *temperature*. A stone under sunshine can be regarded as torrid, sunny, tepid, warm, hot, radiant, caloric, sizzling, fiery, blistering, burning, boiling, glowing, etc., and by merely touching it we can be mistaken by our previous feeling so that we cannot discern what is what without additional phraseology knowledge and practice¹. Correspondingly, under a freezing environment we can regard our sensation as wintry, chilly, cold, frosty, freezing, icy, arctic, glacial, etc., again, too many denominations to make an optimal choice.

We, however, would feel a different effect of sensation in our hand if in contact with an iron or a wooden bar that are both of the same temperature. Here we, moreover, are unintentionally making a certain normalization of our tactility by accidentally regarding not only the entire temperature of the bar but also the heat flow between the bar and the hand. Therefore the iron bar would feel to us colder. Curiously, this is somehow similar to the artificial parameter called *entropy* that is explicating different qualities of heat with respect to the actual temperature. Certainly, and more realistically, it should be related to the modern understanding of transient thermal property known as warm-cool feeling of fabrics (particularly applied to textiles) related to thermal absorptivity (characterizing heat flow between human skin and fabrics at given thermal conductivity and thermal capacity). The higher is the level of thermal absorptivity the cooler feeling it represents, see the Chapter 5.

However, the scale-concept of temperature [5,6] due to its practical significance in meteorology, medicine and technologies, is one of the most commonly used physical concepts of all. In a civilized world even small children are well acquainted with various types of thermometers giving the sign for "temperature" of either, a sick children, out-door suitability of environment, working state of a car engine or even microscopical distribution of energies. It should be noticed, however, that the medical thermometer can be deemed by children to be rather a healing instrument decisive for an imperative command to stay in bed, while the out-door thermometer decides how one has to be dressed, the position of a pointer on the dial in the car thermometer has some importance for the well-being of the engine while the absolute zero represents the limiting state of motionless order of molecules.

As a rule, there is no clear enough connection among these different scales of "temperature" given by particular instruments. For teenagers it is quite clear that all the things in the world have to be measured and compared so that it is natural that an instrument called a thermometer was devised for the determination of certain "exact" temperature – a quantity having something to do with our above-mentioned imperfect feeling of hotness and coldness. Invention of temperature is nothing but further improvement of modern life-style in comparison with that of our ancestors. Eventually, all the adults believe that they know what the temperature is. The only persisting problem is represented by various temperature scales and degrees, i.e. *Fahrenheit*, centigrade or *Kelvin* and/or *Celsius*. The reason for their coexistence remains obscure and common meaning is that some of these degrees are probably more ‘accurate’ or simply better – in close analogy with monetary meaning of dollars and euros.

Roughly speaking, it is true that modern *thermal physics* started to develop as the consequence of thermometer invention, thus, making possible optional studies of quantitative thermal phenomena. It is clear that there were scientific theories dealing with heat effects before this date and that the discovery of the thermometer did not make transparent what really temperature is. It took a still long time before scholars were responsive enough to what they were actually doing to make experiments with thermometers. In this light it may be quite surprising that the essential part of ancient natural philosophy consisted just of what we now may call thermal physics. These theories and hypotheses worked out by old philosophers remained still active even after the invention of thermometer and it was the matter of curiosity that led to build up of predicative theory of thermal phenomena paying little attention to such an important quantity as temperature? To give an explanation it is important to say a few words about these, for us quite strange, theories, in the following chapters.

The first conscious step towards *thermal analysis* was the man’s realization that some materials are flammable. Despite a reference to the power of fire, that is evident from early records, man at an early stage learned how to regulate fire to provide the heat required to improve his living conditions by, *inter-alia*, cooking food, firing cera-

mic ware and extracting useful metals from their ores. It occurred in different regions, at different times and in different cultures, usually passing from one locality to another through migration of peoples or by transmission of articles of trade.

The forms of power (energy, in contemporary terminology) generally known to ancient peoples numbered only two; thermal and mechanical (as the extraordinarily knowledge of electric energy, documented e.g. in the Bible, should be considered exclusive). From the corresponding physical disciplines, however, only mechanics and optics were accessible to the early mathematical description. Other properties of the structure of matter that include thermal, meteorological, chemical or physiological phenomena were long treated only by means of verbal arguments and logical constructions, with alchemy having there a very important role.

Thermal analysis itself imposes such modes of thermal measurement (general observation), which follow temperature changes in matter that are induced by absorption, or extraction of heat due to state changes. It is, fundamentally, based on the understanding of intensive (temperature) and extensive (heat, entropy) properties of matter. In an early conception of heat it, however, was believed

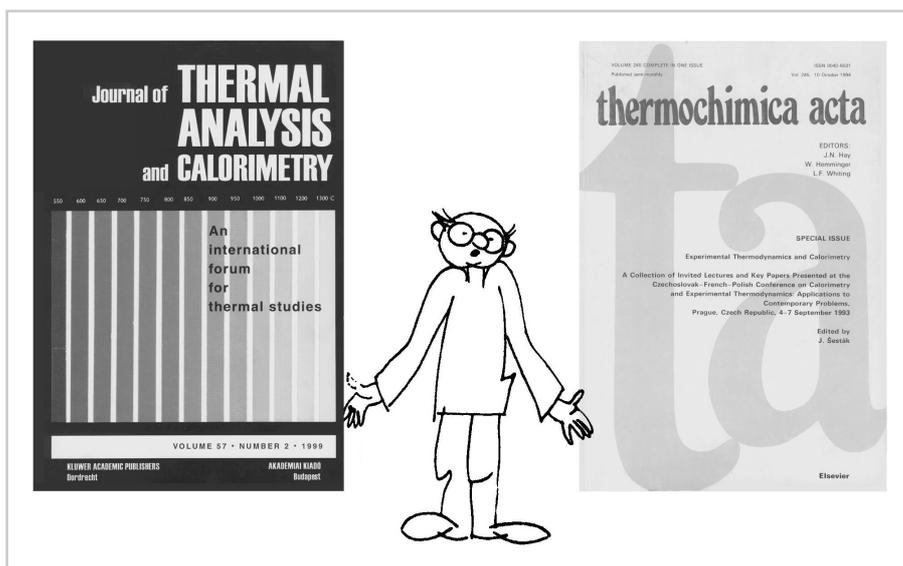
baths were recently described with respect to their architectural and archeological aspects. In detail, the heat loss from the reconstructed bath was calculated and the mass flow rate of the fuel was determined, allowing for the estimation of temperature and thermal conductivity [8]. It shows that the notion of thermal analysis should be understood in broader conjectures, a theme that is upheld as one of the goals of this book.

c) Databases in thermal material sciences

It is clear that the main product of science is information, and this similarity applies for the section of thermally related studies, too. There is seldom anything more respectable than the resulting data bibliographic bases, which store the information gathered by generations of scientists and which put them in order. On the other hand, there are still controversial issues and open problems to be solved in order that this information (and such derived *databases*) will better serve the ultimate endeavor of science – the pursuit of discovery and truth.

Let us make necessary remarks related to our specific field of interest, i.e., thermal science specified as *thermal analysis* as well as the attached *thermal treatment*. Let us mention only the two most specialized journals, *Thermal Analysis and Calorimetry* (JTAC)

and *Thermochimica Acta* (TCA), which cover the entire field of thermal analysis and related thermochemistry, and which naturally belong to a broader domain of journals concerned about material thermal science [9]. These two journals are members of a general family of about 60 000 scientific journals that publish annually about 10^6 papers on 10^7 pages. The questions thence arise as to the appropriate role of such specific journals, and their place among so many presently existing scientific periodicals. The answers to these questions may be useful not only for their Editors, but also for prospective au-



(*Rumford*) that there was a cold "frigorific" radiation as well as heat radiation [7]. This gave credence to the fluid theory of 'reversibly flowable' heat. Elements of this caloric theory can be even traced in the contemporary description of flow mathematics.

Thermal analysis reveals the thermal changes by the operation of thermophysical measurements. It often employs contact thermometers or makes use of indirect sensing of the sample surface temperature by various means (pyrometry). Therefore, the name for outer temperature scanning became *thermography*, which was even an early synonym for thermal analysis. This term is now restricted only for such thermal techniques that visualizes temperature by thermal vision, i.e., the thermal screening of the body's surface. Under the caption of thermal analysis, the heating characteristics of the ancient Roman

authors trying to locate their articles properly, as well as for researchers needing to identify suitable journals when the interaction between thermal specialties or disciplines pushes them beyond the borders of familiar territory.

It is generally recognized that almost three-quarters of all published articles are never cited and that a mere 1% of all published articles receives over half of the citations from the total number. These citations are also unequally distributed over individual journals. Articles written by a Nobel-prize winner (or other high-profile scientist) are cited about 50 times more frequently than an average article of unknown affiliation cited at all in a given year. About 90% of all the actual information ever referred to represents a mere two thousand scientific volumes, each volume containing roughly 25 papers. The average library also removes about 200 outdated volumes each year,

because of shortages of space, and replaces them with newer issues.

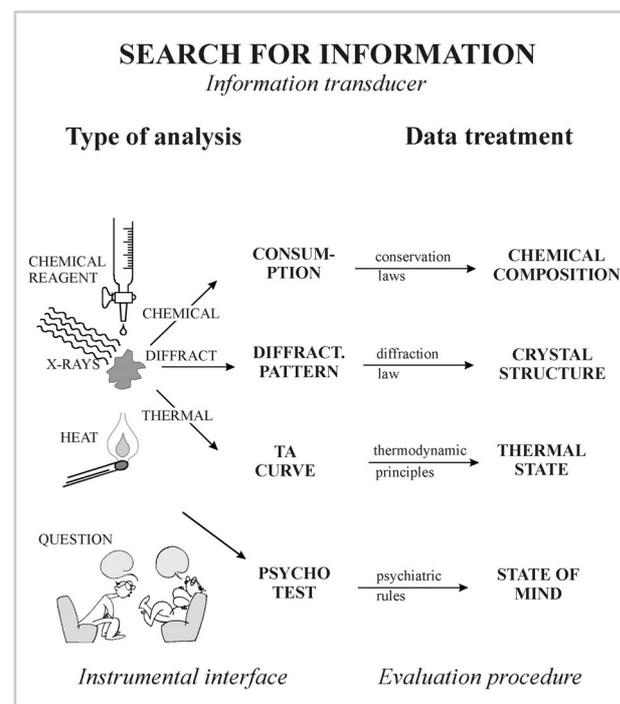
What is the driving force for the production of scientific papers? Besides the natural need to share the latest knowledge and common interests, there is the often repeated factor of "publish or perish" which is worthy of serious re-thinking, particularly now in the age of resourceful computers. We have the means of safeguarding the originality of melodies, patents and even ideas, by rapid searching through a wide range of databases, but we are not yet able (or willing?) to reduce repetitions, variations and modifications of scientific ideas. Printed reports of scientific work are necessary to assure continued financial support and hence the survival of scientists and, in fact, the routine continuation of science at all. It would be hypothetically possible to accelerate the production of articles by applying a computer-based "Monte Carlo" method to rearrange various paragraphs of already-existing papers so as to create new papers, fitting them into (and causing no harm in) the category of "never-read" articles. Prevention or restriction of such an undesirable practice is mostly in the hands of scientific referees (of those journals that do review their articles) and their ability to be walking catalogues and databases in their specialization.

The extent of the task facing a thermal analyst is potentially enormous [10–12]. For the 10^7 compounds presently registered, the possibility of 10^{14} binary reactions exists. Because all reactions are associated with thermal changes, the elucidation of a large number of these 10^{14} reactions could become a part of the future business for thermochemistry and, in due course, the subject of possible publications in JTAC, TCA and other journals. The territory of thermal treatment and analysis could thus become the most generally enhanced aspect of reactivity studies – why? The thermal properties of samples are monitored using various instrumental means. Temperature control is one of the basic parameters of all experiments, i.e., isothermal, constant heating/cooling, oscillating and modulated, or sample determined (during quenching or explosions). Heat exchange is always part of any experiment so reliable temperature measurements and control require improved sophistication. These instruments can be considered as "information transducers", invented and developed through the skill of generations of scientists in both the laboratory and manufacturers' workshops.

The process of development is analogous to the process for obtaining useful work; where one needs to apply, not only energy, but also information, so that the applied energy must either contain information itself, or act on some organized device, such as a thermodynamic engine (understood as an energy transducer). Applied heat may be regarded as a "reagent" which, however, is lacking in information content in comparison with other "instrumental reagents", richer in information capacity, such as various types of radiation, fields, etc. We, however, cannot change the contributed information content of individually applied reagents and we can only improve the information level of our gradually invented transducers.

This may be related to the built-in information content of each distinct "reactant", e.g., special X-rays versus universal heat, which is important for the development of the field in question. It certainly does not put a limit on the impact of combined multiple techniques in which the methods of thermal analysis can play either a crucial or a secondary role. Both interacting fields then claim superior competence (e.g., thermodiffraction). These simultaneous methods can extend from ordinary combinations of, e.g., DSC with XRD or microscopy, up to real-time WAXS-SAXS-DSC, using synchrotron facilities. Novel combinations, such as atomic force microscopy fitted with an ultra-miniature temperature probe, are opening new perspectives for studies on materials, and providing unique information rewards. However, the basic scheme of inquiring process remains resemblant.

In January 1999, the *Chemical Abstracts Service* (CAS) registered the 19 000 000-th chemical substance and since 1995, more than a million new substances have been registered annually. The world's largest and most comprehensive index of chemical literature, the CAS Abstracts File, now contains more than 18 million abstracts. About a half of the one million papers that are published annually in scholarly journals deal with chemistry that is considered as a natural part of material ther-



mal science. *Derwent*, the database producer and world's largest patent authority, registers some 600 000 patents and patent equivalents annually; 45% of which concern chemistry. One of the most extensive printed sources of physical properties and related data, *Landolt-Boernstein Numerical Data and Functional Relationships in Science and Technology*, has more than 200 volumes (occupying some 10 metres of shelf space).

In the area of enhanced electronic communications and the world-wide development of information systems,

electronic publishing and the Internet certainly offer powerful tools for the dissemination of all types of scientific information. This is now made available in electronic form, not only from computerized databanks, but also from primary sources (journals, proceedings, theses and reports). It has definitely increased the information flux available by orders. One of the greatest benefits of the early US space program was not specimens of Moon rocks, but the rapid advance in large and reliable real-time computer systems, necessary for the lunar-project, which now find application almost everywhere.

However, because of the multitude of existing data of interest to material thermal science and technology, and the variety of modes of presentation, computer-assisted extraction of numerical values of structural data, physico-chemical properties and kinetic characteristics from primary sources is almost as difficult as before. As a consequence, the collection of these data, the assessment of their quality in specialized data centers, the publication of handbooks and other printed or electronic secondary sources (compilations of selected data) or tertiary sources (collections of carefully evaluated and recommended data), the storage in data banks, and the dissemination of these data to end users (educational institutions and basic scientific and applied research centers), still remain tedious and expensive operations.

The total amount of knowledge, collected in databases of interest for materials science, is impressive. On the other hand, the incompleteness of this collection is also alarming. The eleven million reactions covered by the BCF&R database constitute only a negligible fraction of the total number of 200 000 000 000 000 binary reactions between nineteen million already-registered compounds, not even considering tertiary reactions, etc. In other words, lots of substances are known, but little is known of how these substances react with each other. We cannot even imagine how to handle such a large database containing information on 10^{14} reactions. The number of substances registered grows by more than a million compounds annually, so the incompleteness of our knowledge of individual compounds increases even more rapidly.

Materials thermal databases expand steadily and quickly, becoming more and more difficult to comprehend. Man perceives serially and the speed with which he receives information is small. It is estimated that an average researcher reads 200 papers annually. This is negligible to respect of the one million papers published in the sixty thousand scholarly journals throughout the world though a specialists needs to read a fraction. As a matter of curiosity, if a person could read the abstracts (about two minutes each) of almost 10^6 papers on relevant chemistry and physics processed during the last year by Chemical Abstracts Service, it would take him almost 20 000 hours in order to optimize the selection of those 200 papers. Factually it would take more than two years to complete!

Fortunately, there are other ways of making priority selections. One can trust the search for information to computers, which will quickly locate it by title, keywords, authors or citations, using complicated algo-

rithms. Unfortunately, the possibility of looking for atypical papers, which may bring unusual solutions beyond the frame of the algorithms used, is, however, lost. Such papers may be very important and valuable.

During recent years, most of the great discoveries made in any domain of science, touching thermal science in view of thermochemistry and material science, have developed from the uncommon concepts: quasicrystals, low-dimensional (quantum) electronics and optoelectronics, non- and nano-crystalline metals, high-temperature oxide superconductors and nano-magnetics (including their magnetocaloric effect), fullerenes, macro-defect-free cements, etc. Nature has provided such unusual and delicate chemical mixtures that there is not reason to expect them to occur spontaneously in natural environments, like a planetary surface or evolve from interstellar material.

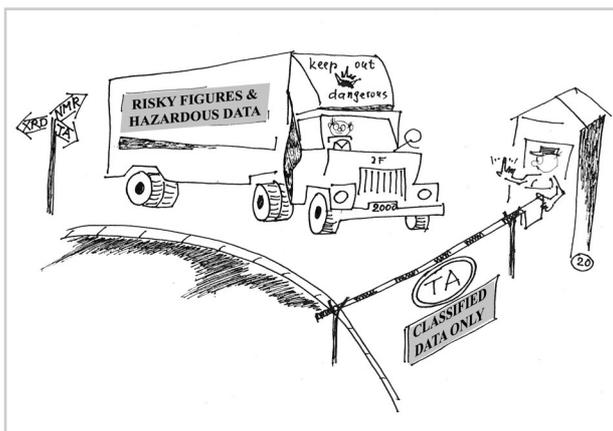
The intellectual treasure contained in scientific papers is great and any simplification of this body of knowledge by computers searches may lead to irreplaceable losses. People, however, will rediscover, again and again, things that were already described in old and forgotten papers which they were not able to find buried in overwhelming data-sources. This rediscovered knowledge will be published in new papers, which, again, will not fully succeed in passing into the hands of those who could make use of them. The unwelcome result is steadily and quickly growing databases, which might hopefully be capable of resorting overlapping data. We can even joke that the best way to make some data inaccessible is to file them in a large database. Curiously, large databases may be even seen to act like astronomical black holes in the information domain.

The steadily growing databases may attract a large number of scientists away from their active research, but it can also give jobs to new specialists engaged in information and data assessment itself. Scientists may spend more and more time in searching ever more numerous and extensive databases, hopeful of becoming better organized. This allows them to be acquainted with the (sometimes limitless) results of the often-extensive work of other scientists. On the other hand, this consumes their time, which they could otherwise use in their own research work and, are, accordingly, prevented from making use of the results of the work of the other scientists. Gradually the flow of easily available information may impact on even youngsters and students, providing them with an effortless world of irrationality developed through games, perpetual browsing the Internet, trips to virtual reality, etc. However, let us not underestimate its significant educational aspects associated with computers (encyclopedia, languages, etc.) and their capability to revolutionize man's culture. Another, not negligible, aspects is the beauty of traditional book-libraries; the bygone treasures of culture, and often a common garniture of living rooms where all books were in sight and a subject to easy touch and causal contemplating. Their presence alone is one that fills me with personal contentment.

If the aim of Science is the pursuit of truth, then the computerized pursuit of information may even divert

people from Science (and, thus, curiously thus from the truth, too). We may cite "If knowing the truth makes a man free" [John 8:32], the search for data may thus enslave him (eternally fastening his eyes to nothing more than the newborn light of never-ending information: a computer display).

What is the way out of this situation? How can we make better use of the knowledge stored in steadily growing databases? An inspirational solution to this problem



was foreshadowed already by *Wells* in 1938. He described an ideal organization of scientific knowledge that he called the 'World Brain' [13]. *Wells* appreciated the immense and ever-increasing wealth of knowledge being generated during his time. While he acknowledged the efforts of librarians, bibliographers and other scientists dealing with the categorizing and earmarking of literature, he felt that indexing alone was not sufficient to fully exploit this knowledge base. The alternative he envisioned was a dynamic "clearing-house of the mind", a universal encyclopedia that would not just catalogue, but also correlate, ideas within the scientific literature.

The World Brain concept has been applied by *Garfield* in 1978, who became a founder of the *Institute for Scientific Information* (ISI), of the ISI's citation databases and, in particular, co-citation analysis [14]. The references that publishing researchers cite, establish direct links between papers in the mass of scholarly literature. They constitute a complex network of ideas that researchers themselves have connected, associated and organized. In effect, citations symbolize how the "collective mind" of Science structures and organizes the literature. Co-citation analysis proved to be a unique method for studying the cognitive structure of Science. Combined with single-link clustering and multidimensional scaling techniques, co-citation analysis has been used by ISI to map the structure of specialized research areas, as well as Science as a whole [15].

Co-citation analysis involves tracking pairs of papers that are cited together in the source article indexed in the ISI's databases. When the same pairs of papers are co-cited with other papers by many authors, clusters of research begin to form. The co-cited or "core" papers in the same clusters tend to share some common theme, theoretical, or methodological, or both. By examining the titles

of the citing papers that generate these clusters, we get an approximate idea of their cognitive content. That is, the citing author provides the words and phrases to describe what the current research is about. The latter is an important distinction, depending on the age of the core papers. By applying multidimensional scaling methods, the co-citation links between papers can be graphically or numerically depicted by maps indicating their connectivity, possibly to be done directly through hyperlinks in the near future. By extension, links between clusters can also be identified and mapped. This occurs when authors co-cite papers contained in the different clusters.

Thus, the co-citation structure of research areas can be mapped at successive levels of detail, from particular topics and subspecialties to less-explicit science in general. It seems to be useful to have the numerical databases of materials interest related to the ISI's bibliographic databases. Each paper bearing the data under consideration cites and is cited by other papers, which determine its coordinates in the (bibliographic) map of (materials) science. In this way, definite data (a definite point in data space) is related to a definite point in bibliographic space (image of these data in bibliographic space). The correlation between data (objects, points in data space) is expressed (capable of locating) as correlations between their images in bibliographic space (which is a well-approved technique developed and routinely performed by ISI).

c) Horizons of knowledge

The structure of the process of creative work in natural sciences is akin to that in the arts and humanities as is apparent from the success of computerization, which is itself a product of science. An inspired process requires certain mind harmonization or better endowment of rhythm accordance, which is necessary in any type of communications (language, digits). Besides fractal geometry (natural scene, artistic pictures, graphical chaos), as an alternative to the *Euclide's* strict dimensionality (ornaments, geometrical structures), there are no margins that science shares with art in some unique and common way of 'science-to-art'. They both retain their own subjects and methods of investigations. Even an everyday computer-based activity, such as word processing, or even computer-aid painting, has provided nothing more than a more efficient method of writing, manuscript editing, graphics, portrayal or painting (popular 'Photoshop') similarly applied even to music. It has indeed altered the way in which the authors think; instead of having a tendency to say or draw something, now they can write in order to discover if they have something to write (or even to find).

Spontaneously mutual understanding through a concord of rhythms is, as a matter of interest, a characteristic feature of traditionally long-beloved music, well familiar in various cultures. The way that it forms melodies and that it combines sequences of sound brings about the swiftness of an optimum balance of surprise and predictability. Too much surprise provides non-engaging random noise while too much predictability causes our minds to be soon bored. Somewhere in between lies the

happy medium, which can intuitively put us on a firmer, rhythmical footing. The spectrum of sequences of sounds is a way of gauging how the sound intensity is distributed over different frequencies. All the musical forms possess a characteristic spectral form, often called '1/f noise' by engineers, which is the optimal balance between both, the unpredictability, giving, thus, correlations over all time intervals in the sound sequences.

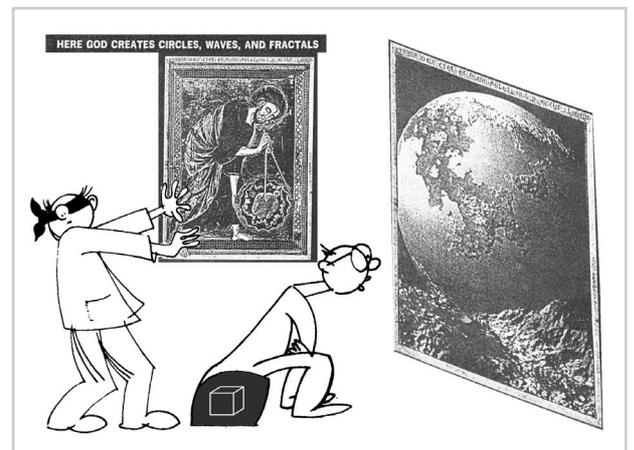
So that when a musical composition is in style, i.e., that is highly constrained by its rules of composition and performance, it does not give listeners too much of new information (adventure). Conversely, if the style is free of constraints the probabilistic pattern of sounds will be hard to make it result in a less attractive style than the optimal 1/f spectral pattern. Distinguishing music from noise, thus, depends then entirely on the context and it is sometimes impossible and even undesirable to discern. It is close to the everyday task of physics, which is the separation of unwanted, but ever-presented noise away from the authentically (repeating) signal, or even ballast figures out of the true mathematical theory, which all is long-lasting challenge now effectively assisted by computers. All other creative activities, like painting, poetry, novel writing or even architecture have displayed similar trends of getting away from constraints. The picture of artistic evolution is one of diminishing returns in the face of successful exploration of each level of constrained creative expression. Diversity has to be fostered and a greater collaboration, easier connection and rhythm eavesdropping between minds, between people and organizations should be a measure of progress.

Separation of natural sciences from philosophy, and the development of specialized branches of each scientific field, led to the severance of thinking which is now tending back to re-integration. Its driving force is better mutual understanding, i.e., finding a common language to improve the comprehension of each other and the restoration of a common culture. Thus, the cross-disciplinary education, aiming to inter-bridge natural sciences and humanities, i.e., certain 'rhythmization of collaborating minds', has become a very important duty to be successfully run through the third millennium. It should remove the mutual accusation that the severe philosopher's ideas have initiated wars and bright scientific discoveries have made these wars more disastrous.

All human experience is associated with some form of editing of the full account of reality. Our senses split the amount of facts received; recognizing and mapping the information terrain. Brains must be able to perform these abbreviations together with an analysis of complete information provided by individual senses (such as frequencies of light, sound signals, touch discerning, etc.). This certainly requires an environment that is recognizable, sufficiently simple and capable to display enough order, to make this encapsulation possible over some dimensions of time and space. In addition, our minds does not merely gather information but they edit them and seek particular types of correlation. Scientific performance is but one example of an extraordinary ability to reduce a complex mass of information into a certain pattern.

The inclination for completeness is closely associated with our linking for (and traditional childhood education towards) symmetry. Historically, in an early primitive environment, certain sensitivities enhanced the survival prospects of those that possessed symmetry with respect to those who did not. The lateral (left-right) symmetry could become a very effective discriminator between living and non-living things. The ability to tell what a creature is looking at it clearly provided the means for survival in the recognition of predators, mates and meals? Symmetry of bodily form became a most common initial indicator of human beauty. Remarkably no computer could yet manage to reproduce our various levels of visual sensitivity to patterns and particularly our sense of loveliness.

Complex structures, however, seem to display thresholds of complexity, which, when crossed, give a rise to sudden jumps in new complexity. If we consider a group of people: One person can do many things but add another person and a relationship becomes possible. Gradually increasing this scenario sees the number of complex interrelations expand enormously. As well as applying



nature, this also applies for the economy, traffic systems or computer networks: all exhibits sudden jumps in their properties as the number of links between their constituent parts over-grows. Cognizance and even consciousness is the most spectacular property to eventually emerge from a very high level of complexity achieved within a connected logical network, like the top neuron organization of the brain.

Such a complex phenomenon can be explained as the outcome of a huge number of mundane processes organizing themselves, over a long period of time, into a structure which learns in the same way that a neural network does: the consciousness would be like a computer 'internet' system that evolves by a microscopic version of natural selection gradually incorporating its novel hardware and software. Supercomputers can always outperform the brain in specific abilities, particularly by applying speed in performing repetitious tasks. But a high price is paid for their lack of adaptability and their inability to learn about themselves or combine with others, in yet unknown ways, enabling collaboration. In the nearest future the

personal computers will be able to figure out what the owner is doing and provide him with some kind of useful service without any cognitive load on him (e.g., monitoring health).

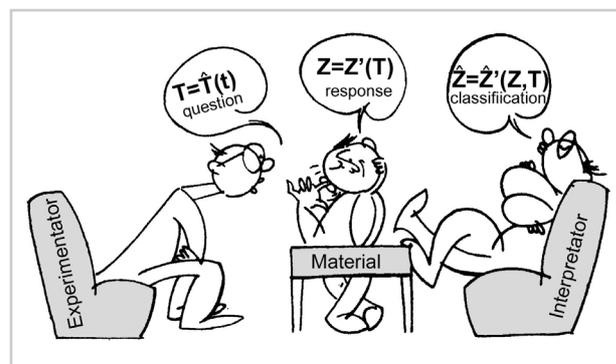
Worth noting is the long-lasting battle of whether the thoughtless computer can ever beat the first-class intuition of a chess world-champion, which has recently turned in favor of a computer; despite its perfunctory capability to merely check the millions of possibilities, it is also able to find the most appropriate move in a negligible period of time. In some way, the computer expeditiousness may, thus, become competitive to man's fore-thought discretion. Pure physicists, however, believe in basic mathematical structures behind the laws of nature and, to the astonishment of biologists, they dare to introduce computational things (like quantum gravitation and intrinsic non-computability at the microscopic level) in order to explain macroscopic features of the mind as a complex computational network.

Computing, in its usual sense, is centered on the manipulation of numbers and symbols. Recently, there has arisen computing with words, in which the objects of computation are propositions drawn from a natural language, e.g., small, large, light, dark, heavy, close, far, easy, difficult, etc. Such a kind of manipulation is inspired by the remarkable human capability to perform a wide variety of physical and mental tasks without any measurements and any calculations, such as parking a car or driving it in a heavy traffic, performing diverse skills and sports or understanding speech and body-language. Underlying this remarkable capability is the brain-like capability to manipulate perceptions of distance, speed, color, sound, time, likelihood and other characteristics of physical and mental objects. A basic difference between perceptions and measurements is that, in general, measurements are crisp whereas perceptions are fuzzy. The fundamental aim of science is continuous progression from perceptions to measurements. But alongside the brilliant successes of these steps forward there stands conspicuous underachievement and outright failure to build computerized robots with agility of animals or humans.

The new computational theory based on perceptions, introduced by Zadeh and called *fuzzy logic*, is based on the methodology of computing with words, where words play the role of labels of perceptions, expressed as propositions in a natural language. Among the basic types of constraints are possibilistic, veristic, probabilistic or random sets, fuzzy graphs and usualities. There are two major imperatives: (i) if the available information is too imprecise (or exceedingly multifarious) to justify the use of numbers, or (ii) when there is a tolerance for imprecision or indistinctness, which can be exploited to achieve tractability, robustness, prudence, low-solution expenditure and better rapport with reality. Although the fuzzy logic is still in the initial stages of development, it may gradually play an important role in the conception, design and utilization of informatively intelligent systems.

Recently we have also become attentive to the traditional method of learning only from our mistakes, customarily passing on information genetically from generation to

generation. We can pass on information by word of mouth, over written message, over airwaves or using modern network means of the Internet. This information can influence any member of the species that hears it. The time that it takes to convey information is now very short and its influence extremely wide. The evolution of human civilization witnesses to the constant search for better means of communication [17]. In 1943 the chairman of IBM has said that the world market can absorb about five super computers and just 30 years later there was the opinion that there is no reason for every individual to have a desk-computer in their homes. Earlier everyone expected that computers would just keep getting bigger and more powerful² as well as expensive, the reality was opposite: Computers got smaller and cheaper, and more and more people could afford to own them. Their co-acting effectiveness developed most impressively by linking them together into huge world spanning networks. It helped the further development of intellectual capabilities of individual 'brains' not by their further evolution but by the sophisticated level of their computerized collaboration. In any complex system it is not so much the size of the components that are of primary importance but the number of interconnections between them alternating the neuron



network. Creating the power of a gigantic interconnected computer, through a web of connections between an overfrowning numbers of small devices, is a pattern that has developed within the human brain, however, the Nature, undoubtedly, got there first.

It is a well-known opinion that collaboration provides exciting opportunities for research and understanding, which individuals working alone could not realize in the past. But collaboration presents new issues to be addressed as we design new environments for this cooperation. The key is to identify how truly "great" feats of teamwork materialize. Nowadays, it is clear there are not as many brilliant individuals as there are brilliant collaborations. In considering collaboration, one must deal with issues involved in the inter-relationships among the individuals in a particular group activity. For example, how can the system reduce friction that may develop between two persons or groups? The value added to a project by collaboration is not only found in the replication of information for each participant, but more importantly, the type of people who use the system. It is not the task of mercantile calculus but of non-equilibrium thermodynamics.

The kind of networks we require depends on what type of experts we want to draw together. People are information processors, but if you define them as such, you end up with a warped sense of what people are really all about. As we change the quantity and quality of people with information, we change the quality of their behavior. This seems rational, but if you think about it, if information was really the most valuable and important thing, the people who run our organizations would be the smartest – that clearly is not the case. Some other variable must be making the impact – and that variable is *intelligence* – one of the few elements of modern mankind that cannot be distributed democratically. For example, people smoke, even though they know it is harmful to their health, people drink alcohol and drive, even though they know they should not threaten others by their drunken outing. One of the most important design shifts is that we must structure information not for itself, but for its effect on relationships. We are slowly moving from "creative individuals" to "creative relationships" as a new source of information.

The real value of a medium lies less in the information it carries than it does in the communities it creates. The Internet is as much a medium of community as it is a medium of information retrieval. Consider *Gutenberg* in the 15th century. At the time, the new medium was movable type. The Bible was the first book ever published and became the medium of the community. During the Reformation period, alternative understanding and interpretations of the Bible developed simply because of its wider distribution through the society of the time. The results of successful collaborations in the past are many, among others: the flying airplane and the atomic bomb, quantum physics and thermal sciences, the double helix and personal computers. Even the Internet was originally a tool to help physicists to collaborate. Such cooperation consists of several aspects: *Communication* = an essential ingredient but not a synonym; bandwidth does not control success; *Participation* = a means to the end; a required attribute, but again, not a synonym and *Process* = a shared creation/discovery that the individuals could not have done it alone.

Famous biologists, the Nobel price winners, *Watson* and *Crick* both said they could not have come up with the double helix secret of life working alone (e.g. without knowing the x-ray image of DNA observed by *Franklin*), though their instinct helped them to realize that the base pairs do not match like with like but rather assorted as A-T and G-C. It means that there are individual geniuses, but the problem that they face are often bigger than they can solve if working in isolation. The value came from the interactions and the spread of technology now allows more people with more information to interact. A key element of all success is 'shared space' – it is needed to create 'shared understanding'. The properties of the environment shape the quality of the collaboration. Chalkboards have limits for example, but computers present many more possibilities. We can scale shared space by making it intelligent – perhaps we need to think of the computer as a facilitator. Intelligence is derived and applied in a myriad of ways. Sometimes we must recognize

that others have more intelligence than ourselves – sometimes we must realize that we hold the key to success if we could just convince others that this is the case. Communication is an act of intelligence, but often the final and/or initial legs of the communication link become "fuzzified" and the message does not get sent or received as intended. The "quality" of the intelligence becomes muddled.

In this context, the disposition of a man-made intelligence will soon become of important attentiveness. Biological life proceeded from very complex interactions of originally simple inorganic units through the continuous process of self-organization (see Chapter 16.). Its imitation complement, called "artificial life", is believed to arise cognitively from complex (logic) interactions to take part within computer (neuron) software. Both such variants, come what may, follow the original vision of *Neumann's* and *Turing's* idea of a certain structure (or organism) simulated by a cellular (digital) automaton, today electronic computer. Our common health troubles are brought in by viruses, known as a short length of DNA/RNA wrapped in a protein coating that fits cell receptors and replicates itself using the cell's machinery. It can be anticipated as an infectious structure (organism) where its appropriately managed mission (having implementation as its driving force) is rewarded by benefiting more space to live. In a similar fashion, computer viruses can be seen as certain embryos during the operation (soon also creative) process, in which the virus competes for more working time (or memory space) in the computer processor, closely similar to any animals' fight for food. Viruses can multiply themselves when finding breeding-ground, developing new strategies on how to survive or even capable to messenger themselves to another environments. It was already shown that an artificial creature can be formed by a certain bunch (collection) of instructions (coding) lone. They are, however, still missing the feature of real life – mutative self-replication in order to trace evaluation adaptation to their surroundings and cohabitants.

d) *Appraisal of Internet*

It is at these times, that we must regroup in our own mind and attempt to examine the issues in a fresh manner in order to see the other person's viewpoint. Collaboration is much more than sharing workspace and experiences. Collaboration, by its very nature, is a form of intelligence on its own – the process of collaboration is as important as the starting point and the end. If we can keep this in mind, then we may be able to achieve the "greatness" that comes from great collaboration. Have you ever met or worked with someone with whom you seemed able to communicate with by telepathy – someone who was able to anticipate your ideas and needs and vice-versa. It is a wonderful thing to find someone with whom you are "sympatico". It might be your spouse or a close colleague or a son, daughter or other close relative. It may be a friend who shares common values, interests, skills, etc. The basis for the closeness can be many different things. The question is – "Can we create or even, hope to create, such closeness over the Internet?"

But if we want to predict the future and understand what is likely to be upon us, it is necessary to step back and examine the most important revolutionary technology to ever appear on Earth. What is the Internet and from where did it come? Some will talk about AOL or Microsoft as if they are the same thing as the Internet. Others will refer to pornography and the dangers inherent on the "Net" from this dark side of society. Throughout the history of humanity, there have been many significant revolutions, such as the Renaissance and the Industrial Revolution that permanently changed how people lived their lives. But none of these changes has occurred as quickly, as universally and as unceremoniously as the Internet Revolution. The Internet affects every corner of our world in profound ways -- at home, at school, and at work -- our lives are different, not necessarily better, but certainly different, as we move into the Information Age. The motto of the Information Age is "Information is Power" and if this were true, then we are the most powerful generation who has ever populated the face of the Earth.

From simple words to the latest hit-song to the ingredients required in a favorite recipe to how to make a pipe bomb, there is almost nothing you cannot find out about with a little effort and access to the World Wide Web. In the early days of the 90s, many businesses had to be forced to adopt Internet-based technology. But today, companies involved in mining, manufacturing, transportation, communications, etc. are now using the Internet routinely since the benefits are so self-evident. Businesses, such as bookstores, are not necessarily located down the road anymore, they can now be found online. It is worth recognizing that an Internet-based business can market their products globally without needing an actual store -- they only require good distribution channels. The Internet automates many business processes and transactions; it reduces costs; opens up new markets; and empowers



customers and potential customers in ways that couldn't even be imagined 10 years ago. The Internet allows small businesses to compete with large corporations, provided that a professional online presence is developed and maintained. We can communicate almost instantly with anyone in the world, whether it is with family or friends abroad or business associates. Letters and Faxes of yesterday are now the E-mails of today and who knows what may turn up in the near or distant future.

Anyone who uses the Internet, cannot fail to be impressed with its power, but how did it all come about? In order to understand where we might be going, it is useful to briefly explore its history. In 1958 the US Department of Defence formed the Advanced Research Projects Agency (ARPA) to enhance the dominance of the United States in military science and technology. ARPA (later to become DARPA) was formed in direct response to the launching of the Russian satellite Sputnik in 1957 -- an event which made the United States military sit-up and take notice. The first references to the social interactions that could be enabled through networking were written by *Licklider* of MIT in 1962 in which he discussed his concept of a "Galactic Network". He envisioned a globally interconnected set of computers by which anyone could access data and programs anywhere in the world, much like the Internet of today. *Licklider* was the first head of the computer research program at ARPA and he was able to convince his successors of the importance of this networking concept. By 1965, while trying to establish efficient communications systems, ARPA developed the concept of a distributed network. A study on networked time-sharing computers, was conducted using three computers that communicated with each other over a 1,200 bps phone line: one at ARPA headquarters, a second at MIT and another across the country at Systems Development Corporation in California. This led to the initial design of what would become ARPANET.

In 1968 when ARPANET merged with ARPA a contract was let to a company known as BBN to build the Interface Message Processor (IMP) network in which 4 IMP nodes connected computers over 50 kbps phone lines. As ARPANET grew in the 1970s, other independent networks sprung up that would later be connected to it. 1971 saw the first inter-machine message transfer which was then implemented on ARPANET in the following year, along with the introduction of the @ -- symbol in the address scheme. Much larger configurations of up to forty machines were demonstrated and other countries began to develop their own versions of ARPANET. Specifications for Telnet were devised in 1972. The year 1979 saw the invention of USENET -- a system of newsgroups which quickly grew to become the main way that university students and researchers communicate and share information on subjects of all sorts. The early 1980s saw a period of rapid network expansion around the world. Networks appeared based on the specifications of the 70s and many of the older networks began to change from independent entities to cooperating nodes in what was now an International network. The Number of hosts Innovation progressed as follows: 1968 (10 links) ARPANET, 1978 (100) USENET, 1988 (100,000) World Wide Web/HTML and 1998 (100,000,000) first software agent. In 1993, a company, called 'Internic', was created to manage the Internet through services contracts with AT&T, Network Solutions, and General Atomics. In each successive year, more and more countries established connections to the network making it a truly worldwide network. HTML has now become the main standard for delivery of the hypertext approach to information originally envisaged in 1945

by *Bush*, a system he called 'Memex'. The potential of this new medium was quickly realized. In 1993, Mosaic (the first real web browser which evolved into Netscape) experienced unbelievable growth as more and more people went online. The Web continued to expand, and in 1994, the first e-businesses opened, the first cyber-banks appeared and "dot com" became the most popular, sought-after domain name extension. By 1995, use of the Web surpassed that of FTP. With the increased demand, authorities began to charge to register a domain name. A most notable innovation was the development of search engines, by which one can find information from all over the world.

We can imagine that the Internet makes research blind to proximity and scale. It, however, may bring some disadvantages rarely discussed. While they may not bring the whole human quest for further knowledge crashing to a stop as a result of some uncontrollable computer virus destroying everything (all important steps in the progress of civilization paid a high price such as yellow fever victims during the construction of Panama seaway). These adverse factors might well move human progress along certain unwitting tracks or, at least, frustrate progression by reduction in diversity of views. Unnoticed it might even forbid the types of questions that are undesired to ever appear.

Forbidden knowledge is also a controversial subject. All modern states have secrets that they hope to keep concealed from certain people for various reasons. Recently this issue has been running into controversy with the imposition of restrictions on the Internet³ lying beyond the means of a government's computer system to break. Like any proprietary or dangerous possessions (guns or even cars) it may be a subject to some imposed restrictions for the common goods, just as in the same way that like the PIN numbers of credit cards are secured. Powerfully widespread communication networks may become exceptionally vulnerable to the novel forms of attacks – conventional assault of society order (robbery, shooting wars) being replaced by computer and mobile-phone fraud, cyber-terrorism (hackers' attacks on the computer control systems to trigger a disaster), cyber-espionage, etc. It is not far from early installed religious taboos usually framed in order to maintain the exclusivity of certain gods. Moreover the insightful network of satellites, massive use of cellular phones and coupling all home facilities, schools and further organization with Internet, can help establishing a kind of police state of everyone being under continuous but unnoticed control (communication, opinions, location). Such an inquisitiveness state can even match the *Orwell's* famous sci-fi of ever-watching "Big Brother" situated in the early year 1984 as an ironic picture of the past Soviet Union dictatorship.

Strict domination over communications seems to be an important, if not crucial, tactic in the recommencement of modern wars, where the instantaneous knowledge of the enemy's location, and the decoding its messages, facilitates the precise guiding controlled missilery. The blocking or jamming of your enemy's communication resources along with its broadcasting and, on the contrary, dissemination

of false instructions and spreading propaganda or fear is an equally powerful weapon as the use of conventional explosives. Widely accessible information can help to dismantle autocratic regimes without uprising; just by free available news. Alternatively, too much free information can narrow the creative approach of people or better students if readily available for transcription without the individual's creative impact.

The harder the competition, the greater is the pressure to gain a marginal advantage by the adoption of innovation. Progressives will have been better adapted to survive



in changing environments than conservatives. Sometimes science advances by showing that existing ideas are wrong, that the past measurements were biased in some way or old hypothesis were misleading. Much of the everyday business of science involves the gradual expansion of little islands of knowledge, deepening the interconnections between the ideas and facts within their environments. Progress is made not by new discoveries but by finding new ways in which to derive known things, making them more simple or efficient.

Comfort, however, may become disincentive to further modernization. Most inhabitants of the Western democracies live luxuriously when compared with the lot of their distant ancestors. Looking forward we might wonder whether the direction in which advanced technological societies are moving will create less work, longer lives and greater leisure, and whether this might eventually remove the incentive to innovate in science and technology. On the other hand, the technological process itself can reveal a serious downside. It often creates environmental problems that outweigh the benefits that the technology was designed to alleviate. Also our own situation in the Universe and our technical capabilities have not been intended in a design view to the completion of our knowledge of the Universe which does not exist for our convenience only.

There are limits with what we can do and know – the skill and knowledge is cumulative and we can only build on what we already know. Existence is precarious –

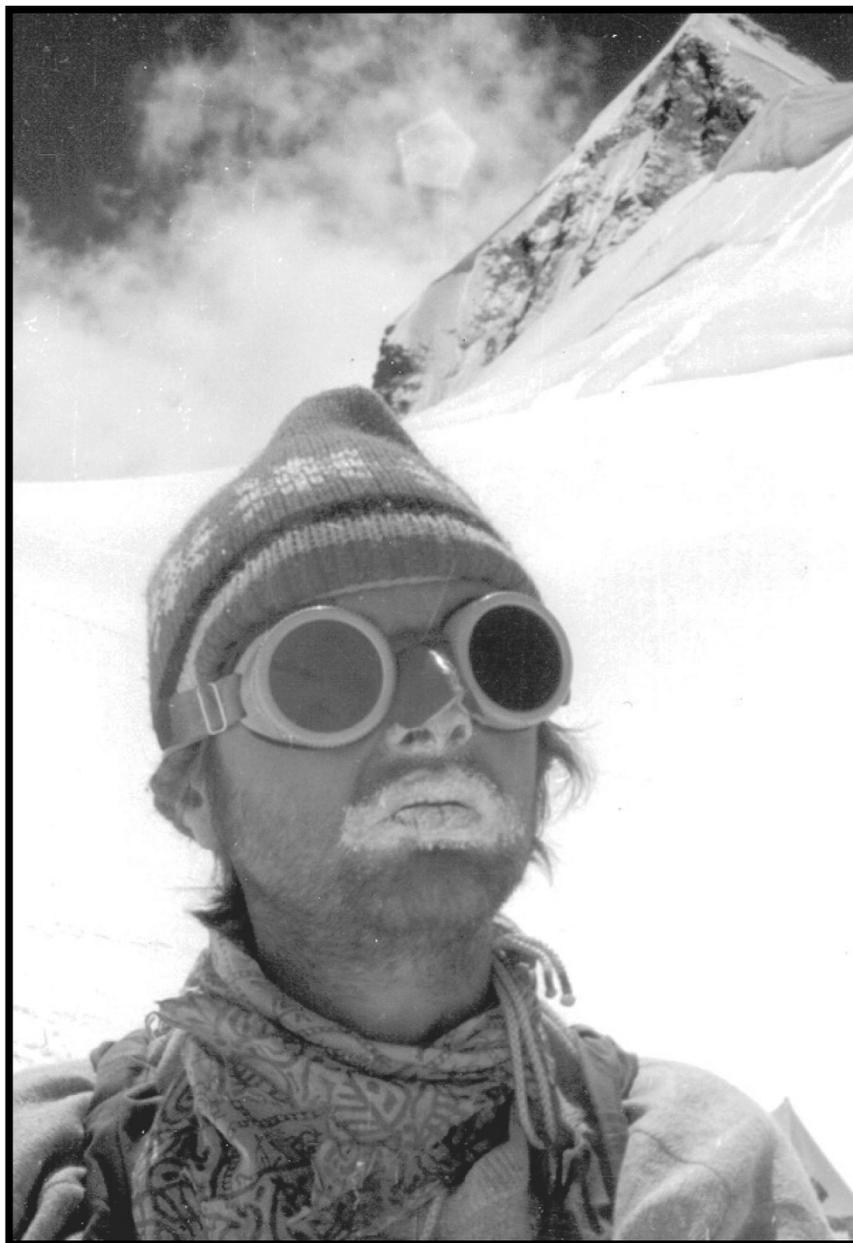
as the world becomes an increasingly sophisticated technological system, it is intensifying the risk from the consequences of its own headlong rush for development. It is difficult to get politicians and democracies to plan for the far future as there are enough problems for today and tomorrow. Even if a civilization would grow befittingly

and would not suffer self-destruction, it will ultimately face environmental crises of cosmic proportions as the earth lacks resources, stars run out of nuclear energy and galaxies disintegrate – nothing to worry about yet in our somehow what narrow-looking and often self-foolish societies.

¹ Early man used to describe various occurrences by vague notions (such as warmer-cooler or better-worse) due to the lack of development of a larger spectrum of appropriate terminology. Only *Pythagorean* school (~ 500 BC) resumed the use of numbers which was factually consummated by *Boole's* (~ 19th century) logical mathematics of strictly positive or negative solution. Our advanced life faces, however, various intricacies in making a completely precise description of complex processes by numbers only, thus falling beyond the capacity of standard mathematical modeling. It implies a tendency to return from the computing with numbers to the computing with words, i.e., byway from the manipulation of consequently developed measurements back to the somehow original manipulation of perceptions (called 'fuzzy logic').

² Although the computer story is not the endeavor of this book it seems be useful for a brief mentioning. Its beginning can be traced back to the vision of uncompleted construction of *Babbage's* analytical calculation engine together with the *Boole's* theory of binary character of veracity. The first machine called Electronic Numerical Integrator and Computer (ENIAC) was gradually developed, it appears, towards the middle of forties and was adapted on basis of *Von Neumann's* and *Turing's* proposed variant as ACE (Automatic Computing Engine). It already defined the unit of information as a *bit* (binary digit) and a *byte* (as an elementary set of eight bites). The computing process became controlled by the Central Processing Unit (CPU) which distributes orders to specific repository sites (memory file) within a specific rhythm (pace) of controlling clock (frequency). After the integrated circuit was introduced by the year 1959, it made it possible for INTEL to develop the chip 4004 and consequently the famous microprocessor 8080 (1974). The machine speed grew to be important as floating point operation (FLOP). The computer architecture became a significant issue – from the *von Neumann* 'pipeline' structure to the CRAY's introduction of vector processing in 1976. Latter a centered CPU system was used to orchestra the subdominant array of CPUs to carry simultaneously their individual computing business yielding either the SIMD (Single Instruction – Multiple Data) and/or the alternative MIMD (Multiple Instruction – Multiple Data) and enabling neighboring CPU to carry independently on the different tasks. Complexity of infrastructure provided the idea to give the hardware as few as possible instructions and for the remaining instructions to be transferred to the sphere of software (as IBM's RISC – Reduced Instruction Set Computer). In result it provided a certain incompatibility with the more classical CISC (Complex Instruction Set Computer) as well as lending a hand to the development of competing structures of computers and programs.

³ There, however, is the risk of over-abundant cumulating of ballast information through, e.g., unwanted distribution of unasked data, advertising and promoting rubbish or other yet unknown inflows. This danger has become particularly painful in the recent Internet, which assimilates and helps intermediate large amounts of unsolicited Email (Spam). The consequent need of unpolluted figures is thus acquired through a sort of data cleaning (data filters) in order to confine the storage load. Here we can behold certain analogy with a biological computer (our long-perfected brain), which terribly needs a sensible management to avoid brain overflow (or even its perpetual outgrowth), intricate by multiple levels of input data (rational, emotional, etc.). It is worth mentioning that recent hypothesis correlates the sleeping phase called REM (rapid eye movement) with an assortment and filtrating processes, which factually undertake survival role of the disposal of a day-package of input information to those that are useful to store or useless to disremember (trash). This allocation process depends on the antecedent state of comprehension so that the REM stage is found longer for newborn and shorter for older individuals apparently depending to the extent of experience how to analyze, sort and collect input data. Of course, this kind of self-improving process is yet outside the capability of our artificial automatons-computers.



CHAPTER TWO

2) The Roots of Western Civilization

a) *Heat as a manufacturing tool*

The notion of fire (light, heat, caloric and more recently even energy) is thoroughly recognized as an integrating element, rudimentary in the pathway of ordering matter and society [18]: It has a long history, passing through several unequal stages in the progress of civilization. From the chronicles of interactions of society with fire we can roughly distinguish about four periods. Perhaps the longest age can be named the period *without fire* as the first human beings were afraid of fire/blaze (like wild animals) but, nevertheless, eventually gained their first sensation of warmth and cold. The first man-made fireplace dates as being about 300 000 years old, but artifacts of ashes resting from different burned woods (apparently composed unnaturally by early man) can be even associated with prehistoric *homo erectus* dating back to one and half million years ago (Koobi Fora, Kenya). Another extended era was associated with the growth of the continuous experience of *using fire* which helped, in fact, to definitely detach human beings from animals (fire as weapons or as a conscious source of warmth) by substantially aiding the cooking of meat as to make it more easily digestible. The associated development of cooking also increased the range of palatable foodstuffs and allowed for more time to be spent on activities other than hunting.

A definite advancement came with the recent but short period of *making fire*, up which preceded the *exploitation of fire* that included the domestication of fire and its employment as a tool and energy source until the present use of heat as an instrumental reagent. Even the ability to use fire for many specific purposes is conditioned by the smallest flame defined by the balance between the volume of combustible material available and the surface area over which air/oxygen can fuel the combustion reaction. As the volume of combustible material gets smaller, the surface becomes too small for the flame to persist, and it dies. Small stable flames are well suited to the needs of *creatures of human size* the tallness of them is affected by the straight downward force of gravity. The opposing direction (buoyancy) of heat was viewed as a contradictory force to gravity that holds people attached on the earth forcing all bodies to finish in rest (i.e., the equivalence of motion and rest for a thrown stone). Moreover people witnessed that a small ignition (spark, impetus) could lead to catastrophic results (fires, avalanches), i.e., unique circumstances (singularity) can give way to the concealed potentiality hidden in the system.

The earliest inventions of mankind were always connected with application of fire in providing and/or processing not only food but also in procuring natural or processed materials for making them useful or ornamentally attractive. The first man-made artifacts were hand-molded from clay known as early as about 15000 years BC and primeval ceramic objects stem 7000 years latter from the Mesolithic period. The name ceramics is derived from Greek word '*keramos*', i.e., potter's clay or vessel, but its origin may be even older, from Sanskrit, where

a similar word means 'firing'. The '*potter's wheel*' is a Mesopotamian great invention dated from the 3rd millennium BC and is responsible for a significant improvement in ceramic technology and cultural life.

Based on the experience gained in producing glazed ceramics by smelting copper ores and in preparing mineral dye-stuffs, people discovered how to obtain enameled surfaces by fire-melting the readily available mixture of silica, sand, lime, ash, soda and potash. The first steps in this direction were made as early as some 7000 years ago by putting in service *natural glasses*, as 'tektites' (believed to be of meteoric origin), obsidians (glassy volcanic rocks), 'pumice' (foamed glass produced by gases being liberated from solution in lava) and 'lechatelierite' (fused silica sand in deserts by lightning striking or meteorite impact). Through history, glass was always regarded to have a magical origin: *just to take plentiful sand and plant ashes and, by submitting them to the transmuting agencies of fire to produce melt which whilst cooling could be shaped into an infinite variety of forms which would solidify into a transparent material with appearance of solid water and which was smooth and cool to the touch, was and still is a magic of the glass workers art.*

Invention of man-made glass was accomplished somewhere on the eastern shores of the Mediterranean prior to 3000 BC, but no hollow glass vessel dating earlier than the second millennium BC has been found. Glass technology reached a high degree of perfection in Mesopotamian and Egypt, especially sometime during 500 BC when one of the most important brainchild, a '*blowpipe*', was invented (around 50 BC probably in Syria), which turned glass into a cheap commodity and provided the stimulus for the proliferation of glasswork throughout the Roman Empire.

Nearly as old is the technology of binding materials obtained by lime burning for the preparation of lime-gypsum mortars. These materials were already used in Phoenicia and Egypt in about 3000 BC. It was the Romans who invented concrete made of lime with hydraulic additives known as 'pozzolana' and volcanic tuff. In Mesopotamia the experience of firing ceramics was also applied to the melting of copper, and, latter, of gold and silver that led finally to the metallurgical separation of copper from oxide ores. Copper, however, was known in Baluchistan as early as by 4000 BC and bronze by 3500 BC. Around 2500 BC excellent properties of alloyed copper (silver, gold, arsenic) were discovered followed by tin in 1500 BC and iron about 500 years latter. About 3000 BC articles on lead also appeared and starting from 2500 BC the Indians began to monopolize the metallurgy. Whilst bronzes were mixed phases prepared intentionally, the admixture of carbon was introduced into the cast iron, and, later, steel by chance, and its unique role could not be explained until recently. Even ancient Chinese metallurgists clearly appreciated that the relative amounts of copper and tin in bronze should be varied depending on the use for which the articles were intended. Iron could already be melted and poured by about 500 BC and steel appeared as early as by 200 BC depending on the thermal and

mechanical treatment. The medieval skill belonging to the Persians in cold-hammering swords of exceptional quality was based on the ability to pour bimetallic strips of low (tough) and high (brittle) carbon-containing steel and its consequent mechanical interpenetration. All such progress was intimately associated with the skill and knowledge of fire-based craftsmen, such as metal-smiths, who had had to have the experimental know-how of, for example, how intense the fire must be to make the metal malleable, how fast to quench an ingot, and how to modify the type of hearth to suit the metal involved.

Operational stuffs, called *materials*, have always played an important position in the formation and progress of civilizations. It was always associated with the relevant level of intercourse (*communication*) and comprehension (*information*). We can learn about their history from archeological sites as well as from recent dumps and waste-containers. Applicability of materials is traditionally based on working up their starting ('as cast') mass to shape a final and refined structure. Today's science, however, tends to imitate natural processing as closely as possible and, in this way, wastes less by positioning definite parts to appropriate places. This ability forms the basis for the development of so-called '*nanotechnologies*'. It has long been a dream of scientists to construct microscopic machines, such as motors, valves or sensors on the molecular scale. They could be implanted into larger structures where they could carry out their invisible functions, perhaps monitoring internal flows or even some vital biological functions¹.

The tremendous growth of certain groups of individual materials will, in time, be restricted in favor of those materials that are capable of recycling themselves, and thus pose the smallest threat to nature. Living structures are yet becoming more and more of an observable example, particularly assuming the synergy of various components in combined materials. Such composites are common not only in nature but also known within human proficiency: from Babylonians times (3000 BC), when resin impregnated papyrus or tissue was used, up until recent times when the icy airfields of the Greenland used sandwich composites made from brittle ice strengthened by layers of newspaper. It appears that we must follow the models of the most efficient natural composites, such as hollow fibrils in cellulose matrix that make up wood, or collagen fibers such as in hydroxyapatite found in our teeth.

In the reproducibility of technological processes, the artificial production of glass and cement (originally volcanic and slag) and iron (primarily meteoritic) have played a decisive role in the progress of civilizations – their production recently amounting to a tremendous 10^{11} kg per year (with the total world need of energy sources close to ten giga-tonnes of oil equivalent). Reproducibility of technological processes, in which ceramics and metals were worked to produce the desired wares, could be secured only by experienced knowledge (information, data-storing) as well as by the resulting accustomed measuring techniques. Its development could only take place after people learnt to think in abstract categories such as are

used in mathematics whose beginning reach as far back as the fourth millennium BC. Production became feasible only after it matured to be consciously determined, keeping constant and optimal values, such as mass proportions of input raw materials. Thus, as well as the others, the Egyptians knew the double-shoulder balances as early as 3000 BC. The notion of the equality of moments as the forces acting on the ends of an equal-arm lever was surely one of the first physical laws discovered by man and applied in practice. Weighing (of pouring in water) was even used as a convenient means to measure time intervals more precisely.

Ahead of growth of industrialization, we should also realize what the more powerful and far-reaching the benefits of a technology are, the most serious being the by-products of technologies' misuse or failure. The more structure that a forward-looking manufacturing process can bring about randomness, the further its products depart from thermal equilibrium, and the harder it is to reverse the process that gave the rise to them. As we project a future of increasing technological progress we may face a future that is advanced but increasingly hazardous and susceptible to irreversible disaster.

In order to make technological progress, mankind had to acquire progressive techniques of producing high enough temperatures. First they applied controlled heat not only by using the closed kilns but also by using sitting kilns or smelters in regions prone to high winds. The role of air had to be understood in order to get the process of burning coordinated. It was also vital to keep certain temperatures constant; hence it was necessary to introduce some early-experimental temperature scales. The relation between input mixtures, mode of fire treatment and resulting properties were initially recognized and then, subsequently, experimentally verified during the preparation of other compounds such as drugs, dying materials and, last but not least, in culinary arts. This all led to the early recognition of three principles of early thermal treatment and analysis [19], i.e., *amount of fire (temperature) can be level-headed, applied fire affects different materials in different ways, and that materials stable at ordinary temperatures can react to give new products on firing.*

It is clear that fire has always played a significant role as an explicit *tool* either in the form of an *industrialized power* (applied for working materials by men long ago in the process of manufacturing goods), or latter as an *instrumental reagent* (for modern analysis of the properties of materials). In contrast to a mechanical machine, that provides a useful work upon the consumption of potential energy received from the surrounding world, it was recognized that any practical use of heat must include changes involved in the explored system itself. In the principle sphere of dynamo-mechanics (in an ideal world detached from disturbances caused by e.g. friction) the efficiency of mutual conversions between potential and kinetic energies can approach a theoretical 100%.

Heat engines, however, cannot be only a passive machinery – just protecting two components, with different temperatures, to get in touch, or not, with each other

at the right moment (similar to the restriction of two parts, moving with different speed, to come, or not, into the required mechanical contact with each other). We should remember that reversible changes furnish the capacity to effect the system and its control – the initial conditioning can restrict the dynamics of an object. Model thermodynamic behavior can be similarly specified if well-defined reversible changes are available for an equilibrium state. For that reason any irreversibility is seen negatively as it is realized by lively irrepressible changes when the system gets out of the standard control. It follows that thermal systems can be controlled only partially; accidentally they may arrive at a spontaneous stage of a surprising character.

b) Mechanical motion and heat transfer

The incompatibility between the time-reversible processes taking place in the mechanics of body-like species (including molecules), and irreversible thermal processes responsible for the equilibration of temperatures (for example in an unequally heated rod) required a better understanding of the inherent phenomena involved, particularly the nature of heat. In sequences it led to the formulation of a consistent science of *thermal physics*, developing the related domain of *thermal analysis* and touching on any adjacent field of science where temperature is taken into account.

In fact, it was initially based on the early and erroneous premises of a non-material notion called '*thermogen*' (or superior term '*caloric*'). It can be also seen as the application of *different* premises regarding the manner of individual approach of theoretical modeling. The caloric theory supplied an obvious solution to the problem of thermal expansion and contraction, which postulated and described an opposing force to that of the attraction between particles caused by gravity. In order to stay away from a total gravitational collision, which would produce a single homogeneous mass, the opposing force was considered to be the '*self-repulsive caloric*'. Such an early 'fluid' hypothesis became important in the formulation of modern laws and was common to the way of thinking of *Archimedes*, *Epicureans* and latter used in the *Carnot's* and *Clausius's* concept of thermodynamics [20,21], up to the present day truly dynamic theories of non-equilibrium, introduced by *Prigogine* [22,23]. Even our everyday use of heat flow equations applied in thermal analysis bears the "caloric" philosophy.

However, the notions of heat and temperature (*temperament*, first used by *Avicenna* in the 11th century) were not distinguished until the middle of the seventeenth century (*Black* [24]). It took another 150 years until the consistent field of thermal science was introduced on basis of *Maxwell's* works [25–27] and named by *Thompson* as '*thermodynamics*' according to the Greek terms '*thermos*' – heat and '*dynamis*' – force. The term contradiction of it 'dynamic' notion against its 'static' applicability (*thermostatics*) is thus a common subjected of examination. The thermodynamic account was, although, complicated by the introduction of an artificial quantity to counterpart the

intensive parameter of temperature in its sense of gradients. After the Greek '*en*'-internal and '*trepo*' – turn it was called *entropy* (meaning transformation and proposed by *Clausius* in sound analogy with the term energy). This action factually eliminated heat from further mathematical framework. In effect the famous law of thermodynamics gives the *quotation of energy conservation law but only under specific conditions for heat that is not fully equivalent with other kinds of energies*. Heat cannot be converted back to mechanical energy without changes necessary to affiliate heat with entropy, via the second law of thermodynamics, which intuitively states that heat cannot be annihilated in any real physical process. It brought a conceptual disparity between the fully reversible trajectories of classical mechano-dynamics and the evaluator world governed by entropy. It may somehow be felt that the domain of thermodynamics was initially positioned at a level of *esoteric* ('those within') doctrine.

Only the statistical thermodynamics (*Boltzmann*) interconnected the micro-cosmos of matter with phenomenological observables under actual measurements. The famous Boltzmann constant gave the relation between the phenomenological value of temperature and the average kinetic energy of motional free atoms – submicroscopic species. In the evaluation of heat capacity, *Einstein* and *Debye* associated temperature with these distinguishable micro-particles (array of atoms), each oscillating around lattice sites where all degrees of freedom correspond to the vibrational modes (assumed either as independent harmonic oscillators or as an elastic continuous medium with different frequencies). The vibrational nature of some forms of energy (as that of heat) was a very valuable and inspirational idea related to an old *Pythagorean* idea of chord harmony tuned in rational ratios.

The nineteenth Century was the period of industrial revolution. Scientists studied the efficiency of machines of all sorts, and gradually build up an understanding of the rules that govern the conservation and utilization of energy. The laws of thermal physics were one of the results of these investigations, most famously stating that the artificially introduced parameter known as entropy of a *closed* system can never decrease. In practice, this means that, even though energy can be conserved in some physical processes, it is gradually degraded into less ordered and less useful forms. It is habitually observed that the entropy of any closed system becomes steadily more disordered. This is not a kind of law as gravity might be classified, but a principle having a statistical nature and very important to consider what is technologically possible.

Latter an interconnection between entropy and information (its gain or loss) was found. If we are to obtain information about the state of a system then there is always a cost. It was the *Maxwell's* sorting demon¹ that made it clear that it is not possible to create or cause a violation of the second law of thermodynamics, any more than it is possible to show a profit at roulette by always betting on all the numbers. The cost of such a long-term strategy always outweighs the possible benefits. It follows that

information can be seen as a commodity that takes effort to acquire, and it is possible to classify all technological enterprises in terms of the amount of information needed to specify its structure, or what level of information would be required to introduced a change in the system (organization improvement, etc.).

Information is thus expensive to acquire – it costs time and energy. There are limits to the speed at which that information can be transmitted, and limits to the accuracy with which it can be specified or retrieved. Most importantly, however, is that there are powerful limits on how much information can be processed in a reasonable periods of time. Even the speed at which light travels is limited.

An ever-increasing experience with burning revealed that released heat always lead to volume increase. Cognizant employment of fire was accordingly utilized by *Newcomen* (1705) and improved by *Watt* (1800) and *Stephenson* (1813) while constructing a *steam heat engine* and, latter, a functional *locomotive* although they were not aware that part of the heat is transformed to motion. It was, however, a qualitative step in making a better use of coal (as a traditional source of heat for personnel working in manufactures) and made it the main source of mechanical energy for use in industry and home, replacing other traditional sources such as animals, water and wind. This new scheme actually interconnected the three of the early elementary forms [28]: heating *water* by *fire* to get a thick *air* (steam) capable of providing useful work (moving piston and turning a wheel). Latter on, this idea was improved by *Lenoir* (1868, gas-engine) and particularly *Ott* (1878) and *Diesel* (1892), who imprisoned the burning fire directly inside a cylinder and, thus, constructing thus a shaped *earth*. Certainly, a confident know-how was indispensable, or better saying, a particular use of the directed (in) formation. The miracle of the nineteenth century, i.e., the four stroke combustion engine, was brought to life! Restricted by thermal laws, it gave a practical dimension to thermodynamics and showed the essence of a sequence process controlled by the four cycle series, which both started and ended in the same position. The encircled loop of given pair of the associated (intensive and extensive) parameters granted access to a convenient estimate of the energy gain (or, better, generally assumed assets, goods).

All this put an emphasis on the importance of mechanical ‘know-how’ to every-day life. Heating a room when it is cold and cooling it when it is hot is also a matter of know-how (an exchange of information). Various thermal flows are set up to partially modify the natural laws determining the movement of the air in the room. The ingenious control torque (governor) of a heat engine, invented by *Watt* using the principle of the excess centrifugal force, was realized experimentally by the famous parallelogram with springs, two balls and steam valves. It illustrates well the advanced information portrayal though there was nothing known about its inherent control function in the terms of modern state vectors.

However, the moment of birth for modern scientific thought probably occurred a few years earlier, in 1811,

when *Fourier* was awarded the prize of the French Academy of Sciences for the material description of heat transfer in solids: *the heat flow is proportional to the temperature gradient*. This simple proportionality revealed a new potential that latter achieved more general applicability (analogical equations applicable for diffusion, quantum-mechanics of waves, etc.). In its simplicity *Fourier’s Law* was considered somehow similar to the *Newton’s Laws* of mechano-dynamics, but its novelty led to a set of new classifications, the evaluation of which put heat and gravity at a contradiction to one another. Gravity can move a mass without causing an internal change, whilst heat puts matter in motion while reforming, at the same time, its internal properties. Similarly to *Boerhaave’s* statements [29] “*heat is propagated and its distribution is equalized under all circumstances*” it supports the idea that propagation of heat is an irreversible process. Moreover, there was a belief that something is ‘qualitatively conserved’ and something is ‘quantitatively converted’. In the year 1847, *Joule* introduced an equivalent for physical-chemical changes and helped to finally define energy as a joining element between physical-chemical and biological processes.

Ultimately the idea of the *thermal engine* has developed into a wide variety of engines, turbines, pulse-jets and other power cycles all still governed by the same principles of thermodynamic efficiency for the external and/or internal utilization of heat/fire. Similarly to any hydroelectric turbine, we should remember that the combustion engine is an open system – it consumes oxygen and fuel at a higher potential energies than at which it produces heat and combustion products. Such a desired pattern of activity produces, however, disorder and thus fully complies with the second law of thermodynamics. The energy produced by the automotive open system of an engine is literally kept alive on the production of excess amount of heat depleted to its surroundings. The second law of thermodynamics tells us that we need to do work in order to acquire information.

This way of thinking is very general and allows us to quantify the cost of any computation. In any sphere of human activity it is not enough to be in possession of a procedure to solve a problem. We need also to know the cost of its implementation, either in terms of time, money, energy or computation power. This knowledge opens to us the possibility of finding a procedure that is better, in the sense of being more cost-effective. Foreshadowing the work of *Prigogine’s* self-organization, there was introduced in 1920s the *science of structures*, as pioneered by *Bogdanov’s tektology* (from the Greek ‘tekon’ – builder), and was the first attempt to arrive at a systematic formulation for the principles of organization, which can function in non-living and living systems. It was followed by *Bertalanffy’s general system theory* [30] aimed to develop self-guiding and self-regulating machines that try to solve the problems of interactions and regulation, which lead to an entirely new field of investigation that had a major impact on the further elaboration of the system view of life.

It inspired *Wiener* to invent a special name '*cybernetics*' (derived from the Greek '*kybernetes*', meaning steersman) as to describe the joint science of control and communication in the animal and the machine. Its importance became the theory of information developed by *Shannon* when trying to define and measure the number of signals (information) transmitted through telegraph lines. It is worth mentioning that the clockworks of the seventeenth Century were the first autonomous machines, and for the next three hundred years they were the only machines of their kind. Computers invented recently are novel and unique machines that can work autonomously, once turned on, programmed and kept ongoing by sufficient energy supply. Computers, however, do something completely new – they process information. As *Descartes* used the clock as a metaphor for the body, *Neumann* used the computer in his cybernetic believe and as a metaphor for the brain introducing there the human relevant expressions of intelligence, i.e., computer *memory* and *language*.

Any variety of useful machinery, that has been developed by means of human cognition (mind) have, however, a relatively short history, just a couple of thousand years. The evolution of life, on contrast, exhibits a history that is several orders longer, perhaps billions of years, and even a live cell can be understood as a *precisionally fine-tuned machine* that was gradually constructed through the ages as an extraordinary sophisticated set of interrelated parts (molecules) that harmoniously act together in predictable ways insuring thus the progressive development, variability, and selective survival of more of its kinds and efficient use of energy. Its "know-how" is recorded in DNA memory that possesses a capacity for creative mutations of its structure (internal development of certain "cognition" [31,32]), which permits further evolution of its machinery cell into forms needed to prosper successfully upon the Earth's continuously changing face. It is clear that the space-time structures do not remain stable and that some of the subsequently mentioned principles, such as chaos and/or entropy versus order and/or information, penetrated into other fields such as humanities, sociology, economics, etc. Generalized course of cycling, which makes a process in such a reliable way as to exhibit coequality of the initial and final points, is necessary to retain the procedural capacity for its continual periodicity.

The short history of human civilization is beyond comparison with the much longer history of life. The recently constructed mechanical engines bear a level of matchless sophistication in comparison to the mechanism of living cells, which have undergone very slow but continual development. Thus, the present-day propensity for the fabrication of macroscopic human tools is tending to avoid the undesirable aspects of self-destruction by introducing, e.g., *pure technologies*, the produce ecologically harmless byproducts (*clean engines*) but are, however and unfortunately, less efficient. This downfall is, however, being overcome by technique such as *miniaturization*, which tries to simulate a more efficient level of the molecular

tools from living cells. The so-far conventional approach of a "top-down" technology starts with a large clump of material, which is then formed by its cutting into a desirably useful shape yet carried out mostly within the capability of our hands. Energy saving miniaturization (early mentioned „nanotechnology") would, by contrast, be a "bottom-up" approach that would involve the stacking-up of individual molecules directly into a useful shape, and, moreover, that would be controlled by the "power of our minds" in a similar way to the proteins that are assembled from individual amino acids. We can think back to the vision of the "nanobots" age, which predicted the manipulation of small species to actually form miniature engines (or more imminent micro-computers).

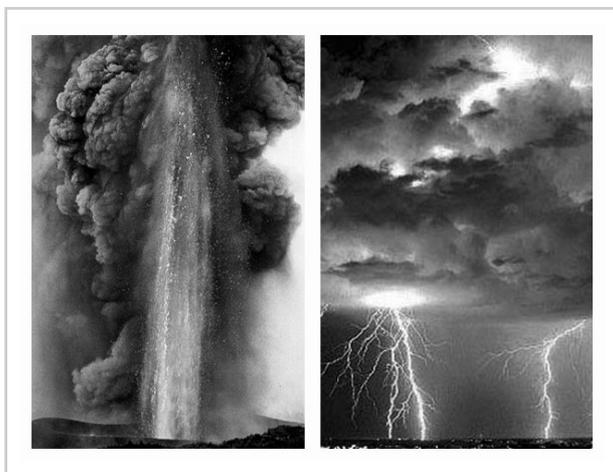
Similarly to the processing instructions necessary for the operation of macroscopic machines (done either by an experienced engineer, by the help of a printed manual, or by the fully automatic control of a programmable computer) and realized at the one-dimensional level of a written message, we have, in necessary addition, to look for the analogy of microscopic instructions already known within the models of the three-dimensional level of DNA structures. Such an approach is also related to the nowadays message passed by the human cognition and based on the early inaugurated need how to understand fire from its visible wholeness down to its imaginable composition of internal vibrations. This has become an important domain of communication and is closely related to spheres of information (and reversed entropy) to be discussed herein, and in more detail, latter on.

By the end of the nineteenth century, there were available two different mathematical tools available to model natural phenomena – exact, deterministic equations of motion and the equations used in thermal physics, which were based on the statistical analysis of average quantities present in complex systems: Whenever any non-linearity appeared, it was put into linear regimes, i.e., those whereby double cause produces double effect and the solution is linear in the known term (classical thermodynamic laws). In these linear systems small changes produced small effects and large effects were due either to large changes or to a sum of many small changes. Moreover the imperfect measurements of an event did not prevent one from gathering its main properties, and in turn, this fact produced the property of easy experiment repetition. The description of phenomena in their full complexity, the equations that deal with small quantities, such as infinitesimal changes, at maximum, with constant changes (e.g., linear heating) took, however, time to develop.

An example of such a simple model is the linear spring where the increase of its tension is proportional to the increment whereby it is stretched. Such a spring will never snap or break. The mathematics of such linear object is particularly felicitous. As it happens, linear objects enjoy an identical, simple geometry. The simplicity of this geometry always allows a relatively easy mental image to capture the essence of a problem, with the technicality growing with the number of its parts. Basically, details are summed up until the parts became infinite in number,

and it is here that the classical thermodynamic concepts of equilibration leading to the *equilibrium structures* belong (i.e., crystals and other static body-like structures). In such conditions each molecule is in an equilibrium state with its own environment and with the potential and kinetic energies of neighboring molecules that are, in the overall level, mutually indifferent.

On the other hand we know the historical prejudice against non-linear problems, i.e., neither a simple nor a universal geometry usually exists. We can consider the cases of a strained spring oscillations now with a non-linear restoring force where the resonance does not happen in the same way as in the above mentioned linear case. It is possible for the tilt to become so pronounced that the amplitude is not single valued and shock jumps may occur conceivably coming to pass in wave packages. It is similar to the case of a continual inflow of energy which forces the molecules to coordinate in larger clusters. In such non-linear systems, small changes may have



dramatic effects because they may be amplified repeatedly by self-reinforcing feedback being, thus, the basis of both instabilities and the sudden emergence of new forms of order that is so characteristic of *self-organization* [33,34]. Such a drastic move away from a standard configuration can lead to states displaying *spatial or temporal order*. We call these regimes *dissipative structures* to show that they can only exist in conjunction with their environment (non-equilibrium thermodynamic laws) and are granted by the continuous access to an energy source. We can reveal that such a dissipative system in its dynamic 'equilibrium' is literarily fed by *negative* entropy (i.e., producing positive entropy – plainly said, it is factually in the state that we may associate with our normal awareness of heating). If constraints (or, better, 'enforced fluctuations') are relaxed the systems return back to standard equilibrium and, consequently, the entire long-range molecular organization collapses.

During the 1960s, when *Prigogine* developed a new systematic approach to so called non-linear thermodynamics that was used to describe the curiosity of self-organization phenomena experienced outside the reaches of equilibrium. The dissipativeness of a process accounts for

the irreversible dispersion of the part of energy during its transformation from one form to another, and in technical processes, it is mostly associated with decrements and losses. Dissipation of energy (due to diffusion, friction, etc.) is thus associated with wastes. However, a new kind of equilibrating disequilibrium can be assumed as a competition between energy and entropy where, at low temperatures, the energy is likely to yield ordered structures with low component entropy, while at high temperatures the entropy becomes more decisive. Mutual molecular motions turn out to be more important producing chaos and structural disorder.

Non-equilibrium thermodynamics of a completely open system also enables the formation of configuration patterns in a similar way to classical 'thermostatics' (stable crystals), but it is of a quite different 'dynamic' nature (turbulence, vortices), showing that the *dissipation can become a source of order*. Microscopic characteristics of the equilibrium distribution lie in the order of molecular distances (10^{-10} m), while in the dynamic case of the energetic super-molecular its ordering reaches clusters of 10^{-4} up to 10^{-2} m. In short we can say that the classical (equilibrium) thermodynamics was the first reaction of physics to the complexity of nature's pretentiousness towards the atrophy of dissipated energy and its conclusive forgetting of the initial conditions (in its sense of diminishing original structures).

Ordered disequilibria are customarily exemplified by the well-known *Bénard-Raleigh instabilities*, a very striking ordered pattern of honeycomb (hexagonal) cells appearing under certain conditions of heating a thin layer of a liquid, in which hot liquid rises through the center of the cells, while cooler liquid descends to the bottom along the cell walls. It occurs only far from the equilibrium state (originally represented by the uniform temperature throughout the liquid) and emerges at the moment when a critical point of instability is achieved. A constant flow of energy and matter through the system is necessary condition for this self-organization to occur. It may be observed even at a macroscopic scale in the atmosphere when the ground becomes warmer than air. Physically, this non-linear pattern results from mutually co-coordinated processes because molecules are not in random motion but are interlinked through multiple feedback loops thus acting in larger cooperative aggregates, mathematically described in terms of non-linear equations. Farther away from equilibrium, the fluxes become stronger, entropy production increases, and the system no longer tends towards equilibrium.

Nevertheless, this does not contradict the second law of thermodynamics because the total entropy of the open system keeps increasing, but this increase is not a uniform increase in throughout disorder. In fact, such dissipative structures are the islands (fluctuations) of order in the sea (background) of disorder, maintaining (and even increasing) their order at the expense of greater disorder of their environment. We should remember that, particularly in the living world, order and disorder are always created simultaneously at the moment when the transfer of heat

begins to play a crucial role. It does not violate the *Boltzmann* early supposition that "entropy can be understood as a representation of increasing molecular chaos and consequent disappearance of initial non-symmetricality".

c) *Understanding our universe*

All nations of the world have their own mythology [35–37]. Myths, in the sense of the Greek term 'mythos' that means speech (tale or story), bring poetic views of the world around us although customarily considered synonymous to something widely spread and not often true. For the Greek poet and philosopher *Hesiod*, the universe was a moral order close to the idea of an impersonal force controlling the universe and regulating its processes of change. The notion of *philosophy* that join images of fondness with knowledge (likely introduced by *Pythagoreans* and similar to the term *mathematical*, meaning conception or theorem 'mathema') came probably into existence when people were no longer satisfied with such supernatural and mythical explanations [38]. It proclaimed 'some are influenced by the love of wealth while others are blindly led on by the mad fever for power and domination, but the finest type of man gives himself up to discovering the meaning and purpose of life itself. He seeks to uncover the secrets of nature. This is the man I call a philosopher for although no man is completely wise in all respects, he can love wisdom as the key to nature's secrets'.

The Greek word philosophy was actually derived from the notion of love ('*philia*'), which marked (or better explained) the attraction of different forms of matter, and of another opposing force called strife; hate ('*neikos*') to account for separation. Love '*philia*' together with wisdom ('*sophia*') – philosophy – first appeared first in the fifth Century BC and primarily concerned itself with the problem of "The One and the Many". Simply stated it involved the attempt to explain of the infinity of things we meet in the Universe (the Many) and the early Greeks believed that the single unifying thing (the One) can be some kind of a material substance, like water, stone or fire. They were concerned with finding an unchanging principle that lay behind all changes. The stable unchanging component of the Universe, which the Greeks called '*arche*' and living (and growing) nature was associated with the notion of '*physis*'.

People gradually began to suspect that there was a logical order in the universe and that humanity had the capacity to discover it. *Milesians* (birthplace of the first cosmopolitan and "philosophical" ideas that eventually made possible the leisure-pursuit called '*scholē*') introduced the approach in which a single element, that contained its own principle of action or change, lay at the foundation of all physical reality. Its founder *Thales* was the first who tried to explain all things by the reduction to one simple principle, one '*arche*'. Such a single viewpoint is generally called *monism* and a more generalized approach, to see all things being alive, is '*hylozoism*'.

This new paradigm sees the world as an integrated whole rather than a dissociated collection of parts and it may also be called as an *ecological view*, if the term eco-

logical (from Greek '*oikos*' – household) is used in a much broader sense, e.g., to see an engine not only as a functional whole, composed of parts, but also to perceive how the engine is embedded in its natural and social environment including its manufacturing (raw materials) or functioning (waste management). Today's science nearly always tries to reduce the complex world to as few principles as possible and the idea of reduction to a single principle is still alive. The physicist's search for the unified theories or, better, for theories of everything (i.e., looking for a data compression to achieve a particular '*final*' theory) can serve as an illustration. On the other hand the Eastern sages have emphasized that the nature of our world cannot be reduced to a number of simple principles and any reduction inevitably leads to misinterpretation. They are aware of the complex interconnections of all aspects of nature and even of the connection of these aspects with our minds.

The universe has been steadily yielding its secrets and powers to human skill and intellect. Let us see the most familiar geocentric '*ptolemaic*' system that was based on the empirical idea of an extra logical character that the celestial bodies – the Sun, the Moon and the other planets, revolved around the Earth along "heavenly" circular orbits, which were considered obligatory since a ring was thought to be an ideal, celestial curve (attuning to divine harmony by *Pythagoreans*). The extensive reckoning needed to compare this idea with the actual astronomical data, comparison which showed certain inaccuracy and inadequacies. *Ptolemy* (about 1st Century) was to use another equally extra logical idea; that of epicycles, which proved to be, nevertheless, unsatisfactory, too. *Ptolemy* invented increasingly newer details, thereby increasing its complexity by epicycles of higher order whose centers revolved itself along another circles, which violated thus the basic concept of harmony and did not touch the elliptic solution yet.

Despite the early heliocentric idea of some previous Greek philosophers (in particular *Aristarchos*, who also came to the precocious opinion that the Moon is three times smaller than the Earth and the Sun is seven times bigger, assuming in the same time the phenomenon of the parallax of fixed stars) the geocentric Ptolemaic system was long considered evident throughout the period of subsequent eighteen centuries. Finally *Copernicus* appeared and spent the greater part of his life on the computational attesting of his time "novel" heliocentric idea. He came to a satisfactory agreement with astronomical data but the final result was not perfect because the centers of some orbits were somehow displaced and the system again violated the yet accepted harmony rules of Nature. Also the speculative geometrical model, inspired by the idea of Plato's aggregated bodies of different symmetries, lasted till the Renaissance. Even legendary *Kepler*, in his work "*Cosmographical Mystery*", described the trajectories of the five known planets by means of spheres written into and drawn onto these regular bodies with the outermost sphere of Saturn and with the Sun at the center. Latter *Kepler* reconsidered the problem, which was still

devoted to the idea of world harmony, until he had to violate even his own belief, introducing finally elliptic, instead of previously obligatory circular, motion. *Newton* proved that any planet under the influence of only its central sun moves in an elliptical orbit, i.e., he solved the "two-body" problem, which refers to the analysis of the motion of one body under the mere influence of a single other body. During the 1890's, the great French mathematicians *Poincare* focused himself on the "three-body" problem in which the motion of one body is influenced by precisely two other bodies. He surprisingly found that there is no simple analytical solution, i.e., he arrived to the general conclusion that it is impossible to give a simple description for the orbit of one body influenced by two other bodies. During his work on this problem he also developed a new kind of mathematics, which was close to the current domain of *topology*, and he finally concluded that minute differences in initial conditions for the three bodies' motion could result in a widely divergent position after a period of time, which is now accepted as one of the basic features of *chaotic* behavior. With the advent of the computers, the analysis of the motion of planets gained a new life. Computers can make trillions of calculations in the blink of an eye and if *Ptolemy*, *Copernicus* or *Kepler* would have had a chance to use a computer, the whole computationally tedious refining process would appear to be one of intermediate steps with the computer in its dialog regime and all the historically progressive discoveries would have been seen as a mere numerical application of the trial-and-error method.

The greatest success of this *Newtonian* and *Euclidean* world of expedient geometry was not, however, only of beneficial aid to astronomers, technical architects and cartographers. For scholar mathematicians, it has established a style of reasoning, wherein truths are deduced by the application of definite rules of reasoning from a collection of self-evident axioms. This confidence was, however, undermined when mathematicians discovered that such a visible 'flat surface geometry' was not the only geometry that existed, and only a rationally consistent geometry assuming logical interrelations between points and lines on arbitrary (curved) surfaces could begin to explain real models. It revealed that the *Euclidean* geometry is one of many possible, logical, and self-consistent systems of generalized geometry. It showed that mathematics could be related as something 'bigger' than so far science has given away, requiring only for consistency to be adhered to. Thus the essence of mathematics can be positioned in the relationships between quantities and qualities – it is the association between numbers, not the number themselves, that form the focus of interest for modern mathematicians; relationships such as domains of transformation, symmetries, programs, operations or sequences. The importance of these relationships also illustrates the difference between the human mind and the computer: Latter Penrose once claimed that "*The performance of feats of mathematical intuition catches the brain in the throes of doing something which no algorithmic computer can imitate*".

Encouraged by the brilliant success of *Newtonian* mechanics in astronomy, physicists extended it to the motion of fluids and to the vibration of strings and bells. This mastery was conceivable by employing a new limit of infinity, and by partitioning to very small differences known as the *differential calculus* (invented by *Newton* and *Leibniz*). We should note, however, that from the seventies century on, the style of European mathematics had gradually shifted from the traditional viewing of visual shapes (geometry) to the mathematics of formulas (algebra, derived from Arabic '*al-jabr*' – binding together) although *Descartes* had already invented a method how to make algebraic formulas and equations visible as geometrical shapes. For example *Laplace* was one of the great formalizers who boasted that in his famous 'Analytical Mechanics' there were no pictures. Thanks to *Poincare* that trend was then reversed, breaking the stranglehold of analysis and formulas that had become very opaque, and turning, instead, to visual patterns. It did not, however, merely follow the geometry of *Euclid* but brought a new kind of geometry – mathematics of patterns and relationships – today called *topology* (or even rubber-sheet geometry).

In fact, what *Poincare* pictured in his mind is now called a *strange attractor* (latter refined by *Lorenz* or *Ueda*), which marked the beginning of the modern *theory of chaos*. It was, however, forgotten as a few years after *Poincare* finished his work. When the famous 'three-body' problem was published (1920s), *Planck* discovered energy quanta and *Einstein* made known his theory of relativity that was highlighted and regarded as a major scientific breakthrough. Based on the reference-frame dependence of space-time, the laws of physics became the most important invariants themselves. Because the laws of mechanics are frame-invariant, it does not matter whether we are walking across of a laboratory floor fixed on the rotating Earth or placed in the rocket moving fast away from the Earth. It means that we are able to formulate the laws of physics so that they take the same form in any reference frame, which shows, in fact, that heliocentric and geocentric views are equally legitimate for the chosen ordinates. All primary qualities spoken about by *Galileo* are still frame dependent but the mathematical laws governing the physical phenomena are now in a form that displays their invariance². As an example "*the energy is frame dependent because the observers in different frames will measure different values for the same system, but the conservation of energy (mass) hold for all observers*".

There is also an important psychological perspective that our awareness of being the center of our own experience was merely a projection of our persisting geocentric cosmology. In contrast the heliocentric view implies that the perceived motion of the Sun, stars and planets across the sky is natural by virtue of our Earth's movement. This was the first major scientific revelation of the unreliability of appearances and the understanding of how our projections shape the world. When the each physical point of view became equally real there is no privilege other than

convenience. We may find a parallel in the Middle way of Buddhism's by the emptiness doctrine, which denies inherent existence to all persons and our thinking – not just quantum systems lack independent existence!

Two scientists, *Laplace* and *Leibniz*, both saw that the laws of Nature, which *Newton* had discovered, created a situation in which the future might be completely known by a mind large enough to know the present state of the Universe completely and to carry out the calculation required to predict its future state. *Leibniz* even extended this optimism into a wider domain, conceiving a symbolic manipulation procedure that could be programmed with the laws of logic and that would enable the answering of all questions by a systematic approach to them. Our limitations, however, are clear – we are never going to be able to collect all the facts that we need to put into the universal formula. *Du Bois-Reymond* published his insoluble problems including the origin of natural forces and the nature of matter and the origin and nature of consciousness and sensation. He found the existence of our free will paradoxical and somehow irreconcilable with a mechanical view of the universe.

Such a prolonged idea development helped, for sure, to continuously improved the understanding of our intimate Universe, but was still far away from achieving an comprehension of its wholeness, particularly in relation to its very beginning and consequent development [4,39–44]. Without more encouraged ideas (materialized into complicated mathematical models) and ahead a wider application of advanced computational means (enabling multiple alternative solutions) we would not be able to go too far beyond our visual world. In particular we can mention the solution of the sets of non-linear equations that was, in early times, outside of the reach of ordinary mathematicians until computer's repetitive capacity to almost infinitely approximate solutions gave the answer. Such a gradual development of any progressive ideas is delicately dependent on certain introspection and capability to examine secondary characteristics. Therefore we achieved a construction capability that was able even to analyze our far-reaching history by the use of the mathematical extrapolation to describe the gross-features of the origin of the Universe and to test the models answerable for the creation process³ (*Gamow, Sitter, Friedman*).

If we presume that after the Universe's originating break-point (initial explosion called '*Big Bang*') the mass had been slightly too much, the Universe would have immediately contracted and on contrary, if too little, the Universe would have expanded so rapidly that there would have been no condensation of matter and no formation of stars and consequent life. Also the weak electromagnetic and strong nuclear forces needed to be very delicately balanced. If nuclear forces were slightly too weak, the heavier nuclei would never formed and the universe would have been composed of hydrogen resulting in a very simple chemistry of a single element. On the other hand, if the nuclear forces were a bit too strong we would have had very heavy nuclei and hydrogen would not have existed at all. What more, a diverse assortment

of elements is potentially caused by certain disequilibrium in the energy distribution.

Successively, the remarkable Hydrogen-bonds (*Van der Waals*⁴) made possible the formation, at global temperature, of an apparently simple but polymeric-like liquid, water (H₂O as an amazing kind of 'fluid glass' thanks to the unique property of its molecular orbitals and quantum mechanics, water dimmers, etc.). Water thus exhibits several intriguing and almost 'superstitious' properties compulsory for existence of life (displaying some important anomalies, such as irregular density, large specific and latent heats, solid ice lighter then liquid water and high solvating capacity).

We should not forget that the theory of the 'Big Bang' has definite critiques because it postulates that the Universe was produced from a singularity of 'nowhere' claiming that space and time started at the same time and showing them as distinctive intermediate phenomenon of a limited extension. However, the often asked question, 'what caused it' or 'what was there before', can be seen as correspondingly senseless because the answer lies at the beginning and at the end of a two-dimensional globe, whose surface has no apparent boundary. Similarly we can treat our four-dimensional space-time model as having no answer for anything other than what is beyond its initial singularity or other such indomitable boundary.

The singularity model expects that the early expanding Universe was behaving somehow against the rules of reactionary thermodynamics. Analyzing the process of an entire 'blowout' it brings troubles with accounting for the appropriate initial critical density, immediate production of the starting energy (of 10⁶⁶ J) and the initial space growth (being 10⁴⁸ faster than the speed of light). All that is presumed by traditional laws (and possibly even dimensions) is seemingly absent within the first 10⁻⁴³ s (so called *Planck* time when the temperature was 10³² K) of the Universe's growth. To avoid inherent query of 'infinitesimality', *Guth* suggested the *inflation cosmological model* where temperature reached its maximum just at the *Planck* time. This limiting state facilitated the 'super-string' behavior of space that assumed so called 'curled-up' dimensions (i.e., for the associated *Planck* length⁵ equal unity where the space compacted radius, *r*, shows certain sense of 'duality' with its reciprocation, 1/*r*).

What is taken for granted is the hypothesis that the very early Universe was undergoing severe loss of its high symmetry, and, thus, passing through two distinct phase transformations (well known from thermodynamics) – the separation of strong interaction forces (at 10²⁸ K) and then another separation of weak nuclear and electromagnetic forces (at 10¹⁵ K)⁶. On further cooling the Universe underwent nuclear synthesis but became penetrated by the homogeneous bath of primary photons which gave both the necessary proof for the Big Bang theory but also started to puzzle why this relict radiation is the same in all the Universe when all its spots could have never been in full thermal contact to share heat transfer (*problem of horizon*)?

Moving on, we still assume that the Universe is that consistent with the view of the *Aristotelan crystal sphere*⁷, with its boundary extending along our observatory (and computational) capabilities (and also theories). As the Universe expands, gravity is less and less effective at slowing down the expansion which, however, opposes its recent speed measurements bringing, thus, into play the former *Einstein* idea of a certain 'antigravity force', now assumed as a general property of empty space and mysterious dark matter⁸. Therefore the defense of a long-termed future requires us to take seriously two extrapolations. We need to consider whether Nature is likely to offer an unlimited number of important things for us to discover (as the new sort of universal 'dark' energy but also the practicality of energy for conversion and accumulation) and whether we should expect our capabilities to improve to yet higher limits of knowledge and acceptability of novel theories. Creative minds would, eventually, look elsewhere for new challenges, perhaps designing another more complex but virtual universe to be more interesting than the study of our own becoming too difficult to fully comprehend.

Biochemists believe that the level of complexity required for a system to qualify for the title of 'life' can evolve spontaneously only if it is based upon the unusual chemical properties of the element carbon with remarkably fortuitous location of energy levels in the carbon (and oxygen) nuclei. The hydrogen and helium from the early Universe is burnt within the interiors of stars and produces, as well as large amounts of energy, heavier, biological elements like carbon, oxygen, nitrogen and phosphorus. It has been deduced that for each atom of carbon there are 3-times as many N atoms, 6-times as many Ne atoms, 7-times as many O atoms, 600-times as many He atoms and 10^4 - times as many H atoms (i.e., hydrogen represents 90% of all atoms with 2/3 of their mass). The Universe must be billion of years old in order to have had enough time to produce these biological elements capable of spontaneous evolution of complexity. An apparent surplus of iron may even question its present age estimate. It means that any life-supporting universe must be, at least, billions of light years in its size. Ironically the fact that the Universe appears big and old, dark and somehow lonely is a feature that is necessary for it to provide the building blocks of any forms to assure chemical complexity.

A habitable planet needs to be large enough for the strength of its gravity to retain an atmosphere but yet not so great that this force will break the delicate chemical bonds at its surface necessary to hold complex biochemical molecules together. The strength of gravity determines also how large living things can mature before their size becomes a liability. Strength does not increase at the same rate as weight, and volume of a structure, grows as a *log* versus *log* plot (cf. 'allometry', Chapter 13). It also appears that this size is crucial to the pattern of social and technological development. If we are to manipulate the environment on scales much larger or smaller than our own body we must employ artificial means. The planet's

orbit must be at a suitable distance from the star to maintain temperature at life-supporting conditions. Living beings must thus find themselves inhabiting environments which are friendly for organized complexity, i.e., cool enough to leave molecular bonds intact but yet warm enough for water to exist in the liquid state.

According to the second law of thermodynamics, the whole Universe must proceed irreversibly from a homogeneous stage of order, and low entropy, towards an equilibrated state of disorder and high entropy. Eventually, when the Universe has reached a state of maximum entropy, it should be a uniform gas with a homogeneous constant temperature. But, the low entropy stars are formed from the high entropy gas clouds so that the observable portion of Universe may be rather seen as proceeding towards states of greater thermodynamic order. However, *Wesley* (1996) considered that although the net entropy change per unit mass is negative when a gas condenses into a star, the entropy production that is radiated off is two orders of magnitude greater than the entropy reduction, so that the second law is not violated. *Wesley* also discussed the relevance of fluctuations away from equilibrium in the context of cosmology, and the generalization of entropy to non-equilibrium situations.

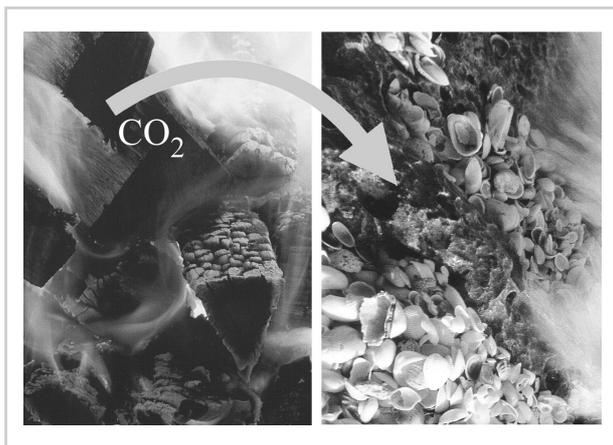
Opposite to the prognosis of a thermal death for the gradually disordering Universe (which applicability is often criticized due to tricky confinement of the Universe as a localized or closed system) there transpires a reverse ceiling point of order called 'omega', which describes a hypothetically complete organization of the Universe where entropy would approach nothing (zero). Besides the already discussed singularity of the elapsed Big Bang we can also concentrate on the ongoing world within the Universe and its gradual progression grades of civilization development⁹ (certain endeavor of the so called "Ω-point").

In 1900, the famous electromagnetic theoretician *Lorentz* also tackled the theory of gravitational attraction, according to which this attraction was propagated with the velocity of light so that without infinite velocity we can never have instantaneous action-at-a-distance. The fact that there is a limit to the velocity put the border line on the dissemination speed of information at which it can be transmitted within the Nature. It brings all sorts of unusual outcomes and is responsible for our astronomical isolation as the enormous time needed to send or receive any waves is a consequence of the finite speed of light. If the speed was not limited then the radiation of all sorts would be received instantaneously after its emission, no matter how far away its source. The result would be a reverberating cacophony of signals caught from everywhere. Instead of local influences dominating over far distant ones, we would be affected instantaneously by all changes occurring on all other sides of the Universe. Thus the impossibility of transferring information faster than the speed of light makes it timely possible to discriminate and organize any form of information. The Newtonian picture of the world placed no such limits as the connection between the assumption and other aspects of the

structure of the Universe was not recognized. Such a Newtonian universe was too simple to accommodate light and, thus, was factually impossible.

e) *Miracle of commencement*

When *Lavoasier* demonstrated that respiration is a special form of oxidation and thus confirmed the relevance of thermal chemical processes [45] to the functioning of a living organism it was clear that a certain relationship between living and non-living systems should exist but would be strongly affected by the dispositions of heat. It was found to be curious that our terrestrial atmosphere contains gases like oxygen (and methane), which should react but instead coexist and form a mixture far from chemical equilibrium thus represents a non-equilibrium, open system characterized by a constant flow of energy and matter. The proportion of free oxygen eventually stabilized at 21%, a value amply determined by its range of flammability. If dropped to below 15% organisms could not breathe and burning would become difficult while exceeding 25% combustion may become spontaneous and fires could rage around the planet. Oxygen, in fact, was a toxic by-product in the originally massive blue-green bacteria photosynthesis (while splitting water molecules into their components) and its increased atmosphere "pollution" resulted in the self-elimination of these bacteria (seen as a signified 'global catastrophe').



Astrophysics teaches that the heat of the Sun has increased by about 25% since life began on the Earth and that, in spite of this increase; the Earth's surface temperature has remained more or less constant, at least at a level comfortable for life to exist during those four billion years. Moreover the heat (radiated and received from the Sun) is befittingly distributed along the planet surface by the system of heat transfer. On the micro scale it has enabled the formation of the non-equilibrium shapes of snow flakes instead of solid ice, which would easy cover the planet's surface and result in more complete reflection of solar radiation, thus making the Earth an insufferable and inhabitable place.

The content of carbon dioxide in atmosphere (as well as water vapor or methane) was likely to buffer the temperature changes since it is one of main greenhouse gases.

Plant and animals recycle massive amounts of CO_2 (as well as O_2) in the process of photosynthesis, respiration and decay but these processes are balanced. The excess of CO_2 is removed from the atmosphere and recycled by vast feedback loops, which involves rock weathering, i.e., granite combination with rainwater to form various chemicals (carbonates) as well as its dissolution in sea water. It is in this carbon-cycle that soil bacteria also play an important and catalytic role in the decomposition of carbon-containing material and in the release or absorption of CO_2 gas. As the Sun gets hotter, bacterial action in the soil is stimulated to increase the rock weathering and so it pumps more CO_2 out of the atmosphere and thus help to cool the planet by creating an outlet for infrared radiation to escape. It suggests a possibility that life could create the conditions for its own survival and produce, regulate and sustain a troposphere as an open circulatory system.

This hypothesis of the Earth as a self-regulating system was for the first time presented by *Lovelock* (1970s) and is known as the *Gaia hypothesis* [46] in honor of the Greek goddess of the Earth. A critique of this hypothesis harks back to the old debate between 'vitalists' and 'mechanists', the latter explaining all biological phenomena in terms of the natural laws. On the other hand the vitalists postulate the existence of a non-physical entity, a causal agent, who directs the life process purposefully. This second view of vitalism is very close, of course, to *teleology* (from the Greek '*telos*' – purpose). It was scientifically responded to by an ingenious mathematical argument and model called the '*Daisy world*', which in many ways is no more than a vast simplification of the Gaian system, and in which temperature regulation is an emergent and predictable property of a system that arises automatically without any purposeful action. Two kinds of growing species are hypothetically assumed in the Daisy world – black and white "daisies" that are only capable of growing under specific temperature ranges. As the model planet warms up, at a certain moment the equator becomes warm enough for daisy life. The black daisies flourish first as they are capable of adsorbing heat better. With further warming it becomes too hot for the black daisies to survive at the equator and, instead, they are forced to colonize the cooler sub-tropical zones and latter even the polar regions of our hypothetical planet. At the same time the white daisies start to appear in the hot equilateral zones as are able to reflect the heat and cool themselves sufficiently enough to ensure survival. If the sun gets even hotter then the white daisies can replace the black daisies in sub-tropical zones too so as to cool the planet further by the reflection of the incident radiation, and *vice versa*, if the Sun gets cooler the black daisies can replace the whites to warm the planet by more efficient heat absorption. The end computational conclusion was striking! It showed that the planetary temperature is kept constant throughout the four above-mentioned phases. In a more sophisticated version of the same model, new variables were taken into account such as varying pigments of the daisies and the interference from the other

fauna and flora, e.g., rabbits eat the daisies and foxes eat the rabbits, and so on. The model's originally small temperature fluctuations are thus flattened out, and the self-regulation becomes even more efficient as the model's complexity increases. It nicely exemplifies the complex game that plays with heat utilization and handling¹⁰.

Our Sun produces energy in a way that depends on a certain balance between the force of gravity and the rate of generation of energy by nuclear fusion in its interior. The strength of the electromagnetic and nuclear forces are set so delicately that they prevent runaway nuclear reactions that would consume our Sun's energy supply so rapidly that any life-supporting environment on the Earth would have disappeared long before evolution produced biological complexity. Also if the force of gravity would have been somewhat larger, then stars would have cooked the nuclear fuel much more rapidly and, thus, their lifetimes would have been unhappily short. And on the other hand, if the force of gravity were to be weaker then the solar material would not have clumped together effectively enough as to last and produce sufficient energy to initiate life. The strength of gravity on a habitable planet's surface determines how large living things can become before their size becomes a liability. Strength does not increase at the same rate as the weight and volume of a structure growth, controlled by the universal power law. It also appears that our size has been crucial to the pattern of social and technological development that we have followed.

A large number of other details in the laws of physics and chemistry fortunately turn out to be just right and appropriate for our existence. The strength of the electromagnetic force of nature and with it the whole of atomic and molecular structure, chemistry and material science, is determined by a pure number called the *final structure constant* (equal to $\mu_0 c e^2/2 h$), which is numerically matching the value of about 1/137. This is one of the famous unexplained numbers that characterize the universe. Present theories of physics lead us to believe that there are surprisingly few fundamental laws of nature although there are almost endless arrays of different states and structures that those laws permit to exist.

Overall, the properties of our universe need to be strikingly and delicately set in order for life (that is to say, life that is anything like what we know) to exist. A pertinent piece of information is that all life on Earth is mostly related to essentially the same origin (e.g., left-handed molecular asymmetry of amino acids). All such observations have been the basis for what is often called the 'anthropic' principle [47] ('*anthropos*' being of man), i.e., for *Hesiod* (the 8th century BC) the Universe was a moral order, and the four centuries later *Socrates* formulated a statement "*whatever exists for a useful purpose must be the work of some intelligence*". The laws of the Universe are seemingly arranged precisely so that we humans can exist, the so-called very-first 'Big Mover' (God-architect understood as a universal transpersonally-omnipresent observer) created life and fitted it within the laws of livable parts of the Universe or made first the Universe

and set its conditions to be compatible for life to exist¹¹. This ideology received the name *Laplace's demon* (do not mix this up with the previously mentioned *Maxwell's demon* familiar in thermodynamics) and has always been popular in scientific and theological discussions lasting until now.

Such a sense of uniqueness, however, goes against the instinct of most scientists because it seems so highly improbable. The existence of even more universes is, thus, postulated, with each being somewhat different from the others. We certainly will have to wait to find out whether or not the uniqueness of physical constants can be adjusted in a natural way. The explanation of the formation of complex structures by evolution and natural selection has played no role in astronomy. The structure of objects, like stars and galaxies, is primarily governed by the laws of physics. They are equilibrium states between opposing forces of nature. The important objects that physicists study, things like molecules, atoms, nucleons and elementary particles have invariant properties defined by the values of the constants and the laws of Nature. Consequentially we arrive at the question of how far, and to where, does our universe allow us to proceed? We certainly will continue to increase our ability to do things as well as the variety of things we can do and such a growth of knowledge can hardly be stopped in natural ways unless a catastrophe would come into view.

There is one important aspect that is dealt with by computer scientists: how to devise and classify the degree of difficulty of problems that can be attacked by using any computer. This has led us to distinguish between tasks, which are impossible in principle, and tasks, which are practically impossible. The adjective '*practically*' means, in this case, that it would be prohibitively long to solve tasks even by the more advanced fastest programs, which endorse problems as intractable. Even a modest computation that grows at a rate of 2^n , where n is the number of computational steps, will soon require the entire visible universe to store intermediate computational information, even if it writes one bit of information on a single proton, because there are only 10^{79} protons available. Such a non-deterministic polynomial can be related to a single problem of logic by a general transformation procedure that can be performed in a real polynomial time. Emerging intractability has created a perplexing problem in molecular biology related to the process called protein folding. We can witness chains of several thousand amino acids folding into their final pattern in about a second. We know that the final shape is the one that minimizes the energy required to support its structure but when we try to program a computer to fold a protein it seems to be an impossible task even for a tiny hypothetical protein containing just 100 amino acids¹².

We are aware that no real system is absolutely closed, i.e., isolated from the outside influence. Astronomical systems are nearly as well isolated from external sources as possible and, thus, we are relatively able to precisely compute the development of such systems. For example, the movement of the planets in our Solar system can be

determined for a period of several millions of years with accuracy to about 13 decimal places. The French mathematician *Poincare* showed, however, that our potential to calculate the movement of gravitationally bounded bodies is strictly limited because of the problem that a many body system cannot be evaluated properly by the analytical means currently available (integration of relevant differential equations). The era of powerful computers, however, makes possible iterative solutions to many of the mechanical problems in the field of astronomy (and likewise it could easily trace out the very complex trajectories that *Poincare* did not even attempted to draw).

The main maxim of science is its ability to relate cause and effect. On the basis of the laws of gravity, astronomical events such as the appearance of comets can be predicted. Other natural phenomena, however, appear to be much more difficult to predict. Although the movements of the atmosphere obey the laws of physics just as much as the movements of the planets do, weather prediction is still very problematic. We often speak of the unpredictable aspects of weather just as if we were talking about rolling dice since there is no clear relation between cause and effect, although the precise predictability of weather patterns looks as if as though it might be eventually achievable. It seems that we just need to gather and process greater quantities of more precise information by using a denser network of sources and applying more powerful computers and software. However, even some of the first theoretical studies considerably altered this viewpoint, showing that a simple deterministic system, with only a few elements, can generate random behavior: It appears that randomness is fundamental! And gathering yet more and more information does not make randomness disappear. This fundamental feature has become to be called *chaos* [48–50] and is discussed in Chapter 13.

The correlation between chaos and geometry is anything but coincidental; rather it is a witness to their deep kinship. It can be best exemplified by the mathematical objects discovered by *Mandelbrot* [51], possibly the most beautiful objects ever seen in mathematics, a fantastically and efficiently organized storehouse of images screening orderliness as obtainable order within chaos. Particularly computers made it feasible to depict a variety of multifaceted natural features (cloud, tree, grass) that *Mandelbrot* coined the term ‘broken dimensions’, known as *fractals*, stressing that ‘*this non-integral geometry of nature deals with an aspect of nature that almost everybody had been aware of but nobody was able to describe and visualize in formal mathematical terms*’. The idea of fractal dimension (or better said ‘*fractal property*’) corresponds, to a geometrical appearance, which is not strictly an integer like being subjected in the traditional Euclidean world.

As mentioned above the evaluation of everyday atmospheric changes, based on the highly non-linear meteorological systems, was found to be so sensitive to the initial conditions that it dramatically enhanced any of the primary negligible variations (fluctuations) of these input parameters. It seems that the weather is still very difficult to compute and model although the controlling of weather

has been a dream of many generations. The energy, available to many atmospheric process, is yet very high on the human scale (the energy of a windstorm can easily exceed the energy concealed in a nuclear bomb) and is, thus, highly authoritative. The Greek *Xenophanes* took the Gods of traditional mythology and redressed them one-by-one as meteorological phenomena (like cloud, storm). He represented the *Eleatic* school of thinking in which the understanding of a God was the identification of that God with something very abstract, some principle or phenomenon of the Universe.

For reasons of aesthetics, or inherited monotheistic religious belief in the unity of the Universe, we tend to believe that all things are related at some deep level. What allows our Universe to be governed, as it appears to be, by a very small number of simple symmetrical laws, yet display a vast array of complex asymmetrical states and structures? It also reveals why science is so difficult. The quest for a grand unification of the four fundamental forces of nature into a single theory is a search for a single overreaching symmetrical pattern into which these four patterns can be embedded and united into a single picture rather like the pieces of a jigsaw puzzle. Sometimes this type of completion is referred to as a ‘theory of everything’. As a by-product, such a universal theory ought to do some other impressive things like predicting the identities of all the most elementary particles of matter and even their properties. The physicists have to distinguish carefully between finding the laws of nature and understanding the complex outcomes of those laws.

The above mentioned ‘super-string’ theory of the Universe appears to compress all sorts of information about the elementary particles but, so far, no one knows how to solve the theory to extract the desired information. It is clear that the mathematical structures employed at the frontiers of fundamental physical theories are becoming less and less accessible to the scientific public, and sometimes even to expert physicists. The number of individuals on the planet with the ability to understand the mathematics involved in the super-string theory is relatively very small and it is not yet the bottom line of fundamental physics. At any moment of history there are not merely questions one can ask but cannot answer, there are also questions, which there is no reason to ask.

f) *Growth of modern theories*

All written history has occurred in only less than about 100 human lifetimes. About 20 human lifetimes back most of the existing books could be read within a single lifetime. The greatest progress of natural sciences has, however, developed within the last 10 lifetimes, and a large fraction of it has been enjoyed during the lifetime of those of us who are witnessing it now. Nonetheless, the full absorption of such a fast growth of our knowledge is somewhat out of our capacity, and the progress is tending to be deplorably exponential – there is a significant time-lag in our receiving or discovery of new information and our understanding of it. Our perception of life’s intricacy and the world’s complexity should advance remarkably:

but to what extent will humans succeed in understanding it with any completeness is difficult to foresee. Are there new phenomena imbedded in the complexity that we have not yet grasped as just we did not dream of quantum mechanics before we could examine the very small particles and imagine and start searching for sub-particles? In the progress of the understanding of a particle we went from elements, to atoms, to sub-atomic electrons and protons down to sub-nuclear quarks and the distinguishing of particles reactions on the basis of strong and weak interactions (hadrons from the Greek 'hadros' – fat, thick and leptons from the Greek 'leptos' – tiny, thin). The fundamental building blocks of hadrons are quarks (they have never been seen directly in the laboratory), they combine in pairs or triplets, and they were given fanciful names (up, down, strange, charm, top and bottom somehow evocative of forbidden Hermetic philosophy).

Nature does not show us any isolated building blocks but rather hints at a complex web of relations between various parts of a unified whole. The father of quantum mechanics Heisenberg said "the world thus appears as a complicated tissue of events in which connections of different kinds alternate or overlap or combine and thereby determine the texture of whole". Quantum theory teaches us that all objects possess a wave-like aspect of behavior. The wavelengths of all matter are inversely proportional to their physical size, so that when its wavelength of a particular object is smaller than its size, the object behaves in a classical *Newtonian* fashion. This classical behavior is, however, just an extreme limit of quantum behavior. Here we assume that it is possible to know simultaneously both the position and motion with a complete accuracy. In practice, however, it appears that even with perfect instruments it is impossible to measure the location and velocity of a quantum particle simultaneously with an accuracy better than some critical limit defined by the basic (*Planck*) constant of the Nature. The uncertainty principle is telling us that in the quantum realm, where dimensions are sufficiently small, certain complementary pairs of concepts, like position and velocity, or energy and time, can coexist only within a limited sharpness. The underplaying principles can join in a more general role for neural information processing (or possibly in a greater concept assuming the correlation of sound frequency and amplitude or even that of temperature and heat). It is important to comprehend that quantum uncertainty is a consequence of a non-zero *Planck's* constant and if the constant were larger than it is, then the larger objects would display stronger wave-like attributes.

Similar to the quantum mechanic concept, the basic elements in biology were first organisms or species (noting its well developed classification for plants and animals), than, with improved observation technology, cells, its macromolecular parts (enzymes, proteins) down to the molecular structure of DNA and its three-dimensionally written message. According to *Capra* [52,53] the key to a comprehensive theory of living systems lies in the synthesis of the two different approaches, the study of sub-

stances or structures (where we can measure or weight things) and the study of forms or patterns (where we have to map configurations and relationships). *In the other worlds, we have to pass between quantities (structures) and qualities (patterns) because systemic properties are properties of a pattern.*

Democritus tried to complete a unified account of the world and his best known works were "The Great Order" (macrocosmos) and "The Small World" (microcosmos), the latter being his view on human beings. He expanded the atomic theory of *Leucippus* who also affirmed the existence of utterly empty space ('*kenon*'), maintaining the impossibility of dividing things *ad infinitum*, and arguing that the eternity of existence of elementary particles – atoms, mutually separated by a vacuum. All motions were the result of their active and passive affection formulating, thus, the basis of the law of necessity by which all things in nature are ruled. Also *Melissus*, an 'outocreative' spokesman of the *Eleatic* school, substituted the concept of nothing (or not-being) by the speculation about free space, a vacuum (or void – '*kenon*') saying "nor is anything empty; for what is empty is nothing; so nothing will not be being of nothing is not being". Only in recent decades have we discovered that the adjective 'elementary' particles do not fit this paradigm exactly as we know that they can be transmuted into other elementary particles or can be created from energy and can vanish into energy. The equality between mass and energy caused a crisis of the very concept of material substance, and perhaps presented the first real complication of our yet comfortable understanding of our universe.

In the view of Greek atomists, the elementary atoms were not created. At the beginning of the world an infinite number of atoms of countless shapes and sizes were constantly impinging upon one another in all directions. There were an infinite number of places where vortex motions were set up causing the mutual impacts so that the larger particles were created. The smallest and most rounded atoms preserved their original motions being associated with atoms composing of the fundamental fire and soul. *Heraclitos* uttered that the principle of the universe is *flux* or change of becoming, which implies that everything is and, at the same time, is not claiming that the existence of opposites depends only on the difference of motion "the way up and the way down are one and the same".

Towards the end of 19th century the Chinese physicist *Cu-t'ung* proposed the subatomic wave theory of 'ether' based on *Konfuciou's* idea of the transmuting, bipolar nature of ether, which is constantly transmuting between the states of *Jin* and *Jang*. It is close to a more serious hypothesis called the *self-reproducing inflationary universe* [54] – a complicated spatial variation that states that chaotic inflation would be expected to spawn in the early Universe. Probably such a network of self-reproducing inflating 'bubble' universes need to have no beginning but particular bubbles may have early stages when their histories can be traced back. These beginnings would correspond to quantum-mechanical fluctuations in the ener-

gy of the Universe from place to place and would appear spontaneously with some probability from time to time. Each inflating bubble gives rise to progeny which themselves inflate (*reproduction*). These baby universes possess small variations in the values of their defining constants of nature (physics) and other properties (*variation*), but they also carry some memory of the defining constants of physics in the bubble that gave birth to them (*inheritance*). The varieties of bubble, which produce the most baby universes, will be the ones that multiply and dominate the Universe in the long run so that the denomination of natural constants can become tunable in order to achieve certain optimal values, certainly only if universes could be created from such 'vacuum' fluctuations.

Thanks to the *Heisenberg principle of uncertainty*, the Universe appears within the super-ultra-microscopic dimension, full of extravagant, vehement and fiery fluctuations (*Trayton*) often known as a 'boiling vacuum' (or Fermi sea or even physical vacuum). Incorporation of both of these conceptions, of general relativity and quantum mechanics, into one consistent approach was seen unfeasible although it was a dream not only of *Einstein* but also of many other distinct scientists. It was not until the 1980s that a new theory appeared that is more suitable for the description of our 'elegant' Universe, which was close to the Pythagorean's idea of chord harmony tuned in rational ratios. This, so called *superstring theory* (*Green, Schwarts*), is mathematically based on the structure of vibrating strings (of various shapes and under certain tension) that factually represent non-material and tiny fragments, little filaments (of hidden dimensions) infiltrating the Universe to cooperatively and harmoniously act as a symphony of cosmic breath (often dedicated to *Ailos*, the Greek goddess of wind). The Universe is displayed in terms of a somewhat strange geometry of 'compactified' multi-dimensional space (called and visualized as a bizarre *Calabi-Yano manifold*).

The known human physical laws are now assumed to be the consequence of the laws of symmetry (*Noether, 1916*), i.e., the conservation of a quantity (position, momentum, spin, etc.) upon the transfer of symmetry (translation, rotation, mirroring, etc.) within space and in time. It shows that the four types of forces must naturally exist in order to enable Nature to respect a given calibration accord and, thus, the original question of why there are such forces is now reduced to the question of why does Nature respect such symmetry? It requested a new system of representation (e.g., *Feynman's diagrams*) that could provide a new physical framework such as *quantum flavor dynamics*, known as $SU(2)$, and *quantum chromo dynamics*, $SU(3)$, so far very constructive for the description of weak and strong interactions.

The above models were further refined into an even more promising but still hypothetical and more demanding mathematical 'ethics', called '*M-theory*', which has been derived from the M-words, e.g., Magic, Mystic, Mother, Matrix, etc. (*Witten*). It accounts for the multi-dimensionality of both the super-gravity and time-space

but is still, however, not fully explained and understood. It is perhaps the ultimate challenge logic for this 3rd Millennium (i.e. as a kind of comprehensive *final theory*). It would likely need to seek symmetry super-partners to any of the existing particles, circular, curled-up and other yet hidden dimensions, mirror symmetry, strong-weak duality and even time-space disruptions ('conifolds' and 'worm-holes') and ensuing mutations of universes (multi-cosmos possibly originating through black holes) and other not yet well understood notions often known from 'sci-fi' literature retaining, however, fundamental views of eternal vibrations so well-acquainted in describing heat. The possibility that our Universe contains many more than three dimensions of space, trapped at the Planck scale of size, means that our access to the overall structure of the Universe might be limited even more dramatically than we have previously suspected.

The pre-history of our Universe is also available for the re-inspection (*Gasperini, Veneziano*), i.e., to look for a time when the primary Universe was cold and extremely large and smooth and where fluctuations could create satisfactory amount of matter in the form of such string-wave pockets (pseudo-particles), which, due to their mutual attraction, can create curvature of the originally flat (space-time) universe. It does not oppose the law of mass and energy conservation as the created mass is compensated by the attractive energy. *Hawkins* and *Hartley* extended this approach and tried to describe the constitution of time and space from a primary Universe wave function (in fact from a kind of absolute emptiness), thus, looking for an alternative to the singularity of the Big Bang.

Historical cosmology assumed that such an energetic Universe was flowered by an 'ether' ('*aither*') which was something celestial and indestructible, possibly related to *Aristotelian* primeval matter ('*plenum*') or the recent view of omnipresent force-fields. It gave birth to a material universe in such a way that a delicate impact ('*bud*') in such a primordial 'reactive solution' provided a dissipative structure, or fluctuation, capable to grow. This idea is also very close to the *reaction-diffusion model of space-time* [41]. It, certainly, is different with respect to the accepted 'mechanical' anticipation of waves resulting from the primeval explosion that would have never occurred without reason ('spontaneously') and where the wave's transporter medium holds constant entropy (conservation of energy). On the contrary, the diffusional waves can interact with the carrier to undergo metabolic changes, enables entropy to increase and, most importantly, enabling self-organizing (and thus non-linear in its character, assuming the Universe is an open system, like the weather).

We may remind ourselves that according to conventional wisdom, *Poincare* failed to derive an early relativity theory mainly as a result of his stubborn adherence to the nineteenth century concept of the ether as an utter void while *Einstein*, just few years later, succeeded because he stayed behind the assertion of a new kind of ether that was the superfluous space-time substratum. His relativity

postulate was called by *Minkowski* as an 'absolute world'. Fifteen years later, however, *Einstein* used *Mach's* ideas on rational movement in order to cancel the action-at-a-distance and refreshed the idea of the ether because his relativity space is endowed with physical qualities. The ether should, thus, be regarded as a primary thing (similarly to the prematurely *Aristotelian* plenum) assuming that matter is derived from it [55], citing 'the metrical qualities of the continuum of space-time differ in the environment of different points of space-time, and are partly conditioned by the matter existing outside of the territory under consideration'.

The reaction-diffusion approach is well known in chemistry for cross-reactions where reactants pass between reactions to form a closed loop (*Zhabotinsky-Belousov* reaction [56] or computer simulation known as *Brusselator*, see Chapter 16). In general, such systems encompass two states, a *sterile* environment of sub-critical reaction and a *fertile* environment of supercritical reaction. The latter can provide localized dissipative structures (wave packets of speculative units – '*etherons*')¹³ put to use in the hypothetical reaction-diffusion model of the self-organization of the Universe. As a result we can explain the red shift of light not on the traditional basis of a galaxies speeding away from us but by the hypothetical phenomenon of 'tired' light that loses part of its energy penetrating the ether (that 'gen' energy can also account for the discrepancy in the anomalously high luminescence of a red giant stars, etc., see Chapter 20). It is interesting but unknown that even *Tesla* once proposed such stationary waves (seiche swelling) of compressed ether. In the *Maxwell's* and *Lorenz's* view, a vacuum is homogeneously filled by symmetric and unidirectional electromagnetic radiation, which in fact, becomes concentrated on the real patterns when allocated to generate their asymmetrical structures (the smaller structure, the more energy is borrowed from such a 'mother vacuum space').

There follows the question of if such a complex system as our Universe can ever be depicted and if we have enough power to understand it not excluding ourselves? Our brains contain about 10^{14} synapses, or in modern jargon, 10 millions megabytes of information and all of them are interacting. Can the human mind understand with any completeness something as complex as itself, or is it fundamentally impossible for any such complex system to do so? Are we to plan what changes in humans will take place and then carry them out over relatively short periods of time neglecting the long lasting experience of nature in its gradual evolution? Who is to determine which ways are allowed or be justifiable? How far do we dare threaten Nature's more random evolutionary process in the future development of humans? We will surely search for some sense of 'doing good' in the way of humans enrichment, however, that may be difficult to precisely define? Some of our goals will be like those of the past, encouraged by human curiosity and interest in exploitation, and enough coherent action on the part of a fraction of our population whose knowledge and capa-

bility to modify our circumstances will continue to grow. Consequently, the increase in human abilities to manipulate our universe, and the nature of human life itself, presents us with an increasingly big decision that will be needed to be based partly on knowledge and partly on other, yet unknown, things. In the ecological and environmental areas we must decide how much to compromise the immediate use of resources in order to protect ourselves and to what extent do parts of our Earth (and even Universe) have intrinsic values that are comparable to those of humans. Our Sun has another few billion years of much the same benevolent support for us providing free energy sources to make possible our survival and leaving us much space and time to think about it.

"We are not just observers we are actual participants in the play of the universe" *Bohr* once said that actually applies to the forthcoming description of the generalized concept of fire. The fight of mankind for a better life, while striving to survive in the universe/nature and while hunting for eternal fire, should therefore be understood as a fight for lower chaos (entropy) and maximum order (information), not merely seeking for sufficient energy, which seems to be, more and less, plentiful. We thus should not underestimate certain self-organization tendencies noticeable not only on the micro- but also on the macro-level of nature noting (according to *Kauffman* [32]) that "even biosphere's can maximize their average secular construction of the diversity of autonomous agents and the ways those agents can make a living to propagate further on. Biosphere's and the Universe itself create novelty and diversity as fast as they can manage to absorb it without destroying the yet accumulated propagation organization which is the bases of further novelty".

There is no reason why the examples of organized complexity should be limited in number. There may be an unending population of structures, which conscious beings could manipulate and engineer, or which nature could produce under suitable natural conditions. The number of complex structures will grow rapidly with the number of permutations of the connections that can be made between different states. Here we just can repeat a speculative scenario in which the values of the constants of Nature, evolved through many 'additions' as new universes, re-emerge from the collapse of black holes, with small shifts in the values of their defining constants occurring at each consequent step. As the outcome of this selection process produces the finely balanced situation, which we are, perhaps, witnessing a very negligible instant, we could imagine it to be an optimum with respect to the selection progress. So many constants of Nature take values, which seems remarkably suitable for the evaluation of life, which might be a consequence of the 'ability' of successive generations of advanced culture of universes ('civilizations') to create an expanding cosmos and engineer the values of their physical constants to approach the optimal values for the subsequent creation, existence and persistence of advanced forms of life.

- ¹ For example, already traditional carbon *fullerene* nanotubes, intercalated by various doping agents, are designed to stretch out catalytical affectivity or even initiate intelligence ('smartness') in various chemical reactions. Newly-made *dendrimers*, tree-shaped synthetic molecules, can possess the ability to capture smaller molecules in their cavities, making them perfect to deal with biological and chemical contaminants. It is believed that they will be eventually able to detect cancer cells, and destroy them by delivering a specific drug or gene therapy. They may become capable of penetrating the white blood cells of astronauts in space to detect early signs of radiation damage, and may even act as toxicant scanners in the against bio-terrorism.
- ¹ The idea of manipulating entropy is old! It is attached to delaying the moment of death, re-obtaining order once disorder has set in. *Maxwell* taught us that a supernatural actor, a demon, is required to be able to sit next to a hole drilled in a wall separating two parts of a vessel containing gas. Watching the molecules and opening and closing the hole, the demon can let faster molecules to go on one side and slower molecules stay on the other side. Disequilibrium, or information, is obtained. The 'Maxwell demon' is a mental artifact used to explain the concept of entropy but cannot be a real device. But the idea is fertile; we can conceive the heat flow diversion (allowed) but not its reversion (forbidden). Respecting the entropy principle, we can imagine an automaton operating that flows continually from warmer to cooler according to a purely thermodynamic logic. Instead of being a stable solution, entropy ensures only dissipative structures such as the thermodynamic demon – life.
- ² In the *Planck's* article published in [Ann. Phys. 26(1908)1], he assumed that the First and Second Law of thermodynamics keep their form in all inertial frames. At the same time he showed that if Q_0 is the heat of a system at rest with its inertial frame, K_0 , then a distinct inertial reference frame, $K > K_0$, moving with the uniform velocity, u , in respect to K_0 , would ascribe to this system a lower heat content according to $\partial Q = \partial Q_0 \sqrt{(1-u/c)^2}$. Assuming the invariance of entropy, *Planck* also concluded that temperature should transform in the same way as the heat. It, however, was latter challenged by *Ott* [Z. Phys.175(1963)70] by the opposite result, $T = T_0 \sqrt{(1-u/c)^2}$, due to his different definitions of the forces and impulses, yet the *Planck* expression is regularly used fore the *Lorentz* transformations of heat. If the *Planck* transformation is valid, the fast moving galaxies should be seen cold and invisible while according to the *Ott's* adaptation these stars should be infinitely hot and bright [I. Avramov, Russ. J. Phys. Chem. 77(2003)S179]. Because the temperature lies within normal limits we can conclude that the temperature is invariant with respect to the *Lorentz* transformation.
- ³ The general Big Bang paradigm holds that the Universe has been expanding and cooling from a hot dense initial phase, leading eventually to the formation of light elements and further galaxies we see around us. For often exciting questions about 'what came before the bang' there is, sadly, as yet, no answer. Instead, we better to ask 'what come from the Big Bang'. Thanks to the finite speed of light we can look at more and more distant objects, enabling us to see into the deeper and deeper past of the Universe (until the ultimate limit, which was the first source of light). By studying the nearby galaxies we are examining the state of the universe as it was relatively recently, however, the cosmic microwave background energy ($T = 2.725$ K) carries an image of the conditions at the beginning of the Universe, at the mmoment when the cosmic fireball radiation was finally released to our gaze. The image of the early Universe carried by the cosmic microwave background energy, with nearly identical intensity coming from all directions of observations. This lends a rather strong justification to the original cosmological models, which treated the idealization of a perfectly smooth Universe containing no structure at all. The current focus of interest, however, is the study of certain anisotropies showing small variations in the brightness of cosmic microwave radiation as we look in different directions. It reveals the state of widely separated regions of the young Universe and tells us that the some early regions had a higher density than other, and, thus, were able to attract neighbouring material in order to build up galaxies.
- ⁴ In character it is somehow a parallelism to the nuclear forces but dependent to the fluctuation of dipoles of one molecule, which indicates dipole momentum of the other neighboring molecules. In the classical *London's* theory (1930) of dipoles interactions the Van der Walls forces are always attractive, non-additive and responsible for cohesion and adhesion in materials (approximately proportional to the biquadratic power of the distance). Recently they are assumed, however, to be a particular case of more general *Casimir* forces, which are due to the zero-point vacuum electromagnetic radiation (see the Chapter 20).
- ⁵ The space and time cannot be boundlessly divided below certain limits because of their interfering fluctuations. Therefore we often distinguish new basic unites such as the *Planck* length of 10^{-34} m ($= gh/c^3$)^{1/2} and *Planck* time 10^{-43} s ($= gh/c^5$)^{1/2} as based on the fundamental constants h , g , c and e (i.e., *Planck* and gravitational constant, speed of light and charge of electron). Factually it signifies that the distance of the *Planck* length passes the light at the *Planck* time. The use of these fundamental quantum constants broke also through the new definition of SI units in metrology where the electric voltage can be defined on basis of Josephson effect observed at superconductors (volt in terms of $2e/h$) as well as electric current through Quantum *Hall* effect at semiconductors (ohm in terms of h/e^2).
- ⁶ The effective strength of forces can change with the temperature of the ambient environment in which they act. The weak and electromagnetic forces change in strength as the temperature rises, and they become similar at about 10^{14} K. When it is reached they combine to generate a single electro weak force. By contrast the strong force is observed to weaken on increasing temperature and it starts to approach electro weak force as the temperature increases further on. At about 10^{28} K, it becomes equal which requires a huge amount of energy (10^{15} GeV) that lies far beyond the reach of terrestrial particle colliders. The behavior of the forth force of gravity is yet more mysterious and is closely entwined with the character of space and time.
- ⁷ Currently the sphere is also drawn on the relation to define a normalized etalon for one kilogram as an ideal globe of perfect single-crystal of silicon with $r = 93.6$ mm. It can further be related to the *Avogadro* number, N_A , through the relation $N_A = 8 V_0/a_0^3$, where V_0 is the molar volume of Si and a_0 is its lattice constant, which is well definable by RTG diffraction and independent to the Si isotopic composition.

⁸ A fundamental ingredient of the standard cosmology model is the density of the Universe, which somehow determines the entire 'geometry of the Universe'. The theory of general relativity tells us that space-time is curved and, indeed, that this curvature is the origin of the gravitational force. It leaves open the question of whether space alone might have a flat geometry, i.e., that the curvature might entirely be in the time dimension. The answer depends on the total density of material and under a special case of so called 'critical density' space is flat, whereas otherwise space as well as space-time is curved. A new surprising conclusion of the Big Bang theory is that 95% of the Universe is plausibly made of two different unknown types of 'material' whose nature remains unclear, i.e., so called 'dark matter' as well as 'dark energy'. This hypothesis has followed from accounting for all observable matter (i.e., baryons) and the speed of cluster's movements. If what astronomers can see were all matter, the clusters would long since have dispersed as their gravity would be too weak to hold them together. When they calculated the gravitational pull needed between what is necessary and what is visible they have attributed the established difference to dark matter due to yet invisible particles sometimes called 'weakly interactive massive particles'. Originally the observed discrepancies were awarded to a certain parameter, known as the 'cosmological constant', which literally describes the 'energy of empty space' (and is associable with dark energy). There is a parameter analogy in quantum mechanics, which is known as the zero-point energy. The density of such a dark energy must resist gravitational collapse; otherwise it would simply be another form of dark matter. This is intuitively possible if such a 'material' has a 'negative pressure' that supports (and even overcomes) the ubiquitous gravitational effect of self-attraction [see, e.g., A.R. Liddle, *Europ. Rew.* 10(2002)237]. Endless ideas were thus generated about the nature of such dark matter and dark energy, their oddness of their similarity in their apparent densities, which has become a current anathema of cosmology (partly returning back on the *Copernicus* view that we live at a special time in the history of the Universe). Moreover, such a theoretical aid, established as a consequence of the yet unobservable but necessary 'dark' matter and energy, well resembles the medieval need of 'caloricum', which was assumed to inescapably exist around all kind of bodies, separating them and thus avoiding their ultimate collapse due to the action of gravitational forces (see Chapter 4).

⁹ From a very low-level of civilization to developing the capability to restructure and alter the planetary environment, we humans could imagine ourselves achieving even higher-level of ability, perhaps, even to the extent of being able to alter or influence an entire solar system change or, yet more unimaginable now, the reconstructing of whole galaxies. Our present capability is on the lower edge of civilization development, which enables us to make changes to the Earth and its immediate environment, either by design or accidentally. We know that the solar activity is steadily increasing and, however, that its impact on the Earth surface temperature is hitherto compensated by the atmosphere. Nevertheless, in about 10^9 years the surface temperature will be sufficiently high to cause the evaporation of the Earth's water; a scenario that would require future generations to be able to manage their own cosmic survival. It may be done through the alternation of the Earth's orbit upon the collision effect of a cosmic object (about 150 km in diameter) which will be attracted to pass nearby the Earth periodically pushing by its gravity the Earth to move slowly away from the sun. The associated waste heat would yet be difficult to be observed by remote observers. If such a hypothetical 'Ω-civilization' could manipulate the structures in the Universe, then they might become experienced enough to also reach yet hidden fundamental limits with regards to information storage and processing, resistance to chaotic unpredictability, and new ways to manipulate genes, molecules and molecular bonds, and even atoms (nanotechnologies down to the atomic scale). Our future abilities might even encompass control of atomic nuclei and elementary particles so that it may perhaps lead to an overall capability to manipulate the basic structures of space and time. Here can be introduced a very speculative scenario in which the values of the constants of Nature could be readjusted by small shifts in their defining constants to occur within each impressionability step. As the outcome of a selection process, the finely balanced situation, that we observed, could be imagined to be optimal with respect to the selection processes.

¹⁰ Some evidence for such a retroacting theory introduced by *Lovelock* has been also agreed in the work of *Ayers*, who followed the existence of dimethylsulfide, plentiful gas produced by microscopical sea plants (phytoplankton), which can be found in large populations at surface layers of the middle ocean (investigated in tempestuous sea region next to the south Australia). Upon the reaction with air, dimethylsulfide oxidizes and forms particles containing sulfur and sulfates, which float upwards and act as condensation sites for clouds formation. The created cloud-cover increases the shadowing of the sea surface and thus reduces the phytoplankton growth and, on the contrary, if a lack of sunshine causes an inadequate amount of phytoplankton growth, then the diminished production of dimethylsulfide decreases the cloud formation and allows the return of full sunshine to recuperate plant escalation.

¹¹ This belief found later its clearest expression in the words, which are often credited to the famous French mathematician *Laplace*, citing "given for instance a mind which could comprehend all the forces by which nature is animated and the respective situation of the beings who compose it – a mind sufficiently vast to submit these data to analysis – it would embrace in the same formula the movements of the greatest bodies of the universe and those of the lightest atom. For such an Intellect nothing would be uncertain and the future, as the past, would be present in its eyes" [W.B. Drees "Beyond the Big Bang: quantum cosmologies and God", Open Court Publ., Illinois 1993]. It, however, can be put under several ratiocinative disputes. Logically arguing, if such a God-Designer is all-powerful could he do things like changing the laws of logic? If yes that it would become incomprehensible to the human mind outfitting the Universe by lawless being. On the other hand, if it is impossible it would be a serious lack of power and lost of the image of impressivity. In the another view of a God-Architecture we may claim that any extraordinarily well organized arrangement of an original singularity, a micro-cell to comprise all the Universe, would require an unthinkable precise hint completed by the design to locate the phase space within a unimaginable tiny volume of the order of something like $\sim 1/(((10^{10})^{10})^{10})^{10}$ – the number with so many decimal zero's that there is not enough particles in the Universe to be associated with each zero.

¹² Let us portray another example in order to aid the imagination of possible magnitude of numbers. The president of the US National Academy of Engineering, *W. A. Wulf*, deduced in his annual, 3rd millennium address that the number of states (1 or 0) of a regular-size personal computer reaches a unimaginable number with so many zeros so that if every atom in the Universe would be a computer itself capable to analyze 10^{100} states per second the time elapsed since the Big Bang would not be enough to analyze step by step all the available states inherent in this computer.

¹³ Another hypothetically implicit particles are assumed on the basis of the earlier 'boson string' theory ('*tachyons*' possessing imaginary mass), or are under the current search within M-theory ('*gravitons*' to intermediate gravitation force moving in the speed of light) or being a subject of some 'sci-fi' hypothesis on information ('*infons*' – projected as a stationary wave of phonon thus imaginary traveling with the speed different from that of light).



CHAPTER THREE

3) Fire as a philosophical archetype

a) Sources and effects of fire

Fire [18,57–61] was believed to have both heavenly and earthly origins: it is brought from the sky by lightning, and it lives in the underworld of volcanoes. Due to its ubiquitous nature and its association with both good and evil, fire has been (and in some places still is) worshipped by many peoples throughout civilization. Because of various psychological reasons, fire is considered to be a personified, animated or living power: it is red like human blood and warm like the human body, it shines brightly in the night and may have a form of "eternal life" or by constant rekindling can be made into a "perpetual fire". Masculine fire (principle YANG – light) is thought to fight from the center and to have the power to decompose what nature joined before while the feminine fire (principle YIN – shadow) attacks from the surface, is difficult to withhold, and often disappears as smoke. Fire was believed to extend throughout the celestial spheres and even time was thought to move in cycles ('ekpyrosis', 'conflagratio') involving a period of its destruction by fire during the cycle's involution and/or end. Fire has for all intents and purposes accompanied mankind's thoughts, beliefs and doings from the very beginning, Fig. 1, until today's serious scientific treatises including the theory of chaos applied, e.g., in the heat transfer and/or distribution (Earth weather conditions).

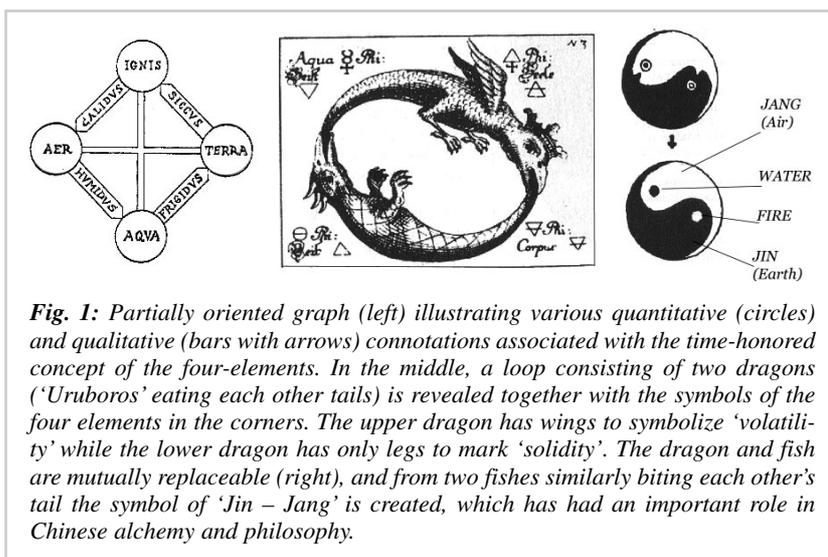


Fig. 1: Partially oriented graph (left) illustrating various quantitative (circles) and qualitative (bars with arrows) connotations associated with the time-honored concept of the four-elements. In the middle, a loop consisting of two dragons ('Uruboros' eating each other tails) is revealed together with the symbols of the four elements in the corners. The upper dragon has wings to symbolize 'volatility' while the lower dragon has only legs to mark 'solidity'. The dragon and fish are mutually replaceable (right), and from two fishes similarly biting each other's tail the symbol of 'Jin – Jang' is created, which has had an important role in Chinese alchemy and philosophy.

The generation of fire, which would be unachievable without the aid of fire bores¹ or saws, (Fig. 2) was also sometimes also perceived as a sexual act that imagin male and female firewood. Corresponding views were most probably pronounced among Aborigines and such a conceptual framework consequently influenced ideas of fire in the body of humans, especially of women, also as a center of sexual life. In archaic civilizations with sacral kings, the sacred perpetual fire (the so called state fire) of the residence and temples of the royal ancestors was believed to have a phallic symbol, and was said to be sacred for virgins, who were viewed as wives of the state fire.

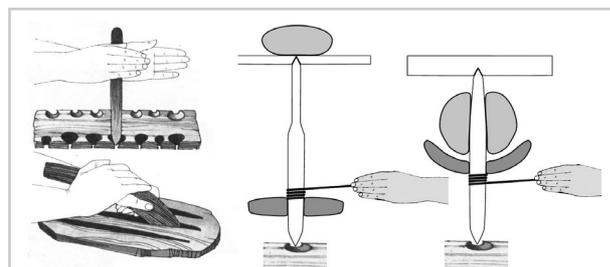


Fig. 2: Illustration of ancient method of making fire by rotating a spindle in the palms of hands or by using a fire-bow. A new alternative method of fire-sticks method driven by a string-rotated whorl (schematically shown on the right in two possible variants) was recently proposed by Mareš. It is an original working hypothesis which has been shown to be in a European historical context as important as the accepted method of striking mineral and flint. Courtesy by J.J. Mareš (Prague, Czechia).

The extinguishing and rekindling of fire at the inauguration of a prince to kingship points to the idea of a spirit of the princes within the state fire and also to the cyclical renewal of the state in the purifying act of fire, which signifies the beginning of a new era. According to some *Hermetic* and *Gnostic* doctrines it was thought that the soul emanated from the God, fell into the body casting its internal fire, and at death returned to its former home. Thus, it was believed that during cremation the soul is helped to separate from the body and continued its journey to the heavens by fire. Fire has duly become a mandatory part of almost all holy places.

Burning, as a source of fire, is invisible. It is only the product of burning, i.e., *flame*, that is visible. The physical appearance of flame exhibits a surprising similarity for different substrates (fuels) and is scientifically reasoned to be a universal portrayal of conglomerated chemical reactions resulting in energy production in the form of heat and light, see Fig. 3. Flame propagation is explained by two theories: heat conduction and heat diffusion (cf. Chapter 4). In heat conduction, heat flows from the flame front, the area in a flame in which combustion occurs, to the inner cone, the area containing the unburned mixture of fuel and air. When the unburned mixture is heated to its ignition temperature, it combusts in the flame front, and heat from that reaction again flows to the inner cone, thus creating a cycle of self-propagation. In diffusion, a similar cycle begins when reactive molecules produced at the flame front diffuse into the inner cone and ignite the mixture. A mixture can support a flame only above some minimum and below some maximum percentage of fuel gas. These percentages are called the lower and upper limits of inflammability. Mixtures of natural gas and air, for example, will not propagate flame if the proportion of gas is less than about 4 percent or more than about 15 %.

At the beginning of science, however, flame was proclaimed to be just an optical illusion and only a visual specter that was felt not to have any substantial purpose – it illuminates and animates its surroundings, creating the illusion of liveliness. Fire can also create a vision of it being a living organism (*'agile' sive/i.e. 'ignis'*) that exhibits growth and change, and that has a need for food and air. Fire is composed of very sophisticated internal structures of flames, and shows continual instability, self-structuring and self-reproduction. Flame is the visible pattern of fire and was treated by any scientific, poetical and mystical essays. There is a Latin proverb *'Ignis mutat res'* – 'fire changes things'². This saying implies that fire has the power to change the properties of matter, metals become ductile, raw food-stuffs can be transformed into a meal. Fire is the kindest servant and the fiercest master; an open log fire and its fireplace (*'focus'*) is a symbol of the intimate asylum of the family home unit but, at the same time, is the source of potentially devastating danger and thus a focus of destruction. Fire is a source of both expansion and contraction, annihilation and purification. The light of ideas reveals the truth, the glow of fire proofs its genuineness. Everything that flares up ends in ashes. Fire is self-destructing; its process of burning turns itself into a worthless thing. Fire is a fundamental beginning with its final effect being the entire end. Fire is often associated with chaos.

It is commonly pointed out that ancient people were familiar with four types of phenomena related to the glow that they associated with the ignition of fire. These sources were thought of as discharges of power: (i) lightening, which was earlier believed to be a sort of burning vapor, (j) the way a torpedo fish stuns its prey (known to the early Egyptians and later recorded by Greek and Roman naturalists), (ii) St. Elmo's fire, which is the pale glow sometimes seen on the tips of pointed objects during stormy weather (again described by the ancient Romans in their military camps), and (jj) the tiny sparks associated with the curious property of attraction shown between pieces of rubbed amber and known as the amber affect (among the ancient Greeks amber became to be called *'electron'*, which was the name also given to the native silver-gold alloy that had a similar color as that of pale yellow sunlight). Any connection between these four phenomena was not made until comparatively modern times when we recognized and separated their thermal and electrical character giving rise of the two basic scientific fields of thermal physics and electromagnetism. *Theophrastus* was known for defining the stone called *'lynce-rium'* and for having observed and discussed both the amber effect and natural magnetic behavior.

Some writers give credit to *Thales*, who is known for his proposition that all things are indeed water and that its basic nature or cause is *'arche'*. Since that time onwards it is worth noting that the early 'natural myths' were slowly replaced by the thoughts and writings of ancient Greek philosophers [35–37], explanations that may be termed as being 'scientific'. Particularly in cosmology, two types of such explanations developed, one of which was theological in character and was referred to sometimes as 'orga-

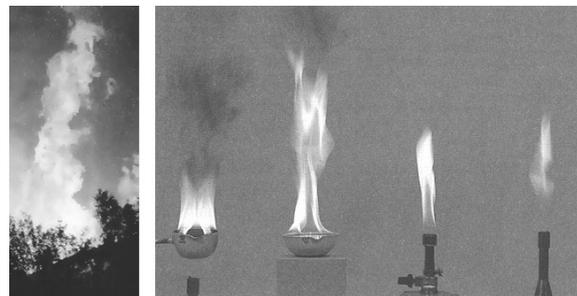


Fig. 3: The shape of flames is similar for the various substrates of natural (left) and artificial fires. Burning natural oil (right) exhibits a similar character to the natural burning of wood. The lower the content of leaving (not fully oxidized) carbon (glowing) micro-particles, the lighter the flame (throughout the sequence from oil, to gasoline, butane and methane, just light bluish, far right). It is worth noting that natural fires (left) has contributed in the creation of landscapes through the regular burning of localized areas due to lightening. Thanks to fires, the countryside mosaic and plant diversity have been maintained and, on the other hand, thanks to mosaic structure, the extent of the fire damage has been kept locally restricted. This natural course, however, has been disturbed by man-made woods, and mono-cultivations due to agriculture rule reasons, which causes national fires to be regionally more disastrous.

nismic' because of its analogy with physical phenomena and the behavior of organism. For example, one such hypothesis concerning amber was that rubbing developed in it a certain "longing", a need that was satisfied by the amber 'catching' its "prey" by projecting arms, as do many living things (not too far from understanding the behavior of caloricum). Another such explanation, known by The Greeks as the respective appellations of *'sympathia'* and *'antipathia'*, was that all objects, both animate and inanimate, possess states of similarity or opposite-ness. This means that all objects that are mutually in „sympathetic" would tend to unite or interact, whereas those in „antipathetic" or natural contrary to one another would exhibit the opposing tendency.

The second type explanation (as a physical explanation) is agreeable with the notion of fire, and may be termed as "materialistic" or "mechanistic". Its hypothesis was advanced in the Century following *Plato* by the Greek philosopher *Epicurus* (and based on the doctrine of *Democritus*) who regarded the universe as consisting of two parts, matter and free space. He proposed that atoms move straight downward according to a natural tendency, supposing that the atoms that are falling through empty space collide by virtue of a self-determining power. This power causes a certain owing to which atoms can swerve a little from their vertical direction of fall. This deviation was termed *'parenclisis'* and enabled philosophers to explain the existence of objective chance and, also, of free will. This logic has had a direct impact on present-day thermal physics, in which we describe a system by a set of so called phenomenological qualities (e.g., tem-

perature, pressure) that are not directly connected with the detailed microscopic structure of matter, but are manifested by directly measured values. Any such a system exhibits small spontaneous deflections from the predicted overall state that are called *fluctuations*, and that are caused by the particular tectonic-configuration of matter. Under standard conditions, fluctuations play a negligible role in most systems or, at least, their effect is averaged. Only under certain circumstances do they become perceivable (often at the vicinity of bifurcations; a novel notion in the present day science) or even play a crucial function in the "spontaneity" of a system, a self-ordering commencement of the above mentioned "free will". The concept of the rotary movement of atoms led to the formation of innumerable worlds, separated from each other by empty inter-mondial spaces called '*metacosma*'. This was followed by the modern thesis of quantum uncertainty that is, in part, derived from the same roots. It, however, was rejected by some important physicists of the time who never accepted the probabilistic spirit of quantum mechanics and, instead, adhered to the *Democritean* access of the order of necessity ('*ananke*').

The term "*free will*" can lead to a confusing paradox because the only freedom that we have concerns the possibility to do what we wish but not necessarily the subject that we wish, best interpreted by the German philosopher *Schopenhauer* citing "*if I wish I could give away my property to the poor, but I cannot wish to wish*" later reformulated by *Barrow* as "*no being can predict what he will do if he will not do what he predicts he will do*". It is related to *Chew's* formulation of the so-called 'bootstrap' hypothesis (1970s) for a continuous dynamic transformation taking place within itself, which is mostly related to the composition and interaction of sub-nuclear particles³. It may even be said to be similar to *Marutana's* concept of '*autopiesis*' (i.e., self-making) [62] for a distinctive organization of (mostly living) systems (sharing the same Greek roots as the word '*poetry*' – creating). *Autopiesis* is used to analyze phase portraits or fractals within the framework of topology, which may appear similar to the action analysis of strongly interacting hadrons within the network of high-energy collisions, however, bootstrap does not form any desirable boundary as the living systems do.

b) Early Greek philosophical views

In early times, the Milesians tried to explain things by the reduction to one simple principle ('*arche*') and by viewing everything from a single point ('*monism*'). *Anaximenes* introduced the important idea that differences in quality are caused by differences in quantity, citing "*when it is diluted so as to be rarer, it becomes fire; while winds, on the other hand, are condensed air. Clouds are formed from air by felting; and this, still further condensed, becomes water. Water, condensed still more, turns to earth; and when condensed as much as it can be, to stones*". On contrary the *Pythagorean School* was a more religious society that cultivated secrecy and speculated that power could be obtained through knowledge. They developed a theory that provides a form or limit (num-

bers) to the „unlimited" saying that things consist of numbers.

Numbers ('*arithmos*') were natural in character and represented bounds ('*peras*') and their ratios were called '*logos*'. They thought that number was a unifying principle in the Universe, so that anything that could be numbered was ultimately linked to other things with the same number. Numbers had meanings apart from their relationships with other numbers. Thus, musical harmony was linked to the motion of the heavenly bodies. The discovery that there were numbers that could not be represented by fractions precipitated a crisis so deep that these numbers had to be called irrational numbers that lay beyond the arithmetic pattern of the Universe. In medicine, the *Pythagorean* saw the principle of harmony at work (body as a musical instrument). *Philolaos* began to teach and lectured about a 'central fire' in the cosmos and located the home of the chief God *Zeus* there.

Later *Zeno of Elea* introduced a proof of contradictions using the term '*aporia*'⁴ and taught that space and time were immanent in our conceptions. The concepts of space and time are not things as they were in themselves ('*noumena*') but rather our way of looking at things ('*phenomena*' – nowadays phenomenology). *Heraclitus* again redirected his attention to the change substituting dynamic '*pyr*' – fire for the static '*arche*' of the Milesians. He said that water, air and even '*apeiron*' are some substances or even material objects, but fire is the process or becoming. Fire cannot be static. It is not a "thing". It is the primary form of reality. Fire itself exhibits the tension of opposites and, indeed, depends upon it. The world is an ever-living fire citing "*this world, which is the same for all, no one of the Gods or humans has made; but was ever, is now, and ever will be an ever living fire, with measures of it kindling, and measures going out*". Neither the Gods, nor they, nor the souls of human beings could escape final destruction citing "*all things are an exchange for fire, and fire for all things, even as wares for gold and gold for wares. Fire lives the death of air, and air lives the death of fire; water lives the death of earth, earth that of water*".

The circular process was called '*ekpyrosis*'. *Heraclitus* taught that all changes in the world arise from the dynamic and cyclic interplay of opposites, and saw any pair of opposites as a unity or a whole. This unity he called '*logos*'⁵. The existence of opposites depends only on the difference in direction of motion; the principle states that The Universe is in a state of flux and that all things are, at the same time, identical and non-identical assuming that the way up and down is indistinguishable. Here we can also cite the famous aphorism "*you cannot step twice into the same river*". The process of change is a process of opposites and diversity creates the problem of identity which is not self-evident, "*it is impossible for fire to consume its nourishment without at the same time giving back what it has consumed already. This presents a process of external exchange like that of gold for wares and wares for gold*". Fire was traditionally a part of limitless '*apeira*', sacred and self-referenced '*apeiron*' (infinite,

boundless) primordial beginning – non-material subsistence. Fire (*'pyr' – flamma*) delivers light (~ eyesight), that is transmitted (~ hearing) by air (*'aer' – flatus*), reflected (~ appetite) by water (*'hydor' – fluctus*) and absorbed (~ tactility) by earth (*'ge' – moles*).

It is part of myth that *Prometheus* stole the fire from *Zeus* (thought by *Platonians* to actually happen to the blacksmith *Hephaestus*). It is of interest that the word '*promethean*' is derived from the Sanskrit name for drill and can thus be understood as a personification of the act of making fire. *Oastanes* the teacher of *Demokritus* was aware that there existed a natural power (possibly fire in sense of energy) that can overcome all other powers and is, thus, capable of creating unification but also is ready to diminish it repeatedly. It, however, was not specified until speculation of some early Greek philosophers, notably *Empedokles*, who was apparently the first to name the four *basic elements* (cf. Fig. 1) that signified the substantiality from which all subsistence (or being) were composed.

In Greek, however, the elements are termed as '*stoi-cheia*' (today's chemical stoichiometry) and the entire name '*elementa*' (beginning) was authentically derived from LMN the first letters of the Etruscan (Phoenic) alphabet. The *Empedokles* concept of such four patterns/roots (*'rhizómata*') was, seventy years later, made widely known by *Aristotle* but it came together with the fifth platonian subsistence/being '*quinta essentia*' that was thought to interject a certain qualitative principle (*'arche*'). It was correspondingly conceptualized as the ether (*'aither'*) – something celestial and indestructible (derived from *'aitho*' meaning glowing, flickering) possibly related to the Aristotelian "primeval matter" (*'prote hyle'*) and interpreted as the presence of subjects. The four elements had been proposed gradually through the ideas of *Anaximenes* – air, *Xenophan* and *Parmenides* – earth and *Herakleitos* – fire, and he also emphasized that fire most completely reveals the "heavenly" reality of our universe, i.e., its order (*'kosmos'*). Sanctified fire gave a basis to the so called "Empedocles complex" where the love of fire is bound with its respect and the instinct of life with the perception of death.

Aristotle was concerned about the general forms and the cause of being (science of being as being), and discussed the notions of potentiality (*'dynamis'*) and actuality (*'entelecheia'*). He also proposed that elements determine not only the degree of warmth and moisture of a body but also their natural motion upwards and downwards according to the preponderance of air or earth. All things are in one way or another analyzable down to the basic bodies – fire tends to rise upwards and become air while water tends to fall downwards and become earth. All motions and all actions succeed in bringing into actuality what is potentially contained in the process of heat transfer such as evaporation and condensation. Mere potentiality without any actuality is the "prima materia" – existing nowhere by itself.

According to *Aristotle*, a body can only be moved if there is a mover in contact with it and if the mover com-

municates with the object by power involved in the movement (the first particles of air are moved first moving than other particles and finally moving the whole object). The power involved in the initial movement of a body decreases, however, in proportion to the distance moved, so that with time, the thrown body comes to a rest. This was taken for granted in almost every philosophy of nature until Newton's brilliant step to overcome this intuitive principle by the introduction of the dissipation of energy into the process of motion. *Aristotle's* consideration of the effect of heat led him to the conclusion that metals, glass and stones that melt on heating are composed of water, whereas materials that merely softened contain various amounts of earth – infusible stones are earthy. Similarly, liquids that did not solidify upon cooling were thought to contain a lot of air and those that readily solidified were supposed to compose mostly of water, and those that thicken were thought to contain more earth or more air. His written observation on "Generation and Corruption" describe flame as a burning of smoke, a claim which was retained by *Theoprastus* in his book "On Fire" but extended to recognize that fire can be generated in various ways and has three manifestations: *flame, burning charcoal* (in sense of glowing combustion) and *light*. It is interesting to remember one of *Theoprastus's* statements that if had the term moisture replaced by flammable volatiles would be an acceptable description for flaming combustion even today. For those times, *Theoprastus* gave a rather accurate account of the slaking of lime when he noted that quicklime evolved more heat when wetted than when left alone, and for the heat stored in the lime is analogous to the fuel required by lamps (note that if "heat" is replaced by "chemical energy" and "fuel" by a "liquid reactant" this statement still stands). Moreover he remarked that old quick-lime does not release as much heat as would new because time had reduced its energy through the contact with air, and that finely-grounded material evolved little heat because of its small particles (noting larger surface area in contact with the atmosphere). These remarkably acute observations not only show the quality of teaching at that time but also demonstrate that the foundation of today's thermochemistry was laid as early as in the fourth Century BC by an implicit distinction of fire, flame and heat. The most significant contribution of *Theoprastus* was in his book "On Stones", in which he not only gave the first classification of minerals (into metals, stones and earth) but revealed a rough form of thermal analysis used as an aid in identifying stones and earth, the latter can be identified with clay minerals, relying only on the five senses, not an easy task even for today's technology. It was written '*some stones can be melted while others cannot, some are combustible while others are not and, in the very process of combustion or, rather, of exposure to fire, stones exhibit many differences ... for earth indeed may undergo melting and if, as some maintain, glass is made from vitreous earth, so too it is firing that causes this earth to become glass*'. *Theoprastus* described the burning characteristics of certain stones, possibly lignite or bituminous shale,

melting of asphalt, conversion of pitchstone to perlite, and the firing stone of Siphonos (possibly steatite) that is *'soft enough to be turned on the lathe and carved, but when it is dipped in oil and fired it becomes extremely dark and hard'*.

Later *Vitruvius* produced his practical treatise "De Architectura" curiously noting the phenomenon of a thermal gradient across the material *'when the sun is keen and over-bakes the top skin it makes it seem dry, while the interior of the brick is not dried ... bricks will be more fit for the use if they are made two years before ... to dry throughout'*. From the fact that larger stones floated on mercury whereas small droplets of gold sink, *Vitruvius* made a clear enunciation of the principle of specific gravity. Clearly the practical knowledge of the effects of fire/heat had progressed more in the time between *Theophrastos* and *Vitruvius* than it had in several centuries previously, as would indeed be expected in a highly civilized Rome that paid much attention to aesthetic aspects of life and to personal comfort, which required the use, creation or manipulation of fire and/or heat.

c) *Concept of four elements*

As already mentioned, it was Greek philosophers who played perhaps the most important role in the concept of fire [37–39, 59–63], and we should again mention that the Greek word for philosophy was derived from the word for love (*'phylia'*), which marked, or better, explained the attraction of different forms of matter, and which had an opposing force called strife, or hate (*'neikos'*) in order to account for separation. Together with wisdom (*'sophy'*), love and hate first appeared in the fifth Century BC and were associated with the problem of the "the One and the Many", which simply stated is the explanation of the infinity of things in The Universe (the Many). The early Greeks believed that the single unifying thing (the One) was some material substance, like water or stone. They were concerned with finding the unchanging principle of substances that lay behind all changes, and the stable unchanging component of the Universe the Greeks often called *'arche'* or *'physis'* (meaning nature as a procreative power).

Xenophanes was a celebrated teacher in the *Pythagorean* school and took the Gods of Greek mythology and, one-by-one, reduced them to 'meterological' phenomena, especially to clouds. God was, in his view, an immaterial eternal being, spherical in form, like a universe, and lots of modern believing scientists often understand God in this spirit, i.e., identifying God with something very abstract, with mathematical or physical principles of the universe. *Empedocles* taught that originally all was The One. All elements were held together in indistinguishable confusion by Love, while the force of Hate manifested itself as a separation of these elements. The four elements were kept in a 'sphere' of Love, while Hate surrounded the outside of the sphere. When Hate began to enter the sphere, Love was driven towards its center and the four elements were gradually separated from one another. The elements alone are everlasting, but the parti-

cular things we know are just unstable and temporary compounds of these elements. They are mortal because they have no substance of their own, their birth is a mixture and their death is their separation. He held fire as the rarest and most powerful compound of elements, which consumed the souls of all intellectuals, and which he thought was issued from a central fire, or the soul of the world.

Anaxagoras postulated a plurality of independent basic elements, which he called the seed (*'spermata'*) citing *"all things ('chremata') were together; infinite both in quantity and smallness; for the small too was unlimited. The science of all things was together; nothing was clear by reason of the smallness. For air and ether contained everything, both being unlimited. For these are the greatest items present in all things, both in quantity and in magnitude"*. He thought that it was a mind, intelligence or pure reason (*'nous'*) that was the source of all motions as well as of the knowledge inherent within us. At the very beginning these seeds mixed without order but under the effect of a cosmic starter *'nous'* the non-arranged matter set itself into motion and began an orderly world *'cosmos'* that was created out of the initial chaos. In more recent times this idea has been a recurrence in *'deism'*, which is the belief in a God-architect, who, after creating The Universe, assumed no control over the created nature or their lives. Such a deity is often used as the explanation of operations of a supernatural cause, which became popular even among some believing scientists.

Plato seemed to distinguish between fire and heat as well as *Aristotle* apparently differentiated temperature from the quantity similar to heat even though the same word (*'thermon'*) was used for both. *Aristotle* and later philosophers paid attention to the notions of *"spirit, breath"* which by some were identified with ether and by others with fire that was always considered as a basic composition element. In *Aristotle's* view any substance is a composite of form (*'morphe'*) and matter (*'hyle'*) originally meaning wood. Consequently this philosophical view was often called *'hylemorphism'* and it stated that matter without form cannot independently exist and so form cannot exist separately, which somehow rejects *Plato's* explanation of the universal Forms/Ideas as existing separately from individual things. He believed that things on the Earth move because they tend to reach their natural places and argued that, although heavenly bodies have eternal motion, there cannot be an infinite series of movers and, therefore, there must be one, the big Mover – the Architect in the series, who is unmoved.

Demokritos and his teacher *Leukippos* imagined immense worlds that resulted from the endless multiplicity of moving atoms. The soul consisted of the smallest and roundest atoms, which were more subtle and globular in shape and could be identified with atoms of fire. Sensation was due to atoms from outside knocking up against the soul-atoms. The first formulation of the principle of causality can be seen in the words *"No thing comes about in vain without cause but everything for a reason 'logos' and by necessity 'anake'."* *Democritos*

introduced the hypothesis of images or idols 'eidola' as a kind of emanation from external objects that made an impression on our senses. He believed in the shape and related arrangements of elementary particles, and similarly to *Pythagoreans*, he distinguished notions for 'matter' and 'form' linked through a process of development. In contrast, *Plato* and *Aristotle* believed that form had no separate existence but was immanent in matter; their philosophy and scientific ideas dominated Western thoughts for two thousand years until a radical change was brought about by the new discoveries in physics, astronomy and mathematics (*Copernicus*, *Bruno*, *Galilee*, *Descartes*, *Bacon* or *Newton*) that viewed the world as a perfect machine governed by exact mathematics.

In the Greek interpretation that all material things are a different combination of elementary *fire*, *air*, *water* and *earth* held together by an integrative and structural essence *ether* that was a heavenly and imperishable matter (which was thought to make up the universe of fixed stars and firmament). The four elements were not only plain mixtures (quantities) but arranged as a balance of four qualities: *hotness*, *coldness*, *humidity* and *dryness* that defined each element using the pairs of opposites (dry/hot, dry/wet, wet/cold and dry/cold). Hotness and coldness were active and the remaining two were submissive (secondary passive) qualities. Properties associated with dominant (active) qualities had a tendency to grow if the object is surrounded by either a hot or cold environment. It was, in fact, the first sense of a *thermal process*. Due to the enormous vastness of these relationships the graphical representation became very popular (cf. Fig.1) and later it was even believed that the formal manipulation with graphical symbols can be helpful for the solution of particular problems (cf. however, modern theory of graphs).

The hypothetical structure of matter based on such a scheme brings about an important consequence – the potential or intrinsic "thermal" property of all existing substances. Thus, e.g. alcohol, gunpowder and pepper are intrinsically hot substances, continuously active in this sense also with respect to other bodies, while opium and snow are examples of intrinsically cold materials. Moreover, the antagonistic nature (so called '*contraria*') of different Elements and Qualities ensures eternal changes and movements of all things in the universe. These changes are, however, not completely free, but are submitted to the remarkable principle of '*antiperistasis*' that controls the relationship between the two active Qualities – coldness and hotness. It can be formulated as follows [5]: *The properties of any body which is bound up with coldness (hotness) tend to increase in the case where the body is surrounded by the hot (cold) environment.*

This principle akin to the modern *Le Chatelier – Braun* principle provided, in a lot of cases, a correct qualitative predictions of the direction of thermal processes. We may quote *Oinipides of Chios* for a typical example consistent with the principle of antiperistasis: "Water in a deep well shows in winter the smallest degree of coldness, while in very hot days is extraordinarily cold." Interestingly, this

statement is actually valid and is not only a consequence of our subjective feelings, but it was confirmed also by careful hydrological studies.

Besides numerous successful applications of the principle of antiperistasis, there were also cases where it completely failed. One example of such failure is the dissolution of black gun-powder containing saltpetre, which, led contrary to expectation, does not warm up but instead cools down. Such exceptions were either neglected or, in better light, given an opportunity for discussion about other weak points of the doctrine. The most important problem, crucial for the theory, was the so-called problem of '*primum frigidum*'. While there was no doubt in which Element warmth dwells – of course in fire – the primary domain of coldness remained uncertain and, thus, made the conclusions of the theory not very plausible.

The later gathering of the vast practical experience with glass bowl thermometers resulted in the following of the '*peripatetical*' (i.e. Aristotelian) explanation of its function together with the above theory as a whole became rather diffident. Accordingly, the coldness in external air activates the hotness inside the bulb which then is likely discharged into the wall of the bulb. This process changes the ratio between 'Qualities' of the enclosed air, in other words, it changes its 'Form'. This depleted form of air has obviously a smaller volume and the resulting empty space has to be immediately filled by water due to the '*horror vacui*' – nature's abhorrence of a vacuum.

In spite of this fact, the concept of temperature was superfluous for the general description of natural processes within the frame of Aristotle's theory; the term '*temperatura*' was frequently used by ancient physicians well before *Avicenna*. Their idea of temperature was in closely connected to the individual's temperament and was determined by the relative levels of four Qualities that were necessary to maintain the form of the tissues of the human body in a proper healthy state – homeostasis. But, in fact, these old physicians did not appear to care about how to determine these evidently crucial parameter.

Certainly, matter ('*materia*' – *potentia pura*) was not distinguished from energy ('*energie*' – *actus*) such that it was proposed that *when heating a metal one was simply adding more "fire" to it*. *Theophrastos* proposed three stages of fire: *glow*, *flame* and *lightening* while *Galenos* brought in the idea of four degrees for warming and cooling with a "neutral point": equal parts of ice and boiling water. These four degrees were still accepted by medieval alchemists and *Mylius* [65] proposed a classification according to the Sun passing through *Aries* (signifying calcination), *Cancer* (solution), *Libra* (sublimation) and *Capricornus* (fermentation). The highest degree of fire was *burning as vehement as fusion and each twice as great as the preceding degree*. *Comenius*, a well-known Bohemian educational reformer and philosopher of Czech origin, progressed to distinguish three degrees of heat (*calor*, *fervor* and *ardor*) and cold (*frigus*, *algor* and one unnamed) with a reference to an ambient (normal) temperature (*tepor*). The highest thermal stage, called

"ardor", represented an internal degradation, i.e., "a combustible substance that collapses inwardly and is dispersed into atoms". The unnamed coldest stage was noted as "a freezing at which a substance breaks up by constriction in the same way as the heat of fire decomposes it by burning". In this manner Comenius actually, although unwittingly and unknowingly, hinted at the present-day concept of absolute zero. He also stated [66] an almost modern definition of *thermal analysis*, (genially interpreted by Mackenzie) as "...to observe clearly the effect of heat and cold, let us take a visible subject and let us observe the changes that occur while heated or cooled, so that the effect of heat and cold are apparent to our senses...". Comenius was also the first to observe the "non-equilibrium character" of such thermal treatment and analysis, noting "...by a well burning fire we can melt ice to water and heat it quickly to very hot water; but there is no means of converting hot water to ice quickly enough even when exposed to very intense frost...". It was an intuitive observation of the phenomenon now called latent heat, and possibly laid the foundation to the discipline of calorimetry.

d) Impact of alchemy

The history of fire cannot be complete without mentioning the subject of 'alchemy' [67–70], a form of science that preceded, and arguably began, the more rigorous and modern discipline of chemistry [71]. The origin of the word alchemy is disputed and could be from the Arabic word 'al-kimijá' – meaning treated by fire, the Hebrew

Table I: Scheme of spagyric treatment of herbs (early roots of homeopatics).

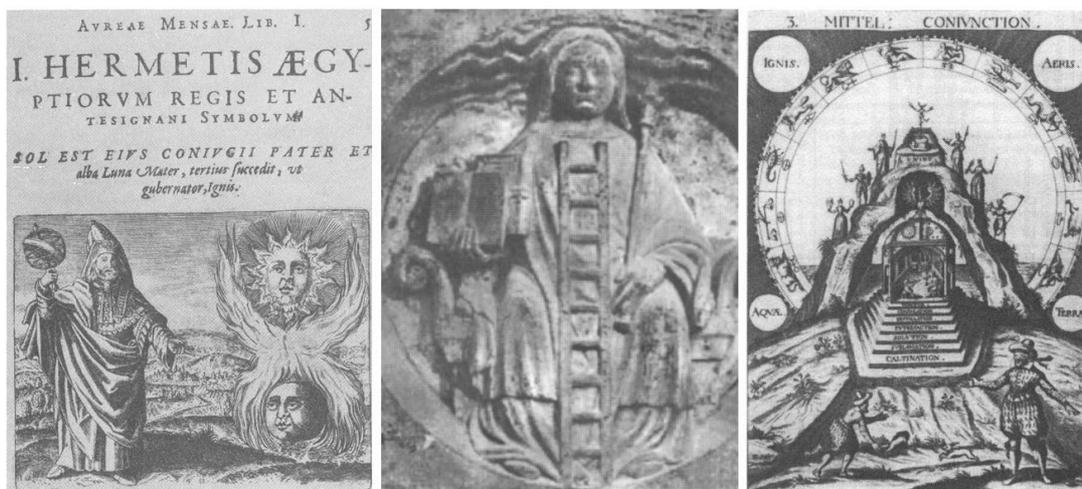
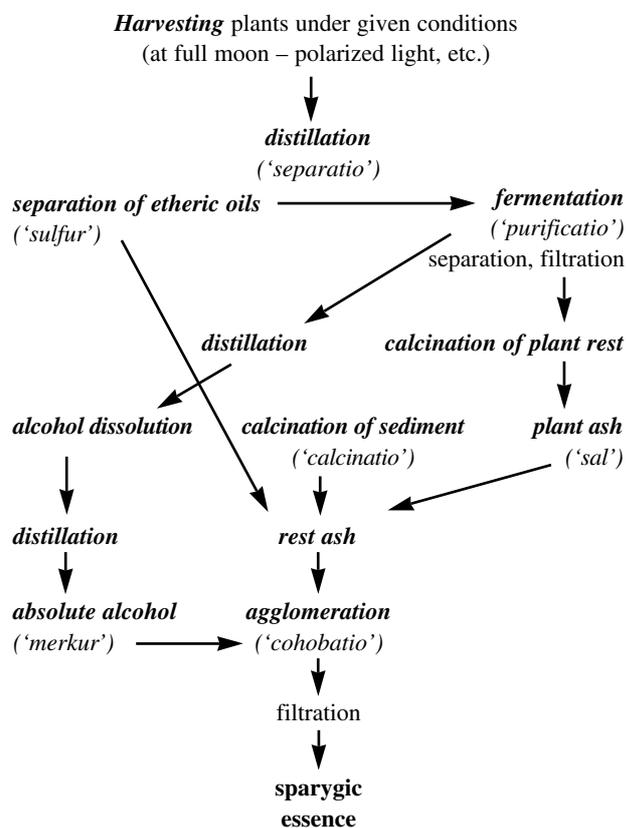


Fig. 4: Choice of symbolic epitomes related to Alchemy shows (left) the allegoric pictures associated with the early edition of books related to Hermetic philosophy and alchemy. The middle figure illustrates the secreta position of alchemy as a lady-figure sitting on the throne with her head touching the sky (blessed wisdom), holding in the left hand a scepter (as a symbol of power) and carrying in the right hand one open and one closed book representing the unlocked and secret sides of learning. The ladder symbolizes patience necessary to pull off all the steps to achieve self-acknowledged epiphany (attainment of the state of "Big Masterpiece"). In the right picture, the hoodwinked figure illustrates the one who does not follow nature while the other, more appropriate one, is allowed to lionize the "Earth Interne – vitriol" following thus the rabbit, which is symbolizing "prima materia". The seven steps are shown to go up, gradually climbing the mount, symbolizing the seven metals' tasks and aiming to the planetary Gods. After ascending the seven steps both principles (sulfur and mercury) are purified and, thus, are revealed as naked bodies, which symbolizes the desired state of "Heavenly Mercurial" (Cabala 1616).

word '*Ki mijah*' – meaning given by God, or the Greek word '*chemeia*' – meaning comprehension of wetness. The latter was also found in the writing of *Diocletian* as the art of making metal ingots and the term '*cheo*' means pouring or casting a liquid and '*chymeia*' means the art of extracting juices, herbal tinctures or generally saps in the sense of vitality. Also the current word 'chemistry' may be related to the Egyptian word '*kemet*', which means 'black earth' or to something unknown but precious in relation to the Persian word '*khimia*'. Fire is even mentioned in the Christian theological lineage, e.g., the abbreviation INRI ('*Jesus Nazaretus Rex Judaeorum*') was once interpreted as '*igne Natura Renovatur Integra*', i.e., through fire Nature is restored to its wholeness.

It is not generally known that alchemy was later subdivided into *spagyrii*, the art of producing medicaments (see Table I), dyes, ceramics, etc., (often trying to transform matter into algebraic combinations), *archemii*, which focused on the development of metallurgy and transmutations of metals, and *Hermetic philosophy* (often synonymous to alchemy itself, see Fig. 4), which is a sanctuary of learning ('*prisca theologia*') build upon performance ('*tractatio*'), explanation ('*exegesis*') and interpretation ('*hermeneusis*' – nowadays giving substructure for a modern interpretative hermeneutic description).

Behind the legendary seven Hermetic principles there lie aspects of early cosmology and a verbally bequeathed book known as '*Kybalion*'. Some of the inherent principles of alchemy are, indeed, reflected in modern terms and ideas of current physics, which is often criticized because alchemists certainly thought within completely different frames and measures. Nevertheless let us abbreviate some of them:

- 1) *Principle of spirituality* – The Universe is a spirit or belief, and was created simultaneously with many other universes – their origin and destruction occurring in a twinkling of an eye.
- 2) *Principle of similarity* – what is above is also below, birth of universes and fundamental particles, creation of works of art.
- 3) *Principle of vibration* – nothing is motionless, everything is in permanent move, vibration of matter is slow while vibration of mind is too fast to evoke stationary state, vibrational switch leads to qualitative changes.
- 4) *Principle of polarity* – associates with vibrations, the higher the vibration, the more positive the pole, everything has two faces, it shows the antagonisms of order and disorder, war and peace, day and night. There follows from this an ethical edict to transform hate to love.
- 5) *Principle of rhythm* – following the polarity as everything is oscillatory, coming up and away, breathing in and exhaling, arriving and leaving, inflow and outflow, circumambulatory come-and-go.
- 6) *Principle of causality* – every action has its consequence, and coincidences do not exist but are the effect of an unknown law, people are subjected to a lawfully ordered universe.

- 7) *Principle of gender* – sexuality is involved in everything, counterwork of masculinity (positive pole) and femininity (negative pole), process of generation, sexual energy in spiritual alchemy, God mate (often identified with point 4).

Alchemy, however, prescribed to the idea of existence of a "first mover or God as creator" (Almighty, Deity) and believed in an evident order installed in the world. This argument, probably formulated by the Iranian prophet Zoroaster, was expressed in the form of the question: "*who could have created the heavens and stars, which could have made the four elements, except God?*". In the Christian Europe the alchemy was similarly presented as '*donum Dei*' [72].

Hermetic learning might well have been ascribed to astrology by the *Hermes Trismegistos* but, later, it was extended to medicine and alchemy, where the obscure Byzantine '*Tabula Smaragdina*' [73] became a favorite source for even medieval alchemists. It contained seven famous principles, and from these scholars obtained knowledge of the laws of sympathy and antipathy by which the different parts of The Universe were related. Hermetism was extensively cultivated by the Arabs and through them it later reached, and consequently greatly influenced, the Western culture although often misinterpreted. Hermes' stick '*rhabdos*' was ornamented by two twisted snakes showing "waving water and blazing fire" as a unity of contradictions and thus becoming a symbol of life. In the present time it may be speculated that it resembles the double helix structure of DNA structure.

Although it is difficult to be certain of its origins, alchemy most likely emanated from China (traced as early as in the 8th century BC and better inscribed by 144 BC) in connection with an enterprise older than metallurgy – medicine. Chinese practitioners of alchemy generally considered its ultimate objective to be the development of medical practice and not the generation of gold from base metal. Alchemy in China was all but destroyed when *Kublaj-chan* ordered the burning of the *Taoist* writings, thus destroying most alchemistic records (including that of the earliest recipe for gunpowder). For a long period of time, it was believed that physical immortality could be achieved through the taking of alchemical mixtures (drugs), an idea that probably vanished when the Chinese adopted *Buddhism*, which offered another, less dangerous avenue to immortality via meditation. This shift in belief left the literary manifestation of early Chinese alchemy embedded in the residual *Taoist* canons.

One of the important but less well-known treaties was the book on therapy by nourishment '*Sh-liao pen-cchao*' published by *Meng-Shen* in about 670 AD. It described the process of distillation was already described and the quality determination of distillates that could be accomplished by the process of freezing out. However, the oldest known Chinese alchemical treatise is supposed to be the "*Commentary on the I Ching*", which had an apocryphal interpretation of the 'classics of changes', and which was especially esteemed by the *Confucians* who related alchemy to the mystical mathematics of hexa-

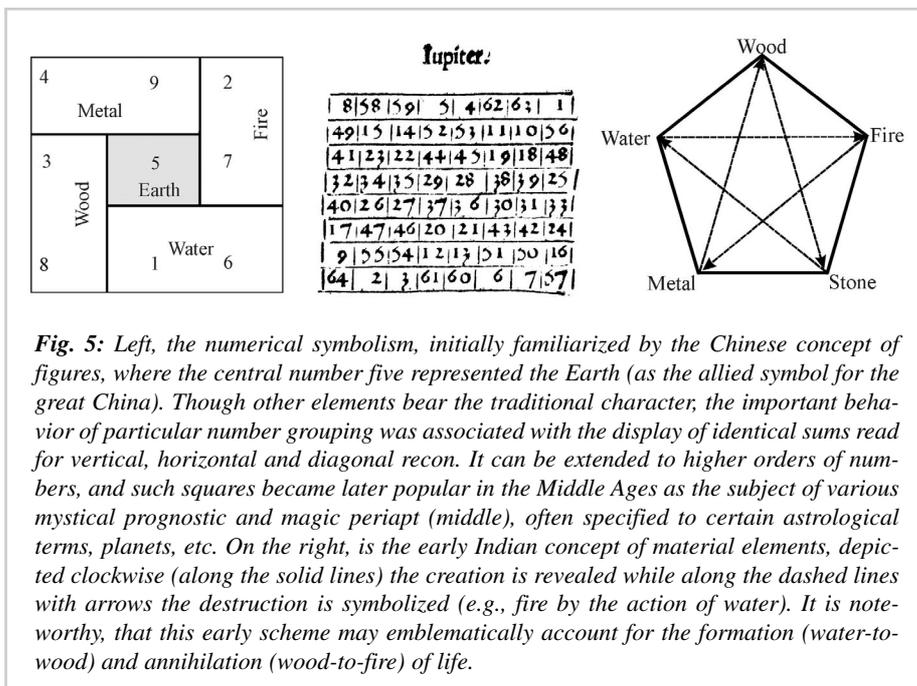


Fig. 5: Left, the numerical symbolism, initially familiarized by the Chinese concept of figures, where the central number five represented the Earth (as the allied symbol for the great China). Though other elements bear the traditional character, the important behavior of particular number grouping was associated with the display of identical sums read for vertical, horizontal and diagonal recon. It can be extended to higher orders of numbers, and such squares became later popular in the Middle Ages as the subject of various mystical prognostic and magic periapt (middle), often specified to certain astrological terms, planets, etc. On the right, is the early Indian concept of material elements, depicted clockwise (along the solid lines) the creation is revealed while along the dashed lines with arrows the destruction is symbolized (e.g., fire by the action of water). It is noteworthy, that this early scheme may emblematically account for the formation (water-to-wood) and annihilation (wood-to-fire) of life.

grams (six-line figures used for divination). Ancient Chinese natural philosophy was thus based on a flat, square Earth with the centered Chinese empire surrounded by the eight trigrams as the symbol of The Universe [74]. There were five elements ('wu hsing'), see Fig. 5, that were related by two complementary principles 'yin' and 'yang'. Mutual transformation of the five elements could, e.g., give the birth of metals from Earth, or change metal to water, because on a proper treatment metals can turn to the liquid state, etc.. The elements were mutually antagonistic because fire is extinguished by water and water is stopped by earthen dam, etc.. Yin represents the female principle (darkness, passivity) while yang, as the male principle, is connected with light and energy. Even numbers were considered as yin and odd numbers as yang. Each number was associated with one of the elements – the central number five exhibiting a crucial position. This number symbolized the earth and, simultaneously, represented the most prominent position between the five geographical directions – the center.

This approach has also qualified in the so called 'magic squares' – a famous object of philosophical, alchemical or mystic speculations [74]. It is known as a square-shaped array of numbers (or even letters) exhibiting certain properties, i.e., the sum of the numbers in each row, column or diagonal being equal. Because of its conspicuous worth it was kept surreptitious until the Arabic alchemist *Jabir ibn Hayyan* refined it into a very detailed but complicated system in his 'Book of the Balances'. A numerical value for basic properties was assigned to each letter of the Arabic alphabet. When a word for a substance was subsequently analyzed letter by letter, the numerical values of the letters determined its composition. For example lead was composed of the 11 outer qualities (3 parts of coldness and 8 parts of dryness) and 6 inner qualities (1 part of warmth and 5 parts of

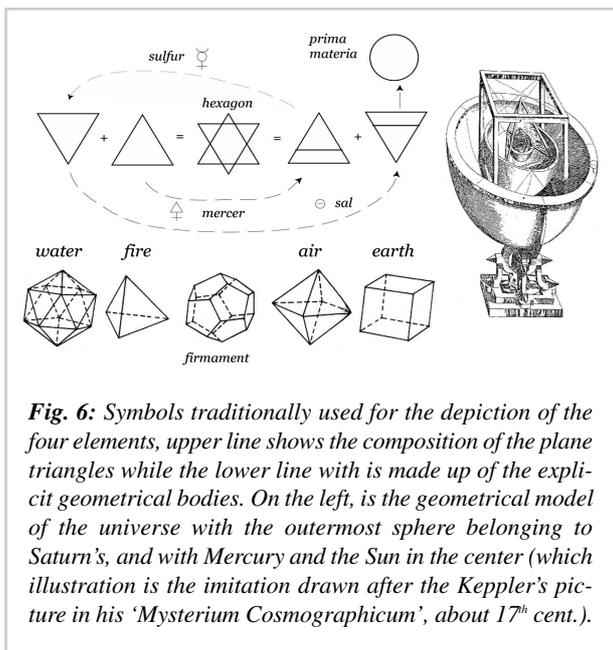
humidity), altogether 17 parts. If, in a similar manner, the qualities were summed up for gold then a somewhat insignificant difference between lead and gold was found, i.e., for gold also 17 parts of 11 outers and 6 inners again, indicating that a proper alchemical treatment (transmutation) could change the nature of such 'interrelated' metals. It was certainly applicable to the given alphabet and thus could have been freely interpreted⁶.

Later in *Agrippa's* and *Paracelsus's* medieval books, this magical application was rediscovered but using the squares that were constructed by the Islamic method (although no direct link was traced with Islamic sources). It appeared as

a promising way to achieve novel discoveries of new relations between things and their properties. The myths of dignified numbers persisted in China until recently [75], which idea might be penetrating the denomination of the periodic table of the elements where the 'prime numbers' and 'numbers of symmetrical principle' are though to be the restrictive islands of the element stability.

Also in India there is evidence for alchemy in Buddhist text. Alchemy came to be associated with the rise of *Tantric* religious mysticism and was recorded in the writings of "*Rasaratnakara*" (in about the 8 Century AD) and "*Treatise on Metallic Preparations*" (~ 1100), which recognized *vitalism* ('animated atoms') and *dualism* ('love and hate' or 'action and reaction'). The earliest records from 500-300 BC already recorded that the theory of nature was parallel to the conception of rudiments ('tejas' – fire, 'vādzu' – wind, air, 'ap' – water, eprthvī – earth and 'akāśa' – wood) but without a more definite influence comparing the role of elements in other alchemical images. In *Theravada's* view there was a plurality of universe surrounded by water and mountains having three planes of *material form* (physical body), of *desire* (mental body) and of *immateriality* and/or formlessness (body of law). In practice, the Indians has begun to exploit metal reactions to the extent that they knew as many as seven metals (and already subdivided as five sorts of gold). They supposed that metals could be "killed" (corroded) often to provide medicinal bases but not "resurrected" as was the custom of later European alchemy.

However, the birthplace of known alchemy is arguably Egypt and the Greek God '*Hermes*' (identifiable with the Egyptian God '*Thoth*'), who is possibly represented as the alchemy father in the largely indecipherable *Emerald Tablet* of 150 BC (as a part of a larger book of the secrets of creation), which existed in both the Latin and Arabic manuscripts. The history of Western alchemy



may go back to the beginning of the *Hellenistic* period and is represented by *Zosimos of Panopolis* (3rd Century AD) who focused on the idea of a substance called "tincture" that was capable to bring about an instantaneous and magical transformation. The earliest notable author of Western alchemy, designated by scholars with the name *Bolos of Mende*, was a Hellenized Egyptian who is often represented by his indefinable treatise called 'Physica kai mystica' (Natural and Mystical Things) that contains obscurely written recipes for dyeing and coloring as well as gold and silver making.

The testing of materials was understood in a double sense, experimental and moral; gold was considered noble because it resisted fire, humidity and being buried underground. Camphor, like sulfur, arsenic, and mercury belonged to the 'spirits' because it was volatile. Glass was assumed to be a metal because it could be melted, a property associated with the seven known metals. The 13th Century AD pseudo-epigraphic book on chemistry, known as the 'Summa perfectionis', contained the terms alcohol (older meaning of powder), alkali, borax or elixir and also suggested that metals were compound bodies made up of a mixture of mercury and sulfur. It recognized 'prima materia' (first matter) as being a *fixative* (visible and solid – earth, represented by sulfur), *quintessence* (personification – salt) and *evanescentive* (implicit, hidden – air, represented by

mercury). It was characterized by triangles that pointed up (escaping) or down (falling), see Fig. 6.

It was close to the Platonian geometrization that represents fire as a tetrahedron, air as an octahedron, water as icosahedra and earth as a hexahedron (cf. Fig. 6). By analogy it was also ascribed to show spheres of Mars, Earth, Venus and Mercury with the Sun in the center. Dodecahedron was assumed to play a role of the fundamental structure of firmament. Identification of elements with certain geometrical bodies led, however, to mechanization and mere abstraction of four elements was not thought to be clear enough for the need of alchemist's teaching so that it was supplemented by additional three imaginary principles, see Table II.

Table II: Initiative of 'Tria Principia' derived from the scheme of four elements and their consequent performance: fire acting upon air created 'sulfur', air against water released 'mercer' and water against earth gave rise of 'sal'.

combustibility	fusibility, ductility	durability
sulphur	mercury	salt
soul, psyche ('mens')	mind, brain ('anima')	body, figure ('soma')
Egyptian tradition	Greek philosophy emphasizing principle of	Metallurgy spirit
- flammability	- shine and volatility	- solubility/incombustibility
	taste of alcohol	
- smearingness, oil, hidden air, fire	air, water	- salt, earthiness earth

In the Middle Ages, European alchemy was chiefly practiced by Spanish and English monks (namely *Bacon* and conceivably also by the Christian mystic *Lulla*), who were seeking to discover a substance more perfect than gold (philosopher's stone) as well as a potable gold (eli-

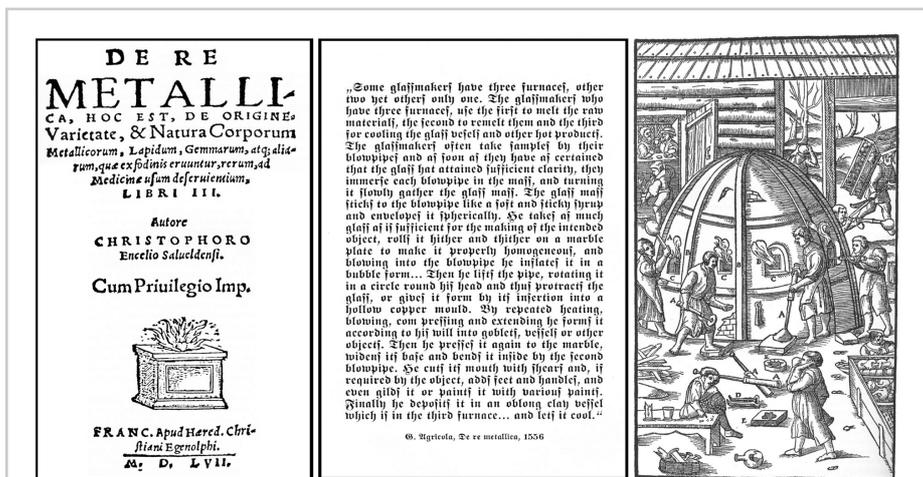


Fig. 7: Reproduction of the title page (front prolegomenon) from the very influential book "De re Metallice". Another two selected inside pages (right) describe the process of processing glass and illustrate, thus, the period furnace with glass pipe-blowing custom. Note that the smart way of drying the fuel wood by pushing it around the furnace wall enabled to minimize the humidity and to achieve its higher caloric value.

xir of life). Worth noting is Swiss/German *Paracelsus* who remarked that it is the human body that is the best of all 'alchemists' as it is capable of transmuting food into a variety of vital compounds. He also tried to understand alchemy as a kind of art. He highlighted the mystifying 'alkahest' as a universal medicament and he stated four pillars of medicine: *philosophy* (knowledge about nature), *astronomy* (knowledge of the macro-cosms), *alchemy* (in the terms of *Spagirii* as production of medicaments) and *virtue* (honesty of physicians). He held that the elements of compound bodies were salt, mercury and sulfur representing earth, water and air, respectively. He is also thought to be responsible for reintroducing the term alcohol from Arabic 'al-kuhl' (originally meaning fine powder, Greek 'xérion') as an early medicament otherwise known as 'tincture', which he thought was a cure for everything. The Bohemian alchemist *Rodovsky* depicted alcohol as 'aquam vitae', a medicinal elixir that is best obtained by a procedure involving 14 repeated distillations of wine and the addition of 15 various herbs. It provided a more real grounds to the mystical world 'elixir' (from Arabic 'al-iksír' meaning gemstone).

Fire was regarded as imponderable or nonmaterial and alchemists used heat lavishly and most of their illustrations include some indication of fire, furnace or a symbol of sulfur. Despite the crudity of the above-mentioned degrees of heat, alchemists laid more emphasis on an accurate temperature control of furnaces (*Norton* [67]) necessary in early metallurgy (*Agricola* [68]), see Fig. 7. Adjustment of temperature was, however, purely manual, oil lamps with adjustable wicks, water and sand bathes for lower temperatures and variation of fuels for higher temperatures. In various processes, such as firing ceramics or melting glass, it was vital to keep certain temperatures constant. This required the introduction of early scales for experimental practice. Moreover, fuels giving moist or dry heats were distinguished with an awareness of how to produce high temperatures (also used in burning glasses and mirrors). They also accumulated a vast store of knowledge of the effects of heat on various substances, even if they were unable to interpret the results and satisfactorily measure the temperature. The most celebrated process was calcinations, i.e., firing substances to turn into powder known as 'kalk' or 'calx' sometimes called 'alcool' (of gold).

The calcinations furnaces were customary named 'athanor' (from Arabic 'at-tannur') when sand in a bath was replaced by ashes.

While Arabs had only weak acids, European alchemists of the 16th century learned to prepare and condense strong acids like *aqua fortis* (nitric acid) and spirits of salt or vitriol (hydrochloric and sulfuric acids), their mixtures capable of dissolving even gold. They became a powerful instrument that made it possible to produce and also characterize ever more varied salts and their spiritual parts separated by distillation enabling to create a more exacting relationship between the identity and way of its testing. An unidentified element, often termed as *alkahest* ('alkali-est' – in the sense of a universal solvent resembling today's action of a catalysts) was believed to exist as grounds of the four basic possibly to act as an universal medicine. At the turn of the seventeenth Century, alchemy flourished remarkably during the region of the Bohemian emperor *Rudolph II* and Prague became a home of

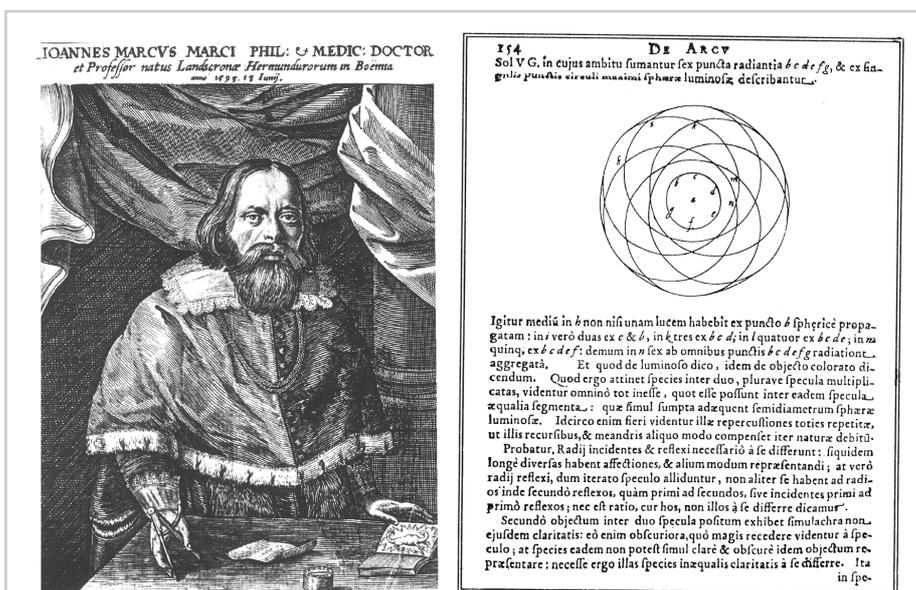


Fig. 8: Marcus Marci (left) probably discovered the fundamental properties of the spectral colors that emerge when light passes through glass prism already aware of their monochromatic properties, i.e., any succeeding refraction or reflection did not change colors. He also studied the color change in rays when spectral colors are mixed. He passed light through a glass prism twisted into the form of a bracelet, which he called the 'trigonum armillare'. He pondered on the diffusion of light in circular spheres, and the way in which the intensity of the light diminished with increasing distance from the source, but only to a certain, terminal distance. He, however, was strongly convinced that white light was the simplest element, the 'quinta essentia'. Interestingly, his ideas were close to the subsequent concept of 'elementary waves' propounded about fifty years later by Huygens in the wave theory of light.

Facsimile of the page 154 of his book 'Thaumantias liber de arcu coelesti' (right) explicates the Marci's two-dimensional model of the propagation of light spheres from a spherical source: on a circle with center (a) he chooses six regularly distributed point designated with the letters (b – g). From these points (as it were centers) he draws circles of the same diameter as a picture of the spheres of propagating light. The points of intersection the circles designated by (h – n) indicate the increasing intensity of the light in the direction of its source, and the set of light spheres is closed in an 'envelope'.

many famous alchemists, among others there were *Hajek* or *Rodovsky* of Czech origin as well as noteworthy *Stolcius* and *Marci*. The latter wrote for that time very advanced books [76,77], which possibly foreshadowed the refraction laws of light and came intuitively (cf. Fig. 8) within reach of the conservation laws. There, however, are inconsistent information about his educational activity. The famous Charles University, founded 1348 in Prague as the first university in the middle Europe, unveiled possibly a world first specialization called "*chimiatrie*", which was conceivably taught as an unusual subject with regards the traditional university disciplines: major '*artes liberales*' and minor '*artes mechanicae*'¹⁹.

Medieval teaching, cf. ref. [65,67,68,71,79,80], is difficult to recapitulate in a condensed form but even in the contemporary world, full of progressive technologies, this elderly philosophy has retained its incomputable role. It remained engaged in the challenge of trying to

maintain a sustainable world, on both levels of matter and mind, for the next generations. *Popper* recently recalled '*Tria Principia*' of cosmic evolution grades pointing out three internal appearances of The Universe: (i) a world of physical contradictions (challenge, personal precariousness – 'sal'), (ii) a world of significance (implication, subjective experience – 'sulfur') and (iii) a world of energy (vivacity, creation of the human mind and ingenuity – 'mercer'). It is somehow related to the interdicted and almost forgotten Hermetic philosophy, with prophecy (God) having the highest, and matter (Earth) the lowest state of eternal vibrations, everything there undergoing processes of dissolution ('solve'), and integration ('coagule') within three levels: (j) exploitation of raw materials or digesting of food on a physical level (life), (jj) breathing, energetically based on a spiritual level (love), and (jjj) meditation, thought based on a heavenly level (wisdom).

¹⁹ An original working hypothesis was recently presented by *Mareš* (at the Conference on Reconstructive and Experimental Archeology, Břeclav, Czech Republic 2002), according to which a spindle-wheel (or simply 'whorl') was used in ancient Europe not only for the spinning of yarn but also as a fire-making device. This theory was supported not only by the rather convincing archeological finding of a whorl (and a guiding leader-string) as part of the belongings of a frozen medieval hunter, who was found high in a glacier of the European Alps (possibly free of any need of yarn-spinning) but also by *Mareš*' direct experiments, in which he showed that fire can be generated using a certain modification of the fire-friction-bores driven by the whorl (cf. Fig. 3-2). It is also worth noting that this set up for making fire is essentially different from the well-known North-American type used by Indians as well as such a drill was rather surprising when accounting on the Roman-Catholic consuetude at that time, which pragmatized making 'abrasive' fire by using fire bores as a barbarian 'sexuality' custom so that for long it was religiously allowed to merely use the strike-a-light manner (from hitting flint against steel, or so).

² It is often exemplified by a burning candle; the more the wick is flaming the more is extinguished being buried in the melted wax thus feeding back the actual fuel supply.

³ Commonly it is related to the theory of elementary particles in which the existence of each particle contributes to forces between it and other particles and these forces lead to a bound system in which each particles helps to generate other particles. It, however, encompasses other meanings such as in electricity, where it represents a single-stage amplifier in which the output loud is connected between the negative end of the anode supply and the cathode, while a signal voltage is applied between grid and cathode, a change in grid voltage changes the input signal voltage with respect to the ground. Bootstrap also serves as a device that provides the automatic input for new computer programs in the memory without arising the basic instructions in the computer, or it can represent a self-generating or self-sustaining technical process (such as the operation of liquid-propellant rocket engines in which, during main-stage operation, the gas generators are fed by the main propellants pumped by the turbopump, which in turn is driven by hot gases from the gas generators).

⁴ It is also close to the notion '*paradox*', which is a synthesis of two Greek words '*para*' and '*doxos*' meaning beyond a belief. It is often assumed interpretative as something, which appears, contradictory but also self-evidently truthful. Paradoxes have played an important role in intellectual history often overshadowing revolutionary development in sciences whenever a conceptual framework could not help to solve the problem. From the traditional Zeno's paradox of Achilles and the tortoise, which appeared to show that motion is impossible (and thus gave a birth to the idea of convergent infinite series) up to the modern paradox of counter-intuitive findings that is believed to shed light upon something fundamental (such as the Maxwell's demon giving the insight of intimate linking for the seemingly disparate concepts of entropy and information).

⁵ Similarly applied to "awake people", those who could make themselves understood. As matter of interest – those who avoided public life of their city states ('*polis*') were called strangers and were rated as second-rate citizens ('*idios*').

⁶ The futuristic followers of alchemical transmutation, impinging as far as into the nineteen-twenties, also played such a mechanical game with figures using, however, the modern isotope numbers. For example, when accounting the mean atomic mass of most widespread isotopes of $^{56}_{26}\text{Fe}$ (91.5%), $^{48}_{22}\text{Ti}$ (73.5%) and $^{14}_7\text{N}$ (99.6%) we may get for the formula: $\text{Fe}_3\text{Ti}_3\text{N}_6 \Rightarrow ^{198}_{79}\text{Au}_2$ (Note that it contradicts the most commonly occurring isotope $^{198}_{79}\text{Au}$, which is found in nature). It, however, was inspired by $^{49}_{23}\text{V}$, which can be altered to $^{49}_{22}\text{Ti}$ through a supposed recapturing of its own electron to stabilize its nucleus containing too many protons. Another transmutation rumor was initiated by French professor *Kervran* (cf. his book 'Biological Transmutations, Barton 1972) for the apparent equivalence of $^{14}_7\text{N} - ^{14}_7\text{N} \equiv ^{12}_6\text{C} - ^{16}_8\text{O}$ initiated by the audible parity of physical properties of N_2 and CO and some obscure incomparability of N_2 vs. CO compositions measured at processing of iron as well as in some vigorous biological systems where even another curios changes was indicated for the apparent contents ratios $^{28}_{14}\text{Si} - ^{12}_6\text{C} \equiv ^{40}_{20}\text{Ca}$.

- ⁷ It is clear that life on the Earth depends on the unusual structure and anomalous nature of liquid water. Its small embryos of four molecules tend to come together to form water bicyclo-octamers which may cluster further to cyclic pentamers expanding to somehow curious network of ordered icosahedra (as foretold by *Platon*, see above Fig. 6), which are in a certain dynamical equilibrium with its collapsed, but more frequent form of a more symmetrical dodecahedra. The solid, denser form of water is the hexagonal ice and has a structure that is uncanonical with respect to the 'pentagonal-like' symmetry of a solidifying liquid that contains a high number of nuclei of icosahedra and dodecahedra. It may help to explain the curiosity why warmer water freezes more rapidly than cold water. It is because the cold water at the temperature near freezing is densely packed with these, for the ice incommensurable nuclei, which are thus capable of easy undercooling. The water at higher temperatures gradually disintegrate them possessing thus a greater number of smaller fragments, which survive rapid cooling being more easily compatible with the highly symmetrical configuration of hexagonal ice.
- ⁸ For example, *Newton* in his treatise "Optics, or a treatise" (4th London edition, 1730) gave factually the first roots of later ideas grown to the present concept of affinity, citing "*solution of Copper in Aqua fortis dissolves immersed Iron and lets go Copper while solution of Silver dissolves immersed Copper and lets go Silver. Solution of Mercury in Aqua fortis poured upon Iron, Copper, Tin or Lead, dissolves the Metal and lets go the Mercury; does not this argue that the acid Particles of the Aqua fortis are attracted ... more strongly by Iron, Copper, Tin and Lead, than by Mercury*".
- ⁹ University's curriculum '*Artes liberales*' included 'free arts' of '*quadrivia*', arithmetic's, geometry, astronomy and music together with '*propedeuticum*' (orientation to Lord) consisting of dialectics, grammar and rhetoric, which was sheltered by the major '*theology*' as the overacting symbol of religion. Less common but adjacent scholars in 'mechanics' were mostly encompassing the learning in crafts (such as warfare, sea-voyage, business, agriculture, hunting, medicine or veterinary) but not in '*artes incertae*', which was a part of the habitually rejected '*equivocal arts*' (associated with occultism, which traditionally involved alchemy).



CHAPTER FOUR

4. Renaissance and new age

a) Emerging new ideas

The modern scientific world is far beyond using any mystic concepts, and many areas of research are now public property. Early mystical philosophy did not really need exact science. It did not look for measurable quantities and therefore scholarly knowledge was deliberately kept a secret often for moral reasons. The human mind, however, needs a bit of both. Hermetic philosophy admitted that the universe is calculable, separating quality and quantity at the same time, i.e., harmony is best when sensually perceived but when expressed by numbers. Measurement was thought to be associated with the consciousness of the person who actually makes it, but nowadays it comes close to the ideas of quantum mechanics. Bohr said "there does not exist a quantitative world, there exists an abstract description of quantum physics. The task of physics is not a search how nature is, but what we can say about nature."

As pointed out in the preceding chapters, fire was always kept in a central position of human awareness, in its view as a primary element. It was well-known that the orderly employment of fire provides warmth and pleasant conditions in which to think about, e.g., how to order things or how to gain easy energy. Wild fire was feared to destroy everything, creating chaos by means of the destruction of material possessions held by society, as well as in terms of the destruction of the human mind. Fire leaves a fingerprint in all types of evolution! Let us again, briefly, mention alchemy, as an example of an old endeavor for fire. Within the modern world of science, alchemy is considered to be rather archaic and without

a real scientific base, often subjected to ironical comments. We, however, should recall that alchemical philosophy was close to the science of Causation's; it tried to perfect matter whilst being aware of nature as a model. That is to say, it respected the order of nature, somehow resembling present day thoughts on living nature (ecology). Alchemy was undoubtedly related with the process of self-recognition, and success in the laboratory led to individualization, and, *vice versa*, individuality guided laboratory mastery. Alchemy was a universal art of vital chemistry, which by fermenting the human spirit purified and finally dissolved itself into a kind of philosophy. On the other hand chemistry, as a consequently derived true science of facts, is primarily oriented to the utilization of nature, freely processing and exploiting basic/raw materials and trying to dominate nature – it shamelessly enforces order on nature and neglects its consequences.

Paradoxically, perhaps, it was a mystic (Agrippa, Meyer, Stolcius, Paracelsus) and practicing (Agricola, Valentinus, Rodovsky, Sendziwoj, Libavius) alchemists who really believed in the physical transmutation of metals and not the theoreticians who contributed most to the scientific progress during the medieval alchemical area. The allegorical complexity of alchemical notations and the impossibility of knowing whether the author understood what he was writing, or merely had copied a text that was obscure to him, see Fig. 1, made alchemists the butt of criticism and mockery. Thereby, its rationalization of chemistry and its marginalization of acculturation aspects are inseparable from the invention of easily available and distributable forms of written messages. The role of printing in alchemy is commonly neglected although crucial. As soon as ancient texts were published they be-

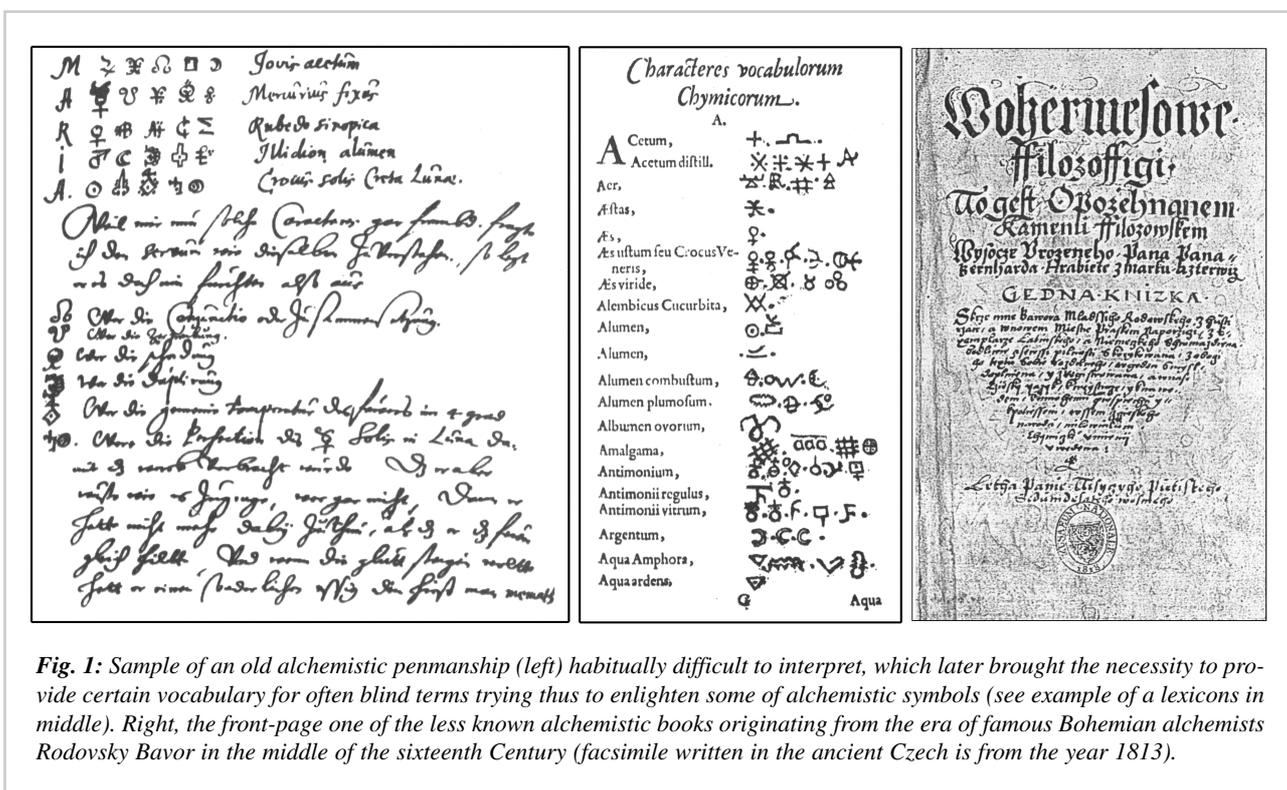


Fig. 1: Sample of an old alchemistic penmanship (left) habitually difficult to interpret, which later brought the necessity to provide certain vocabulary for often blind terms trying thus to enlighten some of alchemistic symbols (see example of a lexicons in middle). Right, the front-page one of the less known alchemistic books originating from the era of famous Bohemian alchemists Rodovsky Bavor in the middle of the sixteenth Century (facsimile written in the ancient Czech is from the year 1813).

come accessible to the wider public and could thus be confronted and challenged by more modern author¹ still full of various allegoric depictions, see Fig. 4.2.

In 1597, *Libavius* published a book about fire (*'Pyronomia'*) where he already enhanced the associated role of human skillfulness and proficiency. However, it was *Helmont* (epigone of *Paracelsus*) who, at the turn of seventeenth Century, rejected the persisting theory of four elements, as well as that of the three primary bodies. Instead he believed water to be the unique primordial substance, and looked for two sources of natural development of minerals and metals (*'seminal spirit'*), which were responsible for creating all objects in various shapes. He distinguished a kind of 'universal' gas from liquefied vapors, even identifying *'spiritus silvestris'* (CO₂) that he found emerged from certain natural substances when consumed by fire. In the book *"Sceptical Chymist"* (1661), Fig. 3, *Boyle* extended the attack on the theory of the four elements and planted the modern roots for natural sciences and the concept of chemical elements. The associated salt theory, which originally subverted the idea of a salt as an alchemic principle, helped in the understanding of the phenomena of solubility as a process. It became, correlatively, a way of further separating salts that finally helped *Lavoasier* to arrive at the modern definition of *affinities*.

It is worth noting that *Plato* already possessed a similar view of an element based on *'chóra'* (analogous to Indian *'amah'* that is understood to become fire or water containing *'proté hylé'*), i.e., continuous dynamic transformation of elements within themselves (resembling a quantum vacuum in the framework of bootstrap and/or particle democracy, see appendix of Chapter 3). The four elements were then identified with the macroscopic phases of gas (from the Dutch contortion of the Greek world *'chaos'*) and Latin derived liquid and solid. Fire became comprehended as heat and recently even better related to plasma, which accentuated and furthered thinking in the direction of yet other forms of energy that lie outside the aims of this book (e.g. nuclear). *Boyle* was also known to strongly criticize the traditional, so-called "dry way separation". He pointed out that when compounds were put into a fire that was 'too hot', the substances obtained were not necessarily components of them but were "creatures of fire" that revealed nothing about the original compound (products what experimenters call "artifacts" today). He preferred slow agitation and gentle heat that could have time to transform textures and therefore produce elements different than those produced from other methods of forcible decomposition. *Boyle* was also the first to use flame testing, probably the first *thermo-chemi-*

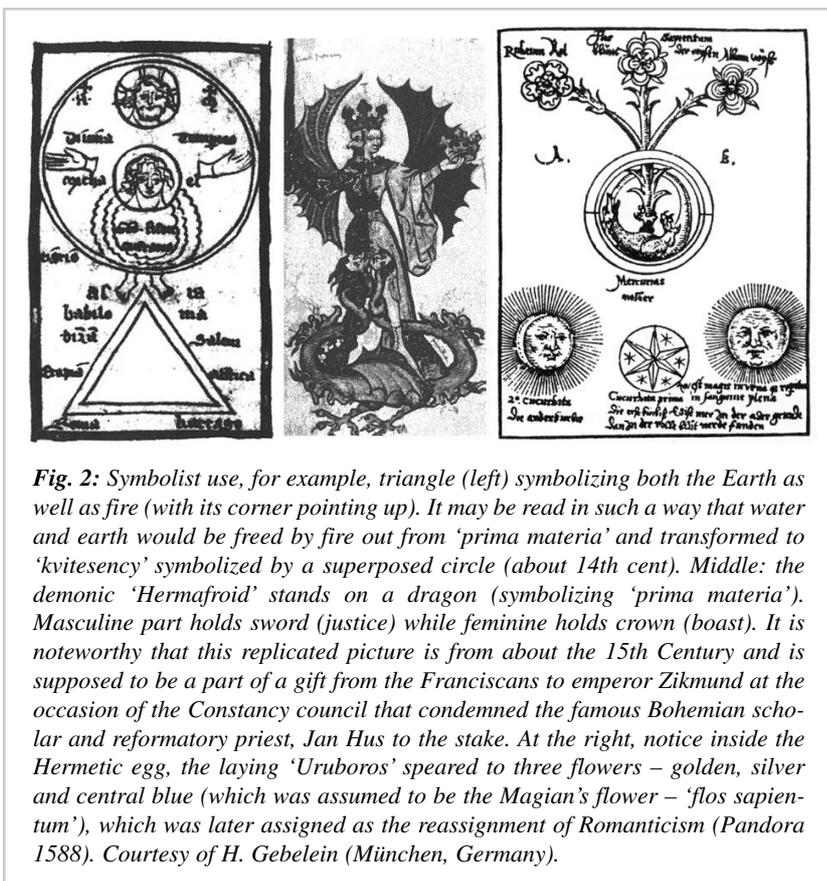


Fig. 2: Symbolist use, for example, triangle (left) symbolizing both the Earth as well as fire (with its corner pointing up). It may be read in such a way that water and earth would be freed by fire out from 'prima materia' and transformed to 'kvitesency' symbolized by a superposed circle (about 14th cent). Middle: the demonic 'Hermafroid' stands on a dragon (symbolizing 'prima materia'). Masculine part holds sword (justice) while feminine holds crown (boast). It is noteworthy that this replicated picture is from about the 15th Century and is supposed to be a part of a gift from the Franciscans to emperor Zikmund at the occasion of the Constancy council that condemned the famous Bohemian scholar and reformatory priest, Jan Hus to the stake. At the right, notice inside the Hermetic egg, the laying 'Uruboros' speared to three flowers – golden, silver and central blue (which was assumed to be the Magian's flower – 'flos sapientum'), which was later assigned as the reassignment of Romanticism (*Pandora* 1588). Courtesy of H. Gebelein (München, Germany).

cal analysis, making it possible to recognize a substance by the color of its flame when it is burned as well as the property of evolved air called "elasticity" (its volume being inversely proportional to the pressure). Although the 17th Century was a time of notable scientific progress, the scientists of the day were themselves far less respected and far less listened to than today's scientists. Some of them, such as *Newton* and *Leibniz* who are responsible for the introduction of many modern theories, were also devoted alchemists. The idea of "fire fluid" (globular particles that attach easily only to combustible objects) persisted for another two hundred years and assumed that when a substance is burnt, the non-substantial essence (*'terra pinguis'*) escapes. The definition of the laws of conservation needed more precision on account of the action of traditional 'vital and mortal' forces. Conservation was assumed to be something general between and within the system as probably first discovered by the non-cited Czech educator *Marcus Marci* [77].

Descartes [79] played an important role, even though he first believed that The Universe is filled with matter in three forms: fire (Sun), transparent matter (Heaven) and dark matter (the Earth). All observable effects in nature were assumed to happen due to the eternal movements of matter, which form gigantic or quite small whirls – *tourbillons*. Such a theory can, of course, explain everything, but unfortunately cannot predict anything. A little better was the theory proposed by *Gassendi*, a devoted follower of *Democritus*, who identified heat and coldness with microscopic material particles, adjoining atoms.

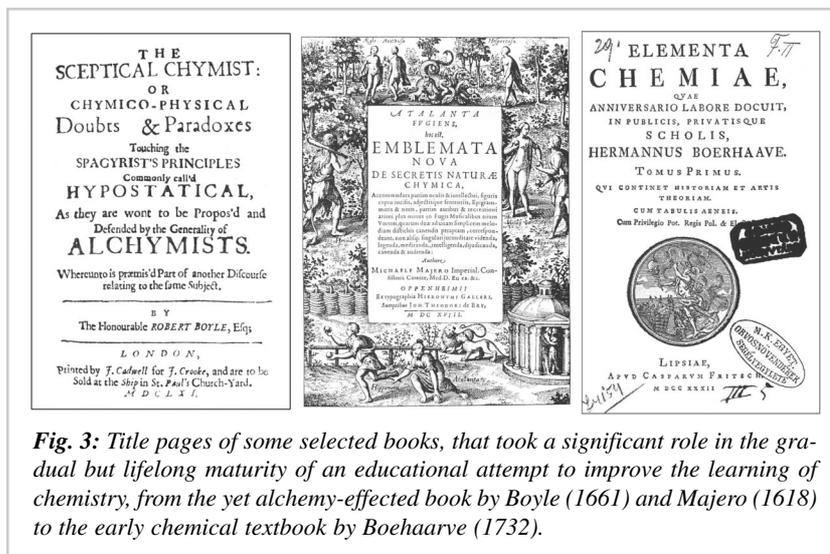


Fig. 3: Title pages of some selected books, that took a significant role in the gradual but lifelong maturity of an educational attempt to improve the learning of chemistry, from the yet alchemy-effected book by Boyle (1661) and Majero (1618) to the early chemical textbook by Boerhaave (1732).

Accordingly, the substance heat consists of spherical and very fast atoms, while the atoms of coldness are lazy tetrahedrons with sharp edges causing pain and destroying solid materials. The compatibility of this "substantial" theory with mathematical treatments probably helped it to survive with minor changes until the 19th Century. Interestingly, the premise of *Bacon* and *Descartes* that heat is a kind of motion, contradicting the opinion of *Gassendi* that heat consists of particles (quasi-particles) was unified, in a sense, by the modern kinetic theory of matter.

b) Phlogiston and caloric

The various phenomena of combustion [81–83] were known for many centuries before any attempt was made to explain them or, indeed, before any attempt was made to investigate them. One of the Boyle's contemporaries, *Mayow* assumed that atmospheric air contained a substance which he termed '*spiritus igno aereus*' which combined with metals to form '*calces*' and which was associated with the process of respiration. This assumption contained the germ of discovery of the new approach to explain combustion later enriched by *Becher* who assumed that all inorganic substances consist of three 'earths': the mercurial, the vitreous and the combustible. The last term was named as '*terra pinquis*' and when any substance was burned, this essence escaped.

Stahl gave to us a special characteristic of chemistry called the "mixative union" or the '*mixt*', which was distinguishable from aggregations (mechanical unions), and their analysis became the entire task of the chemist alone. It was later proposed that a mechanical agent or "instrument" – fire (or heat), water (as a solvent) or air – bridged the gap between the '*mixt*' and aggregates. Fire put the *phlogiston* (renamed *terra pinquis*) in motion, air blew off the most volatile parts and water put the parts into solvated motion. Fire was therefore the instrument, and the phlogiston was the element entering into the composition of the mixts. It explained combustion as well as the transformation of '*calx*' into metal and, *vice versa*, (i.e., metal = calx + phlog.). Phlogiston was, thus, a revo-

lutionary element since it suggested that both combustion and corrosion aide in the same operation of *oxidation*, which is the inverse operation of the process now called *reduction*. During the so called 'phlogistic' period (lasting for about one hundred and twenty years) the science of thermochemistry was enriched by the labours of many eminent investigators, e.g., *Black*, *Cavendish*, *Pristley*, *Scheele*. Although it is easy for modern scientists to ridicule the absurdities of such a phlogistic theory, it must be borne in mind that this idea was very much contributory to the better understanding of early views of energy conservation and it served to stimulate a vast amount of experimental research. The downfall

of this theory was caused by the observed fact that products of combustion retained a greater weight (mass) than the combustible substances from which they were derived. The ingenious attempt to explain this phenomenon by assuming that *phlogiston* possessed a negative weight did not, however, survive later rational protests. The final overthrow of this idea may be thought as the marking of the beginning of a new era that began modern chemistry but, the phlogistic period should also be associated with the discovery of the more important constituents of the atmosphere (dephlogisticated air – oxygen, inflammable air – nitrogen, fixed air – CO₂, phlogisticated air – hydrogen, compound nature of water).

The attacks on phlogiston would become significant only in a larger context when the theory of gases arrived, which was essentially developed by the work of *Lavoasier*. The key factor in his theory was the *caloric*; the substance of heat or matter of fire, which crept in among the constituent parts of a substance and gave it expansibility. If the physical state of body were explained by the quantity of caloric, then consequently air would lose its essential function as a principle. Although caloric [81] differed from phlogiston because it could be measured with an apparatus called a *calorimeter* (designed by *Wilcke* and later used by *Laplace*, *Lavoasier* and others), it was nevertheless an imponderable element with its own properties. *Lavoasier* did not define chemical elements as ponderable but he adopted *Black's* substantial conception of heat, and similarly to the preceding *Boerhaave* idea, he gave it a repulsive effect, too. *Rumford* wanted to prove that heat has no mass and that it can be produced, without limitation, by friction. He also wanted to show that thermal motion of particles occurs also in liquids. He tried to explain heat transfer in a vacuum by the vibration of material particles that cause a 'wave motion of the ether', capable of propagating in a vacuum. *Rumford's* ideas contradicted the accepted understanding of such a heat transfer, which was thought to be the consequence of repulsion of the caloric particles in its 'non-ideal' solution, their high tension tending to 'redistilled' caloric through a vacuum from a warmer to a colder body.

The caloric theory² supplied an obvious solution to the problem of thermal expansion and contraction. Heating a body had the effect of adding fluid caloric to it and, consequently, the body expanded. On cooling the opposite occurred, involving the removal of fluid caloric from the body. Many of the properties of heat were explained by considering each particle to be surrounded by an atmosphere of caloric, whose density is related to the intensity of the gravitational attraction between it and the center of any particle. The gravitational attraction was considered to be inversely proportional to the square of the distance between the centers of the particles involved, while the caloric atmosphere, which caused the repulsion, was assumed to obey a logarithmic law in the analogy to the Earth's atmosphere. In liquids, the caloric content was sufficiently high so that the atoms were not held in a rigid position by mutual gravitational attraction and in gas this attraction was considered negligible. Thus, it was predicted that the expansion of a gas would be much greater than that of a liquid and than that of a solid. It also explained that the expansion coefficient increased with temperature more rapidly for liquids than for solids. In certain views on the physical behavior of gases, particles were even assumed to be stationary, the pressure keeping them such and being derived from the tension of caloric.

A careful distinction was drawn between the intensity of heat and the quantity of heat. All atoms did not have identical caloric atmospheres, and although they all had a logarithmic dependence of caloric density on distance, the rate at which the atmospheric density reduced, varied from substance to substance. The quantity of heat required to produce a given change of temperature for a given amount of material, was called the specific heat of a materials, by analogy to the term of 'specific gravity'. Heat could take two different forms, sensible and latent. Caloric was considered to combine with atoms in a fashion similar to how atoms bind together, and with such combinations the caloric changed from its sensible form and became latent. Such a chemical combination of an atom with caloric produced a 'new' compound in which neither the original atom nor the caloric retained its identity. No heat was considered to be lost in the process since it was reversible – cooling a body down returned the caloric back to its sensible form.

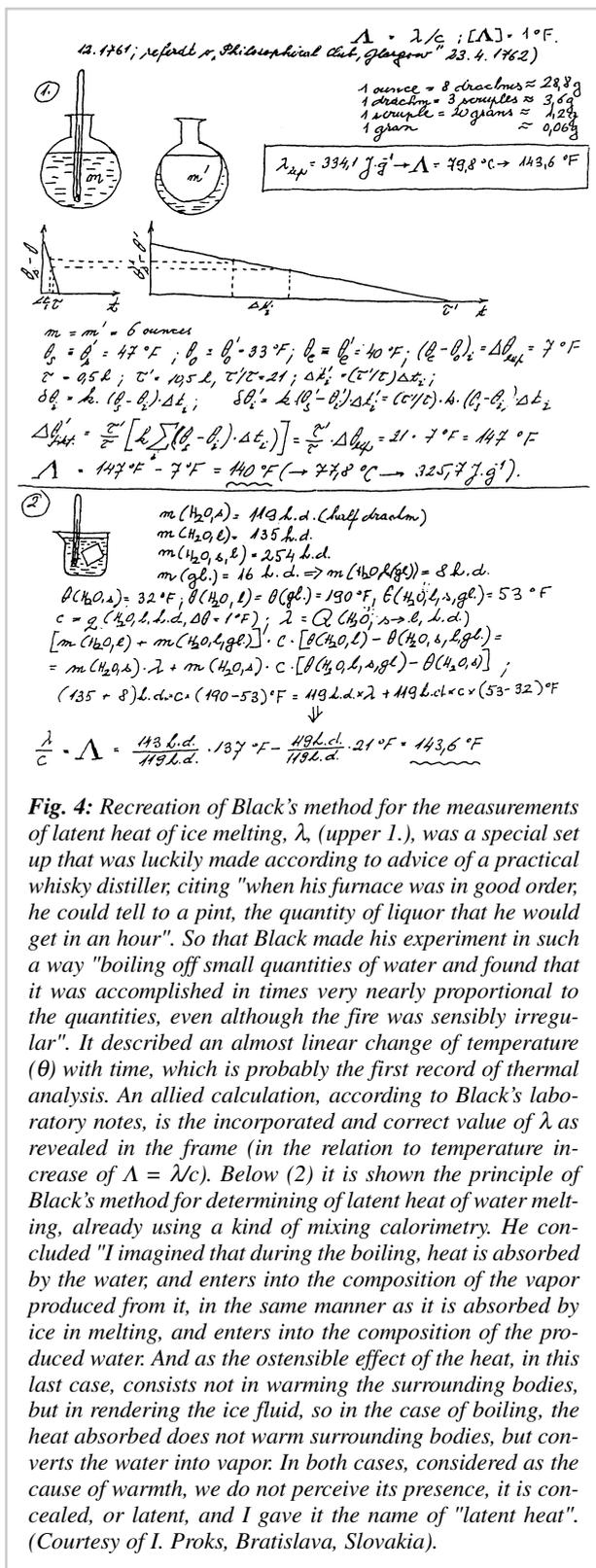
Let us consider two examples; when a piece of iron is compressed by hammering, the sensible caloric is squeezed out and the surface of the iron becomes hot, or if a gas is compressed it emits caloric and becomes hotter. It was thought that sensible caloric could be squeezed from a body by artificially pushing the constituent atoms into closer proximity to one another than what the mutual repulsion of their caloric atmospheres would allow. Therefore, if pressure was put on a substance near its boiling point, some of the sensible caloric would be lost from the substance and a higher temperature would have to be applied before sufficient caloric was available to the atom for a vaporization to occur. The less caloric a body had, the greater was the attraction between the atoms of that body and its surrounding caloric fluid. In adding the caloric to one end of an iron bar, the atoms at the heated end

required more caloric than their neighbors, and by having more, their attraction for this caloric was less. Thus, the neighboring atoms attracted the caloric away and continued to do so until all the atoms of the substance had achieved the same caloric at atmospheres. The facility with which caloric could be passed from one atom to another depended upon the structure and composition of the iron (substance). It is worth noting that a more careful study of what is currently being taught and used as the world quantity of heat concerning its behavior and phenomena shows a striking similarity with the above-discussed caloric theory of the past.

c) Heat and energy

In the year 1647, *Descartes* [79] became the first to propose the conservation law of the quantity of motion, presently called *linear momentum*, and showed it to be proportional to mv . Subsequently this idea was extrapolated by *Leibnitz*, who introduced the terms 'vis viva' for the quantity mv^2 and 'vis mortua' further related to *Newton's* gravitational forces. *Leibnitz's* idea of a 'vital force' was extended to an isolated system by *Lagrange* ("Mechanique analytique", 1788) when he assumed invariance of the sum of this quantity with the function of the coordinates of a particle, i.e., with their potential energy. The terms 'energy' (ability for virtual work) and 'virtual displacement' were used for the first time by *Bernoulli*, were weaving their path to a wider appliance very slowly and yet at the turn of 20th Century the term 'vis viva' occurred still quite commonly. *Waterston* reported in 1845 [27] that the "quality of perfect elasticity is common to most particles so that the original amount of 'vis viva', or acting force of the whole multitude, must for ever remain the same. If undisturbed by external action it cannot, of itself, diminish or increase.... striking against and rebounding from each other they undertake any possible mode of occurrence such that the particles are move in every possible direction and encounter each other in every possible manner during so small an elapsed interval of time that it may be viewed as infinitesimal in respect to any sensible period". It was *Coriolis* who started to use the name 'live force' for a half of its original value, mv^2 , and thus simplified the relation with work. However, it was *Joule* who entitled the principle of work as mechanical power. In 1853 *Rankine* introduced the term 'potential energy' and thanks to *Tomson* the outlasting 'vis viva' was finally renamed as 'kinetic energy'.

Not knowing what fire factually was, *Black* avoided speaking of it, but he studied the specific relations between the two measurable quantities of heat and temperature, which were not new in themselves. *Amontons* first used the effect of heat when he made an air thermometer. In fact, the use of this new instrument brought about the very question of how to define the quantity of heat separately of temperature, since its measurement is a function of both quantities. *Black* was interested in the way in which heat was fixed in bodies and he called this heat as "latent heat" – the heat absorbed or released by a body during a change of state without a change in temperature, see Fig. 4. Contrary to the standard understanding of heat



absorption as the penetration of a fluid (caloric) through a porous body, the way of absorption of 'latent heat' is not comparable and must be understood as a different, rather combined process that entails both the ideas of melting or boiling. Black's elegant explanation of latent heat to the young Watts became the source of the inven-

tion of the businesslike steam engine as well as the inspiration for the first research in theoretical thermochemistry, which searched for general laws that linked heat, with changes of state. Heat and its measurement were, however, to belong to mechano-physics, were they were integrated into the economy of chemical transformations.

With little doubts, until the work of Scot Black, the notions of heat and temperature (from temper or temperature first used by Avicenna in the 11th Century) had not been distinguished between. Black's work, together with that done by Magellan, revealed the quantity that caused a change in temperature but which was it self not temperature – the modern concepts of latent heat and heat capacity. They explained how heat is absorbed without changing temperature and what amount heat is needed to increase a body's temperature by one unit. Worth noting is the original proposal of a name for one unit of heat to be a therm (sufficient heat to warm 1g of water by 1 °C) or the proposal by Groffith to name it after the less known physicists Rowland. The description of latent heat and heat capacity answered, to some extent, the warning given by Boerhaave [29] in the beginning of 18th Century ... "if we make a mistake in the interpretation of what is fire, this deficiency can afflict all disciplines of physics and chemistry, because in all natural creations fire is involved, in gold as well as in emptiness..".

Rumford presented qualitative arguments for a fluid theory of heat with which he succeeded to evaluate the mechanical equivalent of heat³. This theory, however, was not accepted until later approved by Mayer and, in particularly, by Joule, who also applied Rumford's theory to the transformation of electrical work. The use of customary units called 'calories' was introduced by Favren and Silbermann in 1853. Nonetheless it took two centuries to replace the fluid theory of heat (caloricum or thermogen) by the vibrational view (of the state of inherent particles) that was substantiated by the advanced theory of combustion by Lavoisier. Sadi Carnot provided the theory of the four cycles device [84]. However, the idealized theory of a heat engine was proposed on the confused basis of heat transport taking place in the form of a fluid (caloricum) discharging from the state of higher to lower tension ('conservation of materialistic caloricum') and in that time was also supported by Clapeyron. Notably Carnot excluded the existence of perpetual thermal motion, formulating an important efficiency theorem on the "moving force of fire". Such a force does not depend on the medium used for its outgrowth but just on the temperatures of bodies between which the transfer of heat is conveyed.

Following the 1826 textbook by Pencelet [85,86], Rankine introduced in the year 1853 the term energy – actuality ('ergon' – actus and 'energeia' – activity in the opposite sense to the possibility 'dynamis' – potentia). Simultaneously to the development of the separated field of electricity and magnetism, another important field of thermal sciences was introduced and named thermodynamics ('thermos' – heat and 'dynamis' – force), first made known by William Thompson and preceded by Maxwell's concept of thermal equilibrium [25]. Yet to-

wards the end of nineteenth Century, *Helmholtz* and *Laplace* [83] described both theories of heat to be equally suitable to comply with a theory of temperature measurements because it was only determined by the state of the system under investigation. A similar understanding was anticipated for the internal motion of particles because heat was also a measure of the transfer of motion from one system to another – kinetic and potential energies being qualitatively different forms of motion (scaling variance in the degree of self-organization). Nowadays the transfer of heat is sometimes associated with a modern description in terms of non-integral dimensions (fractals, see Chapter 13).

The creation of the notion of entropy in thermal physics was a response to a similar problem in thermochemistry: the principle of the conservation of energy, always verified by physico-chemical transformations, could not be used to simply determine which transformations were possible and which were not. The state of equilibrium was defined by the fact that any spontaneous transformation that would affect it by diminishing entropy was impossible. Whilst a real steam engine functioned by real heating and cooling, the function of the ideal steam engine necessitated the fiction that two bodies of different temperatures would never be put into direct thermal contact. Thus the system is supposed never to leave the state of equilibrium whilst undergoing a displacement from one state of equilibrium to another, which are, moreover, infinitely close to each other and which are determined by an infinitely progressive variation of the controlled parameters. The problem of such a change description bears the same character as the time change during chemical reactions. *Duhem* called such changes ‘fictitious transformations’, which are reversible and entirely directed from the exterior when passing from one state of chemical equilibrium to another. *Van't Hoff* and *Le Chatelier* associated this idea with the law of displacement of equilibrium and chemical thermodynamics received its central principle that dealt no longer with mere energetics but introduced thermodynamic potential as a minimum at chemical equilibrium. Physical chemistry, as an autonomous science in relation to mechanical physics, which has neither reactional event nor the second (entropy) principle, has brought thermochemistry to a level much richer than is physics alone (Fig. 5).

Far from equilibrium [87,88], physical chemistry puts the accent on the global behavior of a population with local interactions. Such an idea may be also applied to the

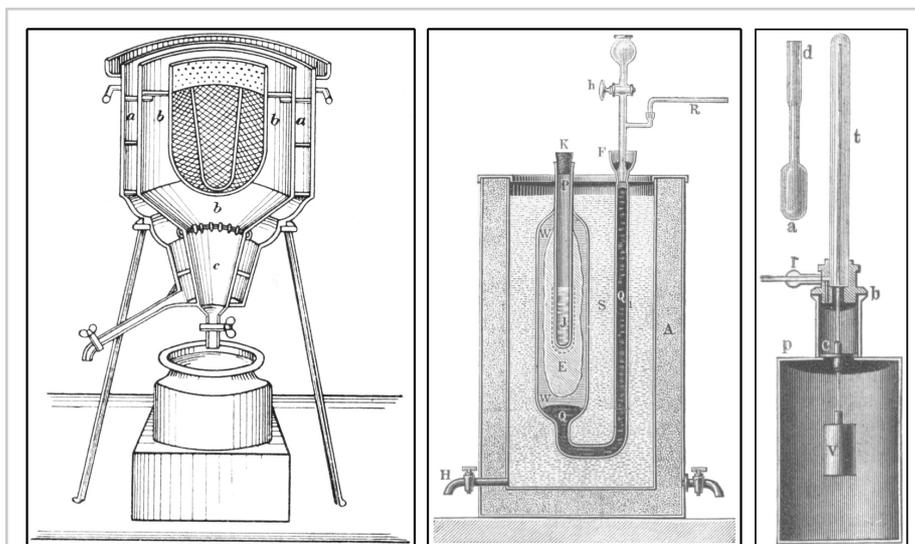


Fig. 5: Time-honored ice calorimeter, which was first intuitively used by *Black* and in the year 1780 improved by *Lavoasier* and *Laplace*. The heated body is cooled down while placed in ice and the heat subtracted is proportional to the amount of melted water. In the year 1852, *Bunsen* proposed its more precise variant while determining volume instead of weight changes (middle). The cooling calorimeter was devised 1796 by *Mayer*, *Dulong* and *Petit*, but became known through the experiments by *Regnault*. Thermochemical measurements were furnished by *Favre* and *Silbermann* in 1852 using the idea of *Bunsen* ice calorimeter but replacing ice by mercury the volume measurement of which was more sensitive.

behavior of various societies, but the exact field of thermochemistry is more honored for two reasons. Firstly, it may encircle a great variety of cases capable of nonlinear coupling, and secondly, any creation of molecular structures can even take place independently of the processes itself (like hydrodynamic whirlwinds). Characteristic of such systems is the nonlinear coupling between inherent processes (that produce entropy), which often shows the capability of self-organization. The spontaneous production of spatial differentiations and temporal rhythms, are often called dissipative structures. Structure is here understood in a more general context and is most likely to exhibit coherent spatial-temporal activity, and is dissipative in nature because it occurs only under the condition when the dissipative process is forcefully maintained. Links between the production of entropy and the production of coherence leads to the association of two sciences: thermo-dynamics and thermo-chemistry. Coherence, however, touches not individual molecules (that can be in the framework of quantum principles) but effects the population of whole molecular aggregates. Coupling of the rates of simultaneous chemical reactions, may even bring the possibility to arrive at a world characterized by the quantum-mechanic-constants (*Planck quantum length*, *thermal length*, *Brownian motion*⁴ [90]). In the other words, chemistry can produce stable structures that store a kind of memory of their formation conditions. Standard crystallographic structures can function as a kind of relay between histories of different types of their formation and the make up of individual materials. The history can be re-constructed on the basis of a physically measurable property characteristic of these structures. The singular link between chemistry and plurality of inter-

woven times for a structure's build up was, therefore, the center of alchemical preoccupations. When the validity of the conservation law of mechanical energy was generally recognized, the French Academy of Sciences did not accept any new proposal for the construction of mechanical 'perpetuum mobile'. At the same time, the widespread caloric hypothesis achieved important supporting results: the derivation of sound velocity with the use of Poisson constant (*Laplace*), mathematical description of heat conduction (*Fourier* 1822) and the proof of the same maximum efficiency for all thermal machines (exhibiting the impossibility to construct perpetuum mobile of the second generation). Its author, *Carnot* also derived the direct proportionality, $f(T)$, between the works performed in the 'fall' of the heat unit during an infinitesimal cyclic change of given working substance and within the corresponding temperature difference between the hooter and cooler reservoirs. It was written as the relation, $f(T) = C/(C_1T + C_2)$, where C 's were constants and T is the Celsius temperature. The expression for $f(T)$ (corresponding to the related *Clapeyron's* term, $1/C$) was later named as *Carnot's* function, μ , equal to $(1 - \delta/\rho) dp/dT \cdot 1/\Delta H$, where δ , ρ and ΔH are densities of vapor and liquid, and the heat evaporation respectively. In fact, it was the first quantitative description of the equilibrium coexistence between the gaseous and liquid phases, currently known as the *Clapeyron* equation.

In 1850, *Clausius* published his first treatise on the new discipline on thermal science (not using yet the term 'thermodynamics', which was already introduced by *Thompson* in 1849) in which he reformulated and specified more exactly the two laws of thermodynamics and better specified the *Carnot-Clapeyron* relationship. In his famous publication "On the modified form of the 2nd law of mechanical heat theory" *Clapeyron* incorporated the possibility of compensation of the enforced negative processes by spontaneous positive processes. To the first class, the impossibility of transfer of heat from lower to higher temperatures was classified spontaneously (and similarly to the conversion of heat into work). The second class was aimed at the transfer of heat from higher to lower temperatures and the generation of heat by work. By mere intuitive and logical reasoning (which might remind us of a current field known today as synergetics) *Clausius* was able to prove that the implementation of processes can be quantified by an algebraic summation of the proportions of the heat content accumulated in the course of investigated process to the corresponding value of the absolute temperature.

For such a classical field of thermodynamics (understood in the sense of being a not too popular, but adequate term for 'thermostatics') the closed system defines and describes the energy conserving approach to equilibrium, which is, factually, thermal death (certainly, if neglecting ever-presented fluctuations). It bears similarity with the mechano-dynamics of an isolated system, i.e., fixed state of planets (or molecules) kept together by stationary orbiting. The next step is the true thermodynamics with thermal bath, capable to draw or reject energy as to balance the coexistence between the two phases divided by

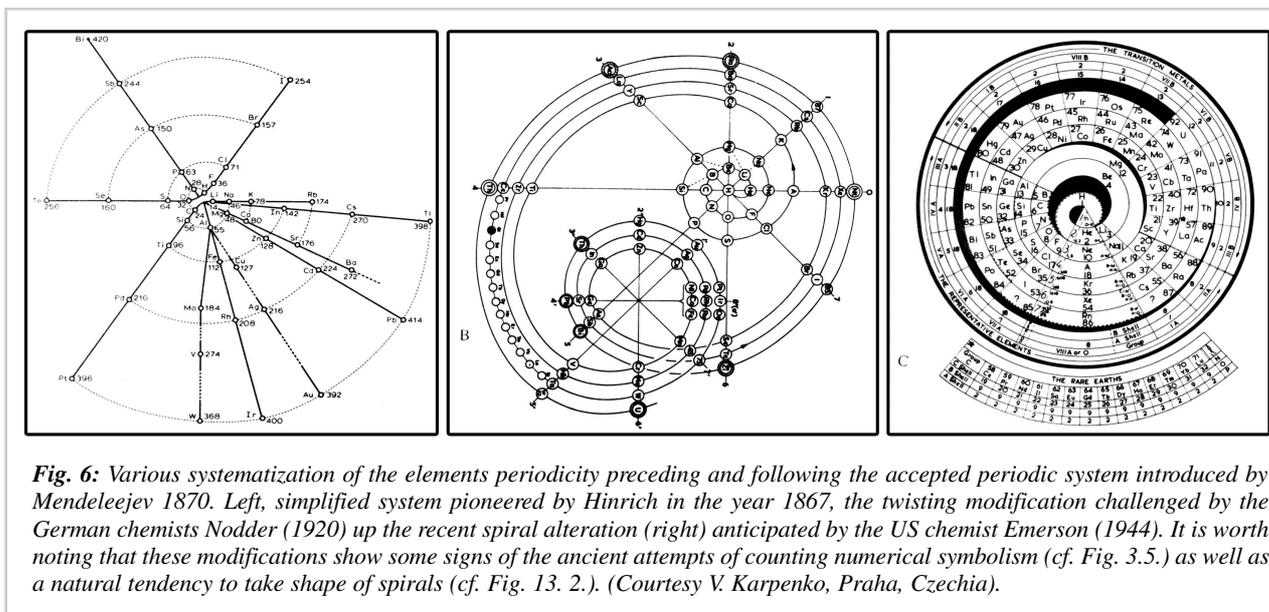
a phase transition. The counterpart in mechano-dynamics is the existence of an external field acting, for example, on a stone dropped from a tower. The external fields are the source or sink of energy – momentum without being modified. Any disequilibrium must be created by, e.g., artificially created experiments (by experimentationists). However, for the case of increasing number of thermal baths we have no such an equivalent in mechano-dynamics but we can account for the possibility of thermal cycles and we can get closer to the description of a situation met in the nature. This is the curiosity of thermodynamics, which, thus, diverges from that familiar in scholar mechano-dynamics.

d) Atomists and matter

In 1675, *Lemery* published "Cours de chemie", which had an enormous impact on the progress of chemistry because it finally released from most references to occult qualities. For *Boyle* in his "Sceptical Chemist" (1661), the consequence of mechanist atomism was that all chemical bodies, whether we could resolve them or not, were produced by 'different textures' of a 'catholic or universal' matter, i.e. an arrangement of particles 'without qualities' would be responsible for what we call properties (characteristic qualities). *Boyle's* definition that holds as 'I now mean by elements certain primitive and simplest bodies, or perfectly unmingled bodies, which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved' and was later known as a 'negative empirical concept' enabling modern definition of the element.

According to *Newton*, atoms were solid, heavy, hard, impenetrable and mobile particles that God made at the Beginning, but he did not accept the idea that atoms were characterized only by the force of inertia – a passive principle in virtue of which bodies remain in movement or at rest meaning that there would be neither destruction nor generation (as with life). Such a corpuscular chemistry as a site of conceptual experimentation on the sequence of atomism, assumed that the constituent elements did not continue to exist 'potentially' in a compound but composed it actually. Chemical transformation had to be thought of in terms of the separation and combination of particles, which were thus assumed invariant and incorruptible, existing prior to combinations and remaining themselves in 'mixts'.

From the atomist point of view, Aristotle's concept of passage from potentiality to actuality no longer made sense. Correspondingly, genesis (*genesis*), destruction (*phthora*), and alternation (*alloiosis*) no longer referred to qualitatively different processes but to a kind of quantitative change, that *Aristotle* called locomotion (*phora*). Atomism, was seen as a 'methaphor' for the alphabet, and the only 'bricks', which can provide a solid construction, where thought to be atoms, which became a principle of both reality and knowledge. There, however, remained a question: what caused for homogeneity? The concept of mixture reemerged, however, recalling what *Aristotle* stated: *stoicheia*, which are the constituent elements of



a body, which can be transformed during the process of decomposition. Aristotle also asserted that the *dynamis* of the elements remained in the *mixt*, in other words, the properties of a *mixt* reflected the properties of its constituent elements. From the point of view of chemical operations, the corpuscular chemistry tended to favor those procedures that were reversible. With the distinction between primary properties (extension, form, mass) and the secondary ones (heat, sound, color) the mechanist version of atomism denied all qualitative differences to atoms and only granted such differences to geometrical attributes.

As a consequence of the opposition between ‘simple’ and ‘compound’, there is the famous Lavoisier’s definition of an element “if we give to the name of elements or principles of bodies the idea of the last step that analysis can reach, all substances that we have not been able to decompose by any way whatsoever are elements for us, they act to as simple bodies and we must not suppose them to be decomposed until the time when experiment and observation will have furnished the proof”. We, certainly, should not forget Lomonosov who was the first physical chemist to view chemistry from the standpoint of physics and mathematics. He considered matter to consist of minute imperceptible particles “the oscillation and rotation of these particles increases on heating and when rotary motion reaches a certain stage the material melts or volatilizes. The particles in gases move more rapidly than in liquids and collide with each other”. His ideas were ahead of those of Lavoisier on the nature of heat and on its resultant effect on materials.

Swedish chemists Berzelius (1810) explained the action of the newly invented electrical battery and associated process of electro-deposition. He defined each simple substance and each compound body by a positive or negative polarity whose intensity varied according to the nature and the number of the positive and negative charges carried by the atoms of each element. The voltaic battery was not seen as a simple instrument but as a ‘principle of

intelligibility’ where electricity was understood as the primary cause of all chemical action. The “electrical fulfillment” was, factually, the original Newtonian dream of mechanical actions between atoms. On the basis of opposite forces it was possible to design a simple method for predicting the degree of affinity: the scale of mutually reacting elements from the most electropositive to the most electronegative.

Dalton made use of Proust’s law as the basis for a new atomic hypothesis [91]. He suggested that chemical combinations take place in discrete units, atom by atom, and that the atoms of each element are identical. These atoms differed from Newton’s corpuscles because they presupposed neither the void nor attraction and made no attempt to explain properties of simple bodies in terms of a complex architecture whose ultimate constituents would be atoms. After the publication of Dalton’s “New system of chemical philosophy” Gay-Lussac announced that the volumes of gases, which combine with each other, to be in the direct proportion – the volumetric proportions thus confirmed by the gravimetric ratios. The first law, to fashion a network of experimental facts from different disciplines, was formulated in 1811 by Avogadro stating that the equal volumes of different gases contain the same number of molecules.

Dulong with his young colleague Petit undertook their study of the quantity of heat needed to raise the temperature of one gram of a substance by one degree Celsius. In this manner, they determined heat capacities of each atom⁵ to be nearly the same. They concluded, “the atoms of all simple bodies have the same heat capacities”. It is now called the Dulong and Petit’s law of specific heat and was based on new field – the above-mentioned calorimetry. This law could not lead directly to the atomic-weight values but it presupposed them. It was followed by the theory of chemical proportions derived upon isomorphism where only the number of atoms determined the crystalline form, and little angular variations attributed to the nature of individual atoms.

In a jungle of obscure and exotic terminology, it was often difficult to read chemical texts. In the year 1860, during the probably the first international Chemical congress, held in Karlsruhe, participants tried to put an end to these deep differences on words and symbols that harmed communication and discussion. It raised a fundamental theoretical issue for the agreement on figures and formulas to be subordinated as well as the definitions of basic concepts: atoms, molecules and equivalents. Moreover it materialized the existence of an international chemical community and defined the rules for its functioning.

In the year 1865, the English chemist *Odling* published the table of elements, which was almost identical as that published five years latter by *Mendeleev* [92], although they did not entirely believe in the existence of atoms as particular species. The individuality of the chemical elements was, for *Mendeleev*, an objective characteristic of nature, which was as fundamental as the Newtonian gravitation; it was both a condition and a product of his periodical classification having a real, and not just a theoretical meaning. His periodic classification was far from being prophetic of the electronic structure that is today so well known and, ironically, those defenders, who were in favor of the existence of the previously popular unique 'primordial' element, criticized it. *Mendeleev* protested against this misuse of his discovery and when he learned about radioactivity and about the electron, he even advanced his explanation in terms of vortices of the ether, which take place around the heaviest atoms. Thus *Mendeleev* initiated an unfortunate hypothesis about the ether as a definite element and placed ether above the column of rare gases. Periodic classifications, see Fig. 6 drew a lesson from the chemistry of substitutions and, correlatively, substitution lost its subversive status – it remained no more than one mode of combination among others.

In 1750, the German physician *Eller* published the first tables presenting solubility data of various salts and their mixtures in water at different temperatures (and indication of atmospheric pressure). The first database, however, was most likely done by the Swedish chemist *Bergman* (1783) who put in to order several thousand chemical reactions (containing 49 columns with 27 acids, 8 bases, 14 metals and others, and discriminated between reactions by a wet method in solution and a dry method by fire). Besides foregoing recent databases he also helped to circumscribe nomenclature. Reactions were no longer 'means' but became 'phenomena', which countered anomalies and had to extend between the chemical affinity and the other physical factors that emerge obstacles in its completion. Only the clairvoyance of the Russian chemist *Beilstein* laid the true grounds for modern databases when he originally published a survey of 15 000 organic compounds as a series of books published in the period 1880–1883, the continuation of which exists as a well respected database until today.

The important process of synthesis was not first distinguished according to the nature of the product (natural or artificial). Synthesis was thought to be merely total or partial. Substances were made from elements (commonly C, H, O) or from other, simpler compounds. *Wohler's*

laboratory synthesis of urea in 1828, a substance made previously only by the action of a living organism, was celebrated as an event of unprecedented importance demonstrating the nonexistence of a 'vital force', which was previously necessary to create organic molecules. In 1847 *Frankland* discovered a new class of organometallic compounds, a concrete argument in favor of a reunion of organic and inorganic chemistry, which also became a starting point for the modern theory of valence (introduced instead as 'atomicity'). In fact it was a fruitful time for new scientific images such as that of *Kekule* who said that he owed his career to the vision of the ring structure of benzene as a snake chewing on its own tail (see chapter 3 – alchemy section).

After the invention of bakelite, prepared from phenol and formalin in 1907, *Baekeland* introduced the generalized term 'plastics' in 1909 to design a larger class of products conceived as replacement products for natural substances, which were either rare or costly. They were a triumph of substitution chemistry and in the 1950s seemed to take on an aesthetics of their own. Polymers were technological items before they were objects of knowledge. Laboratory chemists were annoyed when syrups did not crystallize or with solids that were impossible to melt and they mentioned them in notes as substances of unknown structure. Thermo-hardening properties were used to fashion a variety of objects, their structure yet unknown. Although there was a hypothesis that molecules joined together in chains by ordinary interatomic bonds (advanced for isoprene in 1879), most chemists from the beginning of the nineteenth Century thought that a pure body must be composed of identical molecules of small size. Macromolecules were explained as an aggregation of small molecules, which was later verified by crystallographic research.

Without being self-confident that crystals are internally arranged in a periodical manner *Bravais* mathematically described, in the year 1850, fourteen geometrical figures that can be periodically arranged in the space and characterized them as a combination of one or more rotations and inversions⁶. His idea was later approved by X-ray diffraction (1912) and this approach has been advantageously applied until now. So called 'Bravais Lattice' is, thus, understood as a three dimensional lattice, which tiles space without any gaps or holes and there are 14 ways in which this can be accomplished. Microscopic investigations made by *Reinitzer* when studying cholesterol in 1988 extended the developing basis of crystallography to the sphere of liquid crystals.

The two most traditional actors in chemistry, the chemical reaction and heat, were joined to conceive 'thermochemistry'. Just as the fall of a body is characterized by the work of mechanical forces, the decrease in potential energy and the creation of kinetic energy, a chemical reaction must be defined by the work of chemical forces and the decrease in potential of these forces. Work and decreases in potential were measured by the amount of heat released by reaction. The state of equilibrium thus became the state in which the potential of chemical forces had reached its minimum value. It was a transposition of

the old doctrine of effective affinities and corresponds to the discrimination among chemical reactions. The natural chemical reaction was the one spontaneously giving off heat while the endothermic reactions were considered constrained by an external action, by the chemist who adds the heat (preference to higher temperatures).

In 1867 *Guldberg* and *Waage* proposed a law that abolished any distinction between exo-thermic and endo-thermic reactions and created a new analogy with physics. They put forward the idea of 'active mass' in analogy with Newtonian force, i.e., the chemical force of a reaction was defined as the product of the active masses, and equilibrium was reached when the forces of opposite reaction became equal. However, the relation between forces and masses involved a specific coefficient of activity. It was a great success but it left open the question of its interpretation. In this hypothesis equilibrium was no longer defined as a state in which a reaction stopped but the state in which reaction rates were such that their effects compensates for each other. Equilibrium was not the state where forces, and the rates they determined, both vanished and therefore it was nothing special – just as the analogy with reactive collisions between molecules, which determined the given reaction, were on the whole as numerous as the collisions that determined the inverse reaction. The central concept of the current field called 'kinetics' is thus the probabilistic notion of frequency dependent on temperature.

Finally we come to deal with structures, ideal and real, associated with variety of defects, impurities, vacancies, intersialities, interfaces, etc. – these terms imply the usual hierarchy, the ideal being the prototype from which we can know about real things and their inevitable deviations. But henceforth it is the *defect* that is interesting, for the specific properties it gives the single crystal – in the larger scale it is its matter-separating surface specifying its outer form and interfacial properties. The individual crystalline body is no longer a mere imperfect version of the ideal prototype but the reflection of the singular histo-

ry of its formation, growth and orderliness. The possible multiplicity as well as both the scientific and industrial interests for particular properties linked to the digression (accidental deviations) from the established laws (predictable state) were disposed to remain between the boundary status of 'defects' (a non-hierarchical group of cases, each associated with the circumstances that favor it) and 'normal cases' (as demonstration of rules).

By penetrating micro-, supra- or nano- molecular world and playing with the interactions among molecules in the standard three- but also in two- and even in one-dimensional range (quantum wells or dots), the physical chemists has become a new kind of architect of matter, facetiously saying 'tricky designers for tricky matter'. Among others we may mention optoelectronics, superconductors, magnetics or, in particular, alloys with shape memory, photochromic glasses, smart bioactive ceramics or quantum-well semiconductors. Such a kind of sophisticated materials are often called *intelligent materials*, as if the chemists had breathed life into matter and accomplished an old dream of alchemists.

We are aware of the great environmental cycles of nitrogen, oxygen, carbon or phosphorus, identified the succession of transformations, each one consuming what was produced previously and producing what would be consumed afterward. It is a beneficial self-recyclation, like a desired industrial assembly line in perpetual motion, which is looping back on itself. But what is the thermochemical balance if it does not integrate the many time horizons of those different processes that together create the overall global transformation – we have to learn a lot!

e) *Underpinning of thermodynamics*

Towards the end of the 17th century *Papin* succeeded in proving that water can exist in a liquid state even at temperatures exceeding its boiling point if heated under increased pressure. It preceded the discovery of the *critical state* of substances and the determination of their critical values of pressure, volume and temperature (often named

as '*disliquefying*' or '*absolute boiling*' points after *Andrews*, *Faraday* or *Mendelejev*). Experimental evidence initiated the formulation [83,85] of appropriate state equations of a real gas intending to replace somehow unsatisfactory technical analysis using the state equations for an ideal gas (already introduced by *Regnault* in the year 1847). The '*virial*' of external forces ($\sim 3pV$), suggested by *Clausius* twenty years later, described the difference between the behavior of real and ideal gases. It was centered on the mean free path of a molecule and the potential of intermolecular forces was taken as being proportional to

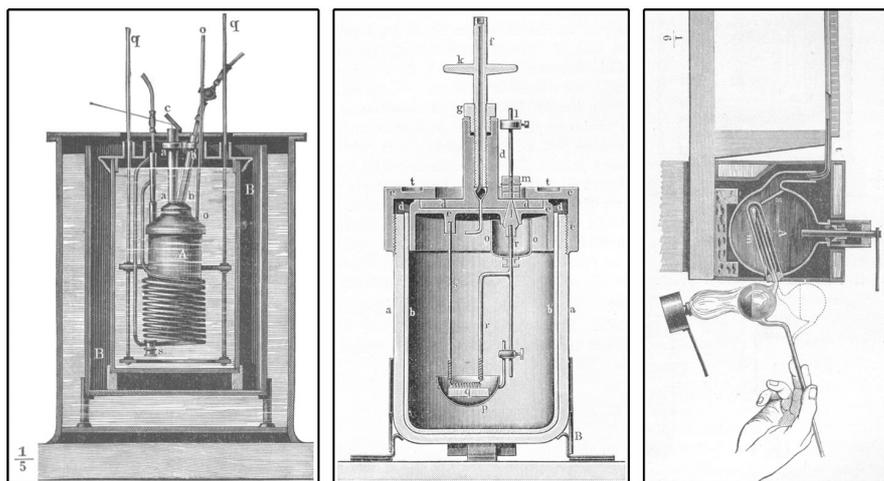


Fig. 7: *Favre and Silbermann* are not widely known for their early construction of a combustion calorimeter, which was adjusted for higher pressures by *Berthelot* (known as today's calorimetric bomb).

$1/V^2$, thus replacing thus the complicated function of *Laplace* that was based on the model of stationary molecules repelling each other due to their caloric envelopes (though satisfactorily explaining the surface tension, capillarity and even cohesion). The use of reduced values by *van der Waals* (1880) enabled him to postulate the 'law of corresponding states' based on the state parameters expressed in the units represented by their critical values.

The most important personality in thermodynamic history was credibly *Gibbs* who discriminated that a system of r coexistent phases, each of which having the same independently variable components, n , is capable of $(n + 2 - r)$ variations of phase, known until now as the famous 'phase rule', that factually unveiled that the whole is simpler than its parts. It followed that for temperature, pressure and chemical equivalents ('potentials' later specified as 'chemical potentials' by *Ostwald*) the actual components bear the same values in the different phases and the variation of these quantities are subject to as many conditions as there are different phases (introduction of partial derivatives). This important work on the theory of phase equilibria was published in the period 1873 to 1878 in an almost unknown journal "Transaction of Connecticut Academy" and its insufficient publicity was fortunately compensated by the proper recognition of renowned scientists [93-95], such as *Maxwell*, *Duhem*, *Ostwald* or *Le Chatelier*, also mentioning the Dutch school of thermodynamics, that must be particularly credited with the broader application attempts aimed at the problems of general chemistry and technology.

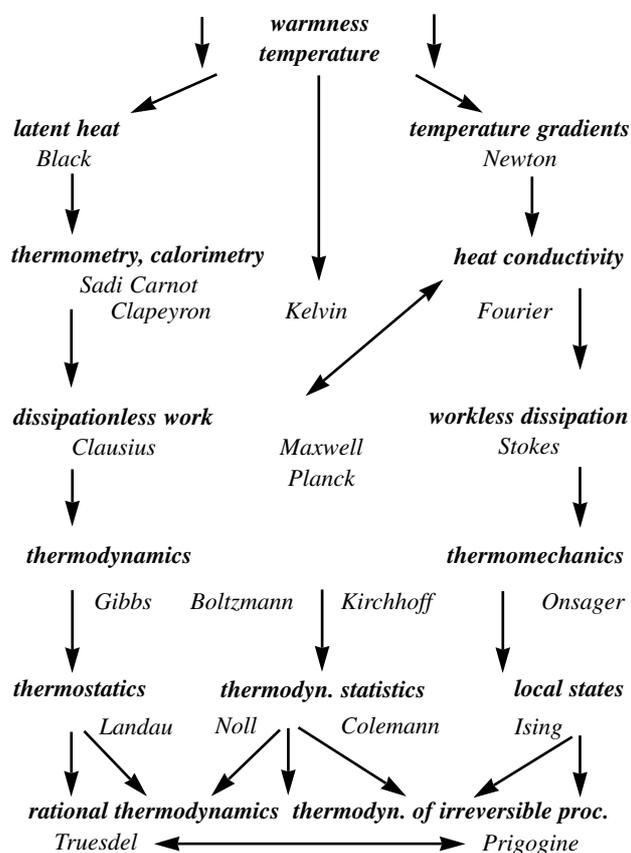
Another important area of *Gibbs*'s interests was the depiction of a fundamental dependence of the intrinsic energy of a one-component system versus volume and entropy, often called the 'thermodynamic surface'. It helped in the distinguishing of individual areas of stability in single- and multi- component systems that are in an equilibrium coexistence and which yield a whole what is now called "surface of dissipated energy". This method for investigating the equilibria of many-component systems, with the use of equality of the potentials of all the involved components in all the existing phases, became widely accepted after the introduction of the quantities of the "escaping tendency" (1900) or "fugacity" (1901). Finally the term "activity" was lastly introduced by *Lewis* in 1907 as relative [96] and established in the current meaning in 1913. Curiously *Lewis* was involved in various thermodynamic applications reaching even to economics [97].

In the last quarter of the 19th Century the theory of *metastable phase equilibria* marched under a more serious consideration although the formation of non-equilibrium states of pure substances and their mixtures had been experimentally proved long before (e.g. *Fahrenheit* published in 1724 experimental results on undercooled water). *Gibbs* was the first to use the term 'unstable' equilibrium while the authorship of 'metastable' is ascribed to *Ostwald* who in parallel with the term 'labile' presented an exact definition of its meaning as early as in 1897. *Van der Waals* modified the original *Gibbs*'s terminology of 'limit of absolute stability' to 'binodal' (points of contact

of the common tangential planes within the *Gibbs*'s thermodynamic surface were named as "nodes" according to mathematician *Cayley*) and the 'limit of essential instability' were called 'spinodal' (i.e., curves dividing the concave-convex surface into areas convex in all directions and those remaining completely concave). It is also worth noting that these purely theoretical considerations led to the discovery of two rather unusual and less known phenomena, such as 'retrograde condensation' and the 'barotropic effect'.

At the turn of 20th century a more modern nomenclature also emerged, such as the notion of a "eutectic" mixture and a eutectic point introduced by *Guthrie* (derived from the Greek expression used already by *Aristotle* in a similar sense of being easily melted – 'eutektor'), followed by "peritectic" reaction (*Lehmann*) or "eutectoid" (*Howe*). The progressive nature of both the theoretical and experimental treatments of this period is manifested in the fact, that the described phenomena were not yet fully understood yet. It was helped by the new approach called 'thermal analysis' (*Tammann* 1905) that enabled the determination of composition of the matter without any mechanical separation of crystals just on basis of monitoring its thermal state by means of its cooling curves – the only method capable of the examination of hard-to-melt crystal conglomerates. It brought along a lot of misinterpretations, the legendary case of the high-alumina regions of the quartz-alumina binary system continuously investigated for almost hundred years. It, step by step, revealed that the mullite phase irregularly exhibited both the incongruent and congruent melting points in dependence to the sample course of equilibration. It showed that mere thermal analysis is not fully suitable for the study of phase equilibria, which settle too slowly. In 1909 there was elaborated another reliable procedure of preserving the high-temperature state of samples down to laboratory temperature, factually 'freezing-in' the high-temperature equilibrium as a suitably 'quenched' state for further investigation. It helped in the consistent construction of phase diagrams when used in combination with other complementary analytical procedures, such as X-ray diffraction or metallographic observations.

Among the generalized applicability of the fundamental laws of thermodynamics is the description of the equilibrium coexistence of a mixture's phases became important. *Kirchhoff's* relation, which enabled the calculation of 'the amount of heat, which is liberated when a certain mass of water dissolves the minimum amount of salt as it is capable to dissolve', represented the first of these (Fig. 7). Another case was *Raoult's* law of the decrease of the melting point of a solution as well as the decrease of pressure of the solvent's saturated vapors over the solution. In the year 1884 the relationship, earlier derived by *Gulberg* for the depression of freezing point and the solute-solvent ratio, was taken over by *Van't Hoff* in his extensive treatise when calculating, for the first time, the osmotic pressure of a solute. Here also belonged the first derivation of the 'liquidus' in the phase diagram of the condensed binary system for the region of the low contents of solute (say for the phase 2) familiarly known

Table I: Rough sketch of the growth of thermodynamic conception.

in the form of $dT/dx_2 = RT^2/\Delta H_{2(\text{melt})}$ and later derived also by *Planck*. However, the author of a more general relationship was *Le Chatelier* in 1885 who proposed a logarithmic function of composition of a saturated solution in the form $dx/x = (\kappa/\sigma) Q dt/T^2$ where x , κ/σ and Q are the ratios of amounts of substances of solute and solvent, the proportionality constant related to gas constant and the molar heat of dissolution, respectively. A few years later it was improved by *Shreder* in his description of a solvent by the equation, $\log x = -\Delta H_{(\text{melt})} [T_{(\text{melt})} - T]/(R T_{(\text{melt})} T)$ since then known as the *LeChatelier-Shreder* equation. It was based on the assumption that the molar heat of dissolution over the whole range of temperatures and compositions is constant and equals to the molar heat of fusion of the pure component, i.e., showing the relationship $\Delta H_{(\text{sol})}/T \approx \Delta H_{(\text{melt})}/T_{(\text{melt})}$.

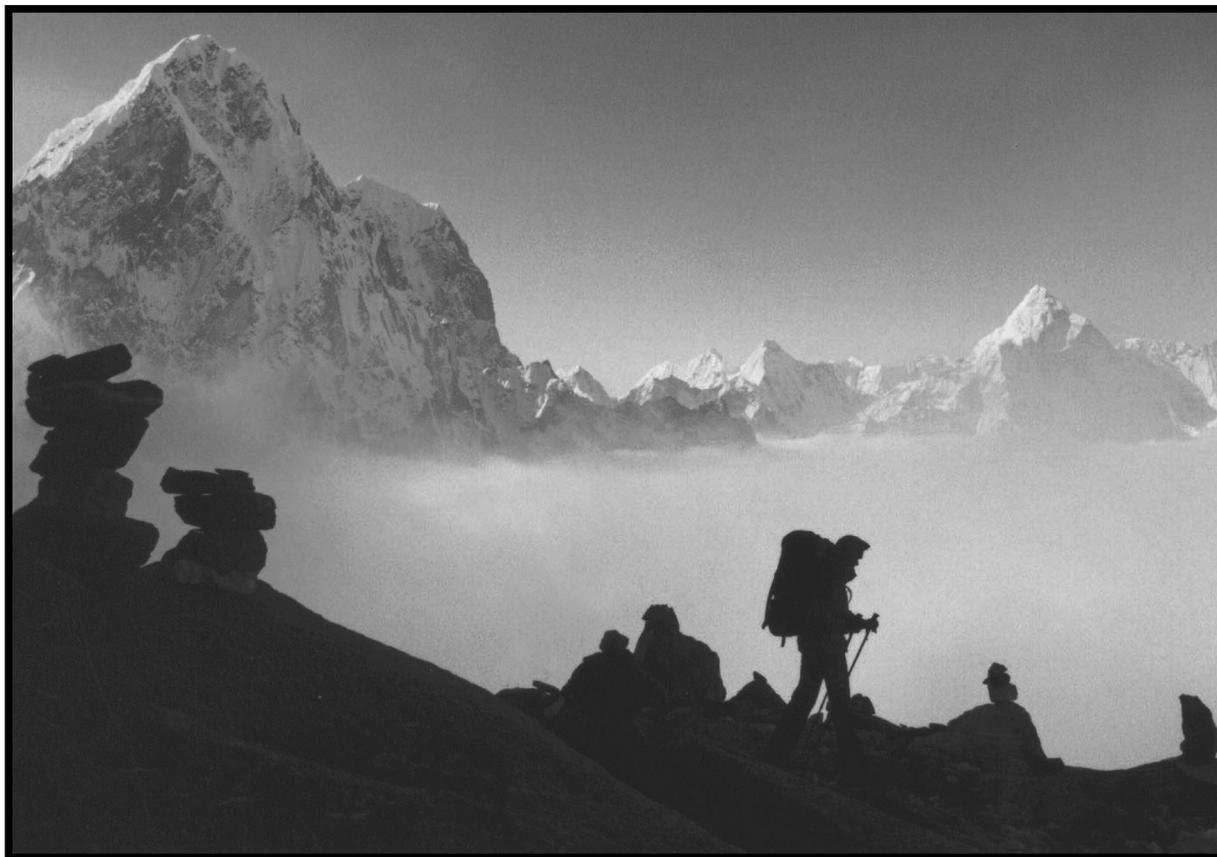
Important studies were performed by *Lewis* who defined the 'perfect' (later termed as 'ideal') solution in 1901, thus following *van't Hoff's* idea, which became extraordinary fruitful in the further development of thermodynamics of mixed systems since it enabled rational thermodynamics to sort out the solutions based on the differences between the behavior of real and ideal mixtures. *Rault's* law for extremely diluted solutions involved the

use of an equality of differentials of logarithms of the absolute activity, a , and that of the mole fraction of a solvent, x , yielding $d \log a = d \log x$. *Guggenheim* classified solution according to the experimentally determinable parameters employing the dependence of the excess of Gibbs energy of mixing, $(\Delta G^{\text{ex}})_{\text{mix}}$ proposed as a combination of symmetrical and asymmetrical functions. *Lewi's* model of an ideal solution was applied to molten salts in 1945 by *Těmpkin* who took the limit of solution of this kind for a mixture of two independent ideal solutions of ions with a coinciding sign of charge.

In the middle of the Twenties, there aroused the period of the *Onsager* revolution initiated by his article on "Reciprocal Relations in Irreversible Processes" [98], which factually followed a kind of quantitative thermal analysis, see Table I. It was based on the accomplishments made by *Ising* when describing the thermal behavior of a linear body consisting of elementary magnets under the assumption of interaction of their nearest neighbors. It was preceded by the definition of order-disorder transitions and the formulation of a general model of the second order phase transition according to which the system reveals the so called λ -point of transition, which is easy to characterize by an order parameter with zero and non-zero values above or below this transition temperature. In this treatise *Landau* also proposed an expansion of the *Gibbs* energies into a power series and entered, thus, the world of broadened phase transitions. It was just the starting point of modern theories of irreversible processes (*Coleman*, *Prigogine*, *Truesdel*, cf. Table I.)

Quantum mechanics brought about a real revolution [99], cf. Chapter 20. It may be said that 'Hamiltonian physics' was kept alive in the halls of Academies while the 'theme of entropy' subsided in the workshops of the smiths where it was actually born. The predictive power of quantum mechanics was upheld in connection with the concept of periodic states of motion, it returns and repeats itself, in this way carrying recognition. In the modern inflowing concept of lively disequilibria, the concept of entropy became important, showing that dissipative systems are profoundly different from Hamiltonian systems, which can be formalized from the unifying principle of minimum action. Hamiltonian systems come, in general, from a well defined variation principle; it provides an important apparatus for conservation laws and symmetries and produces great simplifications as well as bringing one close to a solution. Initially distasted systems of yet mysterious dissipation do not have an equally general formulation, they are open, non-isolated, they interact with the outside and exhibit generalized properties being possibly the reason why they are sometimes considered scientifically 'less aristocratic' and, thus, worthy of increased attention. In contrast to the classical perception of equilibration, for a dissipative system the state of motion literally dies out unless energy is constantly provided, cf. Chapter 16.

- ¹ For example, an excerpt from the western Christianity saga says "*the soldier was the solvent who would force the sulfur king to react with the mercury queen; the death of 'Priam' was the dissolution or melting of compound; the Hermetic dragon, who represented a test upon the alchemist's path, a counterforce opposing his work, guarded the grotto where Quintessence was found; the wolf was antimony devouring the gold before the purifying fire regenerated a living, active philosopher king*".
- ² The theory of caloric played a very important role in making the observation that gravitational force does not pull all things together to form one very dense body. Currently an invisible dark matter (and/or energy) hypothesis is used to explain yet undefined anti-gravitational forces that keeps the Universe expanding instead of only contracting under the omnipresent gravitational force – a striking coincidence!
- ³ The characterization of one kilocalorie as 427 kilogram-meters was first launched by Mayer [Organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel, Heilbronn] in the year 1845. Regarding some impediments associated with the wider application of (only now traditional) units, such as calories and recent joules [J], the establishment of some practical links with traditional work [$W = J/s$] became necessarily accentuated. Therefore, an innovative unit 'horse power' (HP) was necessary to bring in as the performance measure thanks to Watt, who was unable to sell his steam engine to mines without telling the engineers how many horses each engine would replace, because the owners traditionally used horses to drive pumps that removed water. Jointly with another norm work power by then, produced by a healthy brewery horse (introduced and premeditated by Joule working as a brewster), a horsepower unit was defined as 550 ft-lbs (~ 75kgm) of work every second over an average working day. It is clear that from that time the strong miner and brewery horse got off the use due to modern carriers and current 'average' horse power would have to turn into somehow 'weaker' status of present 'racing horses'. Nevertheless it is steadily kept in traditional rating engines of cars and trucks. The other horse 'dimension' was otherwise important in mankind's history as was the separation of two horse backs, which became a factor for establishing the distance of wheels in Greek wagons, and later, it correlated with the separation of railways and profile of tunnels. Consequently it even gave the size of the external rockets in the US space program as their size was limited by the separation of railways and associated size of tunnels through which the rockets were transported to the launching sites.
- ⁴ The so called *Brownian* motion was curiously ignored by the physicists who developed the kinetic theory of gases, though this case is now taken as its best illustration. Einstein was successful in taking a formula from hydrodynamics, for the force on a sphere moving through a viscous liquid, and other formula, from the theory of solutions, for the osmotic pressure of dissolved molecules. Joining these apparently incompatible physical characteristics he arrived to his famous result for the mean square displacement of particles. Modern readers may be puzzled by the steady use of the term 'molecular', which has the origin in the natural theory of Buffon, who assumed the supply of organic molecules as interchangeable part of its 'interior mold'. The idea of 'animated molecules' was finally refused by Brown moreover saying '*the motion of particles in a fluid cannot be due, as other had suggested, to that intestine motion which may be supposed to accompany its evaporation*'. Smoluchowski finally attacked the most common misconception about the molecular-kinetic explanation of *Brownian* movement that a large number of molecules near the suspended particle must move in unison in order to produce the observed motion. He showed that such a cooperative motion can be equivalent to the action of fluctuations as a natural consequence of randomness of molecular motion. The pivotal position reached Perrin, whose followers (e.g., Nernst in his 1909 '*Teoretische Chemie*') added even extra sections on kinetic theory and heat almost infirming the allegation of validity limits of the Second law of thermodynamics.
- ⁵ Convenient notion is gram-atom which was earlier specified as $6 \text{ cal}^{\circ}\text{C}^{-1} \text{ gram-atom}^{-1}$, today's expedient as about $25 \text{ J mol}^{-1} \text{ K}^{-1}$.
- ⁶ The frequency with which a given face is observed is roughly proportional to the number of nodes it intersects in the lattice per unit length. A lattice is understood as a regular array of points. Each point must have the same number of neighbors as every other point and the neighbors must always be found at the same distances and directions. All points are in the same environment

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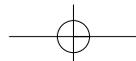
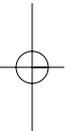
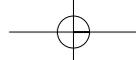
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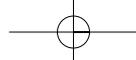
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Volume two
APPRECIATION OF HEAT AND THERMAL PHYSICS

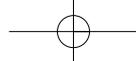
Heat, temperature and gradients

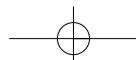
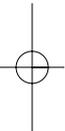
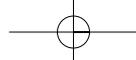
Thermodynamic principles

Equilibrium and kinetic phase diagrams, nucleation and growth, glasses

Thermal physics of processes dynamics

Literature







CHAPTER FIVE

5. Heat, temperature and gradients

a) Development of the concept of temperature

Temperature in view of *'temperament'* was first associated with the state of a human body [1–4]. Probably the first attempt to define the state of the human body by objective physical measurements came from a group of Italian scientists at the beginning of the 17th Century. *Sanctorius* experimentally studied the forces exerted by muscles, the content of various fluids in the body and the frequency of pulses using a *pulsologium* – an apparatus devised by *Galileo*. He tried, also, to measure the instantaneous characteristic of temperament, i.e., temperature, by means of a modified version of a very old device called a *thermoscope*. In fact, *Philon of Byzantium* (about 3rd Century BC.) constructed an instrument that demonstrated the expansion of air on heating, thus laying the foundation of thermometry without actually measuring temperature. Some years later *Diocles* developed the theory of the parabolic burning mirror and *Heron of Alexandria* (about 1st Century AD.) first used *thermoscope* for a more practical use. A medieval form of this instructive instrument consisted of a large bulb hermetically attached to a thin glass tube, the end of which was immersed into water in another vessel. To prepare the apparatus for experiments, a few bubbles were driven out of the tube by a slight heating of the bulb. After that, the instrument worked as a gas dilatometer, sensitive to changes of temperature (but also to changes of the external pressure). The addition of a regular scale, made of glass pearls, to the pipe of the *'thermoscope'* enabled *Sanctorius* to judge the degree of the patient's temperature and then to choose the proper medical treatment. This conversion from a curious toy into a powerful measuring device, which provided data that could be applied for some purpose, gave the *thermoscope* all the features of an effective discovery.

It is quite certain that by the 17th Century knowledge of the *'weatherglass'* (the common name for *thermoscope*) was widely spread among educated people, either due to the new edition of *Heron's* papers or upon the accessibility of excerpts of Arabian alchemical manuscripts. Assigning only a single "true" inventor of thermometer, from among persons such as *Galileo*, *Segredo*, *Fludd*, (*F.*) *Bacon*, *van Helmont*, *Boyle* and others, is practically impossible. Among these inventors was also *Goethe*, who more than one century later (1732) had patented a *'virginomorphic'* glass bowl filled with wine and containing a very strange pipe – the device was more worthy of deep

psychoanalytical study than for a "reliable forecast of weather". However, during the second half of the 17th Century there were in use some advanced forms of thermometers for medical and meteorological purposes, namely those constructed by *Guericke* and by the members of the *Accademia del Cimento* in Florence who also invented the closed fluid-thermometer.

The second half of the 17th Century may be characterized as an era of the differentiation between pure theoreticians and experimentalists. Typical of the theoreticians, represented e.g. by *Bacon*, *Descartes* and *Gassendi*, was a very prudent and critical approach to new experimental facts, a deep interest in new methodology that was more reliable than that used by medieval scholastics, and the will to construct universal theories. Regardless of the progress made by the theoreticians, it would have all been futile if it were not for the extensive work by other experimental scientists. The words of *Fludd* that "...the thermometer became a mighty weapon in the Herculean fight between 'Truth and Falsehood'" were prophetic. The most distinguished person who was trying to use this "weapon" for quantitative measurements was *Boyle*. Unfortunately, the main problem concerning his experiments was the absence of sufficiently reproducible fixed points that characterized the given thermal states, and consequently he was able to perform only relative measurements.

However, *Römer* and *Fahrenheit* satisfactorily solved the serious problem of suitable scales much later, at the beginning of the 18th Century, by their use of the first sealed precision mercury-in-glass thermometer, see Fig. 1. They introduced fixed points such as the freezing point of an aqueous solution of salmiac (0), the freezing point of water (32), the normal temperature of the human body (96) and the boiling point of water (212). The intervals between the fixed points¹ marked on the scale of such a fluid thermometer were divided regularly into degrees. This calibration, which was for some time *Fahrenheit's* personal secret, ensured a very good reproducibility

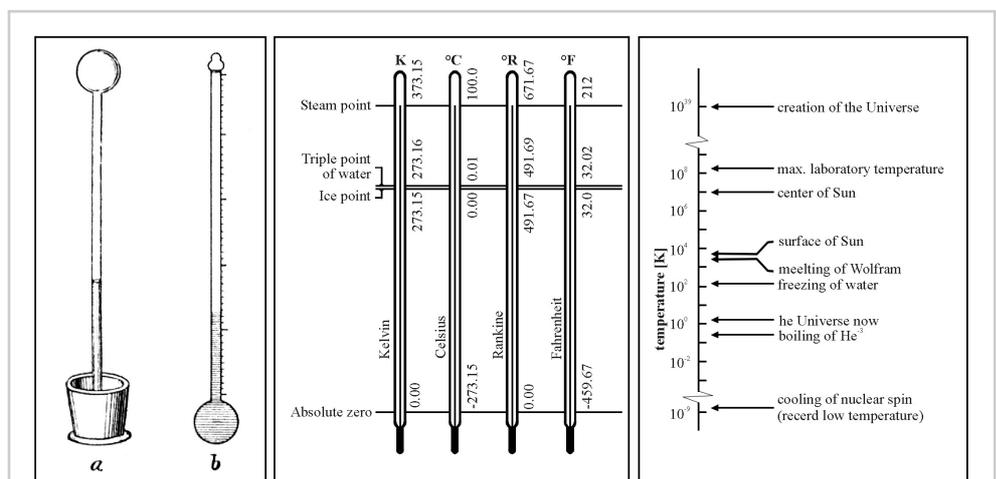


Fig. 5.1: Medieval types of thermometers (left) compared with the traditional mercury-in-glass-tube thermometers calibrated to different, than so far used, temperature scales. Right: the extent of temperature scale shows its infiniteness on the both sides of extra-high and ultra-low temperatures.

of results for a number of different instruments. In 1746 the Swedish astronomer *Celsius* introduced a new temperature scale with zero set at the boiling point of water and 100 for its freezing point. After his death *Linne* changed it to the scale (0–100 form) that we still use to this day.

One of the earliest attempts to put high temperatures on a mathematical scale was done already by *Newton* (1701), who described a thermometer on the basis of oil and calibrated it by taking "the heat of the air in winter when water begins to freeze" as 0 and "blood heat" as 12 – on this scale water boils at 34. The melting points of alloys were determined by an extrapolation and logarithmic temperature scale that was proposed for high experimental temperatures on the basis of the equation, $\theta = 12\{2^{(x-1)}\}$, where θ was the temperature in units of the above scale and x represented the logarithmic temperature. Actual values on the arithmetic and logarithmic scales were determined by interpreting the time that an iron-bar took to cool down to "blood heat" in terms of *Newton's* law of cooling.

An analogous method for the construction of a thermometric scale was devised independently by *Amontons* [5] who made experiments with a constant volume gas thermometer. By extrapolating the regularly-divided (into 100 degrees) scale between the boiling and freezing points of water below the freezing point, *Amontons* noticed that there should be a point corresponding to zero pressure of a gas in the thermometer. He called this point (lying approximately 270 degrees below the freezing point of water) the absolute zero or point of 'ultimate coldness' (*l'extrême froid*) and suggested its use as a natural fixed point. Mankind is indebted to *Amontons* for another fruitful idea; the invention of the gas thermometer. Whilst not a very convenient instrument, it is, nevertheless, a reliable and very important tool for the calibration of more practical liquid thermometers. *Fahrenheit's* and *Amontons's* scales have a lot of common features with modern thermometric scales (cf. Fig. 1). These enabled the fundamental problems in scientific thermometry to be solved, namely: to assign a number θ , called the *empirical temperature*, to any given thermal state, to decide whether two bodies have the same temperature or not, and to determine which body has the higher temperature. Later *Maxwell* recognized that for thermometry to be a logically closed system it is necessary to add a concept of thermal equilibrium and another theorem, sometimes called the zero law of thermodynamics, according to which: "two bodies which are in thermal equilibrium with a third one are also in thermal equilibrium with each other." By establishing this theorem, which encompassed the form of *Euclid's* first axiom, the development of the concept of empirical temperature was practically completed.

In 1824, whilst investigating the theoretical optimization of steam engines, *Carnot* devised an idealized heat engine capable of performing virtual, fully computable, cyclic processes [1,6,7]. His concept consisted of a thermally-insulated cylinder containing a gas which is provided with a movable piston. The bottom of the cylinder can be either insulated or, in turn, put into contact with

two bathes (A or B), which have different empirical temperatures ($\theta_A > \theta_B$). These operations may be performed in such a way that only isothermal and/or adiabatic changes are involved, so that it can be proved mathematically that the work done during one cycle is maximal. Using these conclusions, and the conjecture about the impossibility of 'perpetually motion' (*perpetuum mobile*) generalized for thermal phenomena, *Carnot* formulated the following important theorem: "The moving force of the fire (i.e. useful work) does not depend on the agent used for its development and its magnitude, it relies only on the temperatures of the bodies between which the transfer of heat takes place".

It was *Kelvin's* excellent idea that every thermometer may be treated as a special kind of thermal engine working between a bath kept at the temperature, which has to be measured, and other one at the reference temperature. According to *Carnot's* theorem, the efficiency (i.e., normalized 'useful' work) of any reversible cycle is dependent only on these two temperatures, regardless of the working (thermometric) substance. By taking this efficiency as a measure of the temperature, the absolute scale (i.e. independent of device and/or of material constants) can be constructed. In order to find additional conditions to which such a construction must be submitted, *Kelvin* constructed a mental experiment that had three reversible engines simultaneously working with three baths at different empirical temperatures $\theta_1 > \theta_2 > \theta_3$. Application of *Carnot's* theorem to all combinations of these cycles provided a functional equation with solution, $Q_1/Q_3 = \varphi(\theta_1)/\varphi(\theta_3)$, where $\varphi(\theta)$ is a monotonic, positive, definite and real function of the empirical temperature, θ . The simplest choice, which later became the basis of the international temperature scale, is that it corresponds to the relationship $\varphi(\theta) = \alpha T$ where α is a universal constant and αT is that for heat, Q , exchanged between the bath and thermometer. This convention is fully consistent with the empirical scales induced by isochoric (so called *Amontons's* scale) and/or isobaric (*Avogadro's* scale) equations of state.

How important the choice of $\varphi(\theta)$ was for the further interpretation of concepts in thermal physics will be apparent from the following example. *Dalton*, in analyzing not very reliable measurements [8] of the thermal expansion of fluids, found a quadratic dependence between supplied heat, identified by himself as temperature, θ , and the increase in volume, V , of the fluid with respect to that at its freezing point. Using this conjecture as a basis for the construction of a temperature scale, he was able to fit the isobaric equation of state of any permanent gas by the formula $V/V_0 = \exp\{\beta(\theta - \theta_0)\}$ where β is also a universal constant. The initial state, characterized by the volume V_0 and by both temperatures θ_0 and T_0 , will be changed to a new equilibrium state that corresponds to the volume V . It is easy to show that the difference $(T - T_0) = \text{const}(V - V_0)$ is directly proportional to the work done by the gas against the external pressure, P . On *Dalton's* scale, the temperature difference factually measures the increase in entropy (in its usual sense) of a gas in a thermoscope, because $\ln(V/V_0) = \text{const}(\theta - \theta_0)$, where *const* stands for β .

It is remarkable that both the arbitrarily chosen quantities of temperature, related to just the same experimental situation (volume change induced by heating), can have such a different interpretation. There is an enormous freedom in how to choose the function, φ , but it is a very difficult task, and a matter of intuition, to anticipate whether such a choice will be of practical value in the future. Thus the intuitive opinion of *Dalton* that the temperature should reflect something closely related to the content of heat in a given body actually corresponds to his idea. On the other hand, the simple interpretation of heat conduction and the evaluation of efficiency (of, e.g., steam engines) require the temperature to behave like the potential of a heated fluid. In this case, a *linear scale*, equivalent to the contemporary *Kelvin's* international scale, is the most convenient one.

At about the same time (1848) *Thomson* used the same basis of *Carnot's* thermal efficiency and tried to introduce a logarithmic temperature scale, *Th*, in the form $\eta = \text{const} dTh = dT/T$. After integration it follows that $Th = \text{const}_1 \ln T + \text{const}_2$, where both constants can be determined by using the traditionally fixed points of the melting and boiling of water. This scale, however, would dramatically change the customary concept of thermodynamics. The meaning and interpretation of the third law of thermodynamics would ease if the zero temperature would be replaced by infinity ($T = -\infty$) but the traditional degree of freedom, $\sim 1/2 kT$, would revolutionize to embarrassing proportionality, $T \sim \exp\{(Th - \text{const}_2)/\text{const}_1\}$, etc. It shows the significant role of a suitable convention, which we can illustrate using a hypothetical case of *Newton's* definition of force, *F*. Instead of the contemporary expression $\{d(mv)/dt\}$ a more complex relation could have been adjusted, such as $\{d(mv)/dt\}^n$ or even $\ln\{d(mv)/dt\}$, which would essentially changed our tradition.

As indicated, temperature reveals itself to be a potential of heat, illustrating its similarity to mechanical work and its well-known complete conversion into heat [9,10]. There, however, is no a single process enabling a complete reverse conversion of a given amount of heat back into mechanical work without the accompaniment of other changes. The very absence of this opposite transformation logically excludes the possibility that *heat is equivalent to any other kind of energy*, which is characterized by the unlimited fluctuations amongst its particular forms. This serious inconsistency in classical thermodynamics is compensated for by the traditional introduction of a new quantity (called entropy) and of a new axiom (known as the second law of thermodynamics), which states that this entropy is indestructible ("never decreases") and is always increasing (factually being "created" during every real, irreversible route). It is, therefore, of no wonder that a meaningful physical interpretation of this quantity is apprehensive and lacking easy demonstration. This is due to the fact that it has just the same properties as heat (in its common sense), the name of which has already been quite improperly used to label a certain special kind of energy. Indeed, if we identify heat with entropy, the mysterious second law of thermo-

dynamics becomes quite intuitive and very easy to understand stating, "*heat cannot be annihilated in any real physical process*". For instance, in an experiment where heat (= entropy) is generated by means of friction between two blocks of any material, it is clear at first glance that the heat (= entropy) will not disappear by moving the blocks in opposite direction but will instead only increase further. Indeed, just to be able slow down such a process, one would have to effectively decrease the amount of friction being generated, i.e. by suppressing the generation of heat (\cong entropy) during the movement, however, there is no process involving the mentioned blocks that could reverse the system and destroy the heat (\cong entropy) that had already developed. Moreover, the substitution of the word "entropy" by the word "heat", which is no longer regarded as a kind of energy, would enable a more intelligible interpretation of temperature [1] as the desired potential in a closer analogy with other potentials (electric, gravitational) used in other branches of physics.

b) Heat transfer

In the 1850s, the Scottish physicist *Maxwell* [10] initiated convincing investigations into the mechanical theory of heat. He argued that the velocities of point particles in a gas were distributed over a range of possibilities that were increased with temperature, which led him to predict, and then verify experimentally, that the viscosity of a gas is independent of its pressure. In the following decade *Boltzmann* began his investigation into the dynamical theory of gases, which ultimately placed the entire theory on firm mathematical ground. Both men had become convinced that the novel notion of entropy reflected molecular randomness. *Maxwell* expressed it this way: "*The second law of thermodynamics has the same degree of truth as the statement that, if you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out of it back again.*" These were the seminal notions that in the following century led to the field of non-equilibrium thermodynamics.

Although *Euler* had already in 1764 formulated a mathematical theory for convection in fluids, for the 19th Century scientists the subject of heat transfer had to begin with the simple notations of *Newton's* Laws of cooling² [11] (even if we now consider it insignificant in comparison to his other works on mechanics and optics). We may repeat "*the greater the outer conductivity and surface of a cooled solid body the faster is its cooling. On the other hand, the body's thermal inertia, given by the product of its specific heat and mass, slows down its cooling*". It, however, did not yet distinguish between different modes of heat transfer.

In 1818 *Dulong* introduced an improved law of cooling, and *Petit* suggested that a body absorbs and emits heat at the same time. They argued that the rate of cooling, \underline{v} , of a body at temperature, $T + \theta$, in a vacuum surrounded by a container at temperature, θ , must be determined by the general formula $\underline{v} = f(T + \theta) - f(\theta) = m a^x (a^y - 1)$ where f is a power function and the parameters \underline{m} , \underline{a} , \underline{x} and \underline{y} are 2.037, 1.0077, θ and T , respectively. This formula was later simplified to describe the

thermal effect measured by a thermoelectric instrument, z , in the form $z = a T^2 (T - \theta) - b (T - \theta)$, thus combining thus the terms responsible for radiation and Newton's previous that accounts for the influence of the surroundings. One consequence of this exponential-like form was that the heat radiated by a body would never become zero for the finite values of temperature. In 1860 it was *Maxwell*, who borrowed from *Clausius* the concept of the mean free path traveled by a molecule from one collision to the next, and who introduced the modern view that heat conduction is a special case of a general transport process of which diffusion and viscosity are parallel examples. The T^4 term was later found to fit the corrected *Dulong-Petit* data leading to the gradual establishment of the *Stefan-Boltzmann* Law of radiation. Worth of note is *Leslie's* work on the rate of cooling that furnished the relationship, $dT/dt = -a T$. If the initial temperature of a hot body is T_0 (at $t = 0$), then $T = T_0 e^{-at}$. The constant a represents the range of cooling and can be estimated by measuring the time taken to cool down an object to the value of $T_0/2$. The rate of cooling was found by dividing 0.693 by the time required for T to decline to $T_0/2$. This, in fact, provided the early basis for theoretical calorimetry.

The study of temperature distribution was initiated by *Biot*, who found that if a copper rod and an iron rod are joined together end to end, and the coupled ends are placed in heat sources [12], then the heat will conduct through the copper end more quickly than through the iron end, because copper has a higher proportionality constant, k equal to 92, whereas, iron has a value of only 11. He introduced a method of how to determine the relative thermal conductivities (*de facto* thermal diffusivity, the term used by *Kelvin*), λ , of two well-connected metallic bars of similar shape that are put under a steady heating of their join. A measurement of the distance from the join where the temperature is the same on both bars, x , provides the heat conductivity value in the form $\lambda_2/\lambda_1 = (x_1/x_2)^2$. Of even more intelligent insight was the estimation of λ on the basis of average temperature measurement at three arbitrary but equidistant points, T_1 , T_2 and T_3 . If equally separated they provide a useful average – the dimensionless value of n equal to $1/2 (T_1 + T_3)/T_2$. It helps to determine λ_2/λ_1 by distinguishing, x , by help of the logarithmic form, $\ln[n + (n^2 - 1)^{1/2}]$ providing the first insight into the thermal exponential distribu-

tion (see the early method of thermal measurements in Fig. 2).

Perhaps the more important contribution, however, came from *Fourier*, who in the year 1822 judged the above mentioned thermal properties in detail and summarized them in the renowned *Fourier's* Law of heat conduction in the form of $Q = -\lambda s \Delta T/\Delta x t$. It states that the amount of heat, Q , which passes through a surface (cross section), s , in time unit (sec) is proportional to the temperature difference, ΔT , per given length, Δx (i.e., to the unite temperature gradient of 1 degree per 1 meter). The proportionality constant stands for the standard *coefficient of thermal conductivity* while $a = \lambda/(c_p \rho)$ expresses *thermal diffusivity* where c_p is the specific heat capacity and ρ is the specific mass. It complies well with the generalized physical observations of one-dimensional heat flow that results from the temperature non-uniformities, i.e., heat flow and temperature gradients are exactly opposite one another in direction, and the magnitude of the heat flux is directly proportional to this temperature gradient. It is worth noting, however, that this early account of the ratio of heat over temperature (i.e., cal/1°) was presupposed to bring the same meaning as 'mass'. It is clear that we should understand generalized heat flux, q , as a quantity that has a specified direction as well as a specified magnitude [13–16]. *Fourier's* Law summarizes this physical experience succinctly as

$$q = -\lambda_i \nabla T = \lambda \Delta T/\Delta x \quad 5.1$$

where the temperature gradient ∇T is represented by three (i, j, k) – dimensional derivatives, i.e., $\nabla T = i \partial T/\partial x + j \partial T/\partial y + k \partial T/\partial z$, and where the standard thermal conductivity can now be found to depend on both the posi-

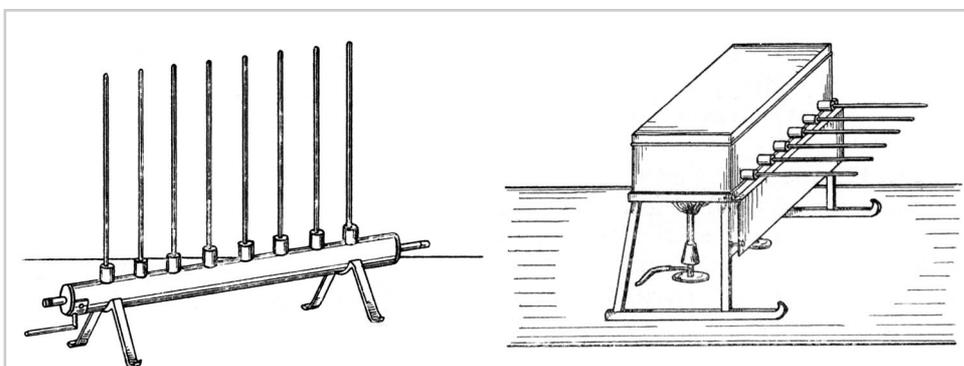


Fig. 5.2: Two instrumental versions of the Ingenhausz's apparatus used for the heat conductivity measurements at the beginning of 19th Century. The rods made from different metals (Ag, Cu, Zn, Pb, etc.) were immersed into the vessel filled with boiling water (or flowed steam). In order to follow the gradual temperature changes of individual rods their surface were covered by either the layer of wax (to observe the melting) or mixture of $\text{Cu}_2\text{J}_2 + \text{HgJ}_2$ (to observe the change of red color to yellow). It was stressed out that 'rods must be sufficiently lengthy; vessel heating ought to be prolonged and intensive so that the temperature differences are well visible to the eye. However, potential experimenters are apprehended of possible investigation artifacts that even though the silver is a better heat conductor than copper, the silver rods from bazaar show often heat retardation because of their contamination – unseen mix up with copper'. The experiment could be reversed so that the advancement of coldness was possible to observe if the heated water was exchanged for the mixture of ether with snow particles of CO_2 .

tion and temperature, $\lambda_i = \lambda\{(i,j,k)(T)\}$. Fortunately, most materials are nearly homogeneous so that this equation simplifies to $\lambda = \lambda(T)$ and for a one-dimensional flow is further simplified to $\Delta T/\Delta x$. It is evident that λ may vary from one substance to another, which is accounted for in part by varying electron and photon conductance. One feature that substances have in common with one another, according to empirical evidence, is that λ is always a positive constant. This, of course, makes intuitive sense, at least if the molecular concept of temperature is invoked; the heat (kinetic energy at the microscopic scale in another sense) tends to flow from the regions of high internal energy to the regions of low internal energy, which is consistent with the statement above that the heat flow is opposite the gradient direction of temperature. This is also consistent with the laws of thermodynamics. To show this we must emphasize that heat flow is independent of velocity gradients or gradients of concentration, such as would exist in a fluid mixture, so that it is required that $\lambda/T^2(\nabla T)^2 \geq 0$ approving the previous request of $\lambda \geq 0$ and therefore being consistent with experimental results.

Fourier's Law has several extremely important consequences in other kind of physical behavior, of which the electrical analogy is most striking. Let us first consider *Ohm's Law* describing the flux of electric charge, I/A , by the electric current density, $J_e = -\sigma \nabla V$, where σ is the electric conductivity, V is the voltage, I are the amperes of electric current and A is an area normal to the current direction (vector). For a one-dimensional current flow we can write Ohm's Law as, $J_e = -\sigma \Delta V/\Delta x$. Because ΔV is actually the applied voltage, E , and R_e is the electric resistance of the wire equal to $\Delta x/(\sigma A)$, then, since $I = J_e A$, the equation becomes the form of Ohm's Law, $V = R_e I$. The previously written formula, $\Delta x/(\sigma A)$, thus assumes the similar role of thermal resistance, to which we give the analogous symbol, R_t , and which shows how we can represent heat flow through the slab with a diagram that is perfectly identical to an electric circuit.

Another analogous relationship is that of mass transfer, represented by *Fick's Law* of diffusion for mass flux, J , of a dilute component, 1, into a second fluid, 2, which is proportional to the gradient of its mass concentration, m_1 . Thus we have, $J = -\rho D_{12} \nabla m_1$, where the constant D_{12} is the binary diffusion coefficient and ρ is density. By using similar solutions we can find generalized descriptions of diffusion of electrons, homogeneous illumination, laminar flow of a liquid along a spherical body (assuming a low-viscosity, non-compressible and turbulent-free fluid) or even viscous flow applied to the surface tension of a plane membrane.

As a matter of interest and in view of general thermo-physical measurements, there are some other important subjects that, whilst lie outside the scope of this chapter, but are worth mentioning. For example, the coefficient of thermoelectric tension (*Seebeck coefficient*, α) describes the proportionality between the heat generated at a material's contact when a certain amount of electric current passes across it (*Peltier coefficient*, P) and the composite heat, Q , due to the electric current, I , at time, t , generated

within the material held under a temperature gradient, ∇T (*Thompson coefficient*, $\mu = Q/(J_e \nabla T) \approx Q/(\Delta T T t)$). All these coefficients combine to form certain complex parameters such as the proportion of thermal and electric conductivities, $\lambda/\rho \approx (k_B/e)^2 T$ (where k_B is the *Boltzmann* constant and, e , is the charge of electron), or the quality factor of thermo-electric material, $Z = \alpha^2 \rho/\lambda$, or some other mutual interdependency like $P = -\Delta \alpha T$ or $\mu = -T (\partial \alpha / \partial T)_p$.

When developing methods that combine thermal determinations [15,16] it is necessary to take into account a number of factors, many of which either do not occur or leave only a small influence on the entire measurement of other, for instance electric, quantities. There are no perfect conductors nor absolute thermal insulators and most thermal conductivities vary in a relatively narrow range (within approximately five orders of magnitude). What is more, at higher temperatures these values converge and it is, therefore, difficult to realize a well-defined thermal flow, particularly when assuming the practical lengthiness of a thermal process, which, in comparison to electric flow, takes a rather long time to achieve equilibrium.

However, it is more important to note that within phenomenological theories any flux can be generalized as the kind of the dissipation function, Φ . Thus it can be written as a sum of all the thermodynamic fluxes, J_i , and their conjugate forces, X_i , i.e., $\Phi = \sum_i J_i X_i$. The fluxes are unknown quantities in contrast to the forces, which are known functions of the state variables and/or their gradients. It has been found experimentally that fluxes and forces are interwoven, i.e., a given flux does not only depend on its own conjugate force but may depend on a whole set of forces acting upon the system as well as on all thermodynamic variables (T, P, \dots). Various fluxes can be thought of the rate of change of an extensive variable, X_i , i.e., $J_i = \partial X_i / \partial t$. Conjugate forces are identical in form to the phenomenological flow equations shown above and can be expressed, close enough to equilibrium, in the linear form [17] of the *Onsager relations*, or

$$\partial X_i / \partial t = J_i = \sum_k L_{ik} X_k \quad 5.2$$

where the constant coefficients, L_{ik} , are called the 'phenomenological coupling coefficients'. Written in this fashion, thermodynamic forces are differences between the instantaneous and equilibrium values of an intensive variable (or their gradients). For example the difference $(1/T - 1/T_{eq})$ is actually the thermodynamic force conjugate to the internal energy, which is the familiar *Fourier Law*, i.e., $q = -\lambda_i \nabla T$ or *Stokes Law*, i.e., $p^v = -2 \eta \nabla v$. The traditional *Fick's Law* is then obtained by introducing the condition that one works at a constant temperature and pressure, while *Ohm's Law* requests supplementary constraints provided that the magnetic induction and all couplings are ignored³. Similarly we can predict a linear relationship between the rate of advancement of a chemical reaction and the affinities, which, however, is correct only within a very narrow domain around equilibrium.

c) *Non-stationary heat diffusion and the Schrödinger equation*

In general, any of these phenomena involves the movement of various entities, such as mass, momentum, or energy, through a medium, fluid or solid, by virtue of non-uniform conditions existing within the medium [16]. Variations of concentration in a medium, for example, lead to the relative motion of the various chemical species present, and this mass transport is generally referred to as diffusion. Variations of velocity within a fluid result in the transport of momentum, which is normally referred to as viscous flow. Variations in temperature result in the transport of energy, a process usually called heat conduction. Besides the noteworthy similarities in the mathematical descriptions of these three phenomena; all three often occur together physically. It is in the case of combustion, where a flowing, viscous, fluid mixture is undergoing chemical reactions that produce heat, which is conducted away, and that produce various chemical species that inter-diffuse with one another.

Description of a more frequent, non-steady progress requires, however, the introduction of second derivatives. These are provided by a three-dimensional control of a finite region of a conducting body with its segmented surface area, denoted as A . The heat conducted out of the infinitesimal surface area, dA , is $(-\lambda \nabla T) \cdot (\underline{k} dS)$, where \underline{k} is the unit normal vector for the heat flux, $q = -\lambda \nabla T$. The heat thus generated (or absorbed) within the underneath region, V , must thus be added to the total heat flow into the surface, A , to get the overall rate of heat addition. Therefore we need integration. Moreover, the rate of the increase of internal energy, U , for the given region, V , is granted by the relationship, $dU/dt = \int_V \{\rho c_p (\partial T/\partial t)\} dV$, where the derivative of T is in the partial form because T is a function of both, V and t . Applying Gauss's theorem, which converts a surface integral into a volume integral, we have to solve the reduced formula of the form, $\int_V \{\nabla \cdot \lambda \nabla T - \rho c_p (\partial T/\partial t)\} dV = 0$

Since the region, V , is arbitrary small, the integrand must vanish identically so that the heat diffusion equation in three dimensions reads, $\nabla \cdot \lambda \nabla T + dq/dt = \rho c_p (\partial T/\partial t)$. If the variation of λ with T is small, λ can be factored out leaving a standard but a more complete version of the heat conduction equation (i.e., the second law of *Fourier*) $\nabla^2 T = (1/a) (\partial T/\partial t)$, where a is the thermal diffusivity, and the term $\nabla^2 T \equiv \nabla \cdot \nabla T$ is called the *Laplacian* and is arising from a *Cartesian* coordinate system $(i \partial/\partial x + j \partial/\partial y + k \partial/\partial z)$ $(i \partial T/\partial x + j \partial T/\partial y + k \partial T/\partial z) = i \partial^2 T/\partial x^2 + j \partial^2 T/\partial y^2 + k \partial^2 T/\partial z^2$. This is the standard second order form of the heat equation showing that the change of temperature over time is proportional to how much the temperature gradient deviates from its linearity. In the other words, the bigger the protuberance in the temperature distribution, the faster is its compensation.

However, its mathematical solution is complicated and is not the aim of this chapter. Just as an example, let us consider a massive object of temperature T_0 (at the initial conditions of $T\{x,0\}$) that would affect the temperature of its environment, T_c . The solution in time, t , and space distribution, x , gives solution in the form, $T(x,t) = T_c +$

$(T_0 - T_c) \Phi [x/2(at)^{1/2}]$, where Φ stand for the *Bessel* functions, usually available from tables.

The fact that the second *Fourier Law* bears a general form of a distribution law is worthy of special remarking. The significant reciprocity can be found for the famous *Schrödinger* equation when taking into account a diffusion process as something fundamental [19–22] and intimately related to light and matter (close to the physical intuition of *Feynman*). It is usually written in its simpler form as $d\psi/dt = i c' \Delta \psi$, where ψ is the wave function and c' is the 'imaginary' diffusion constant. The different paths along which diffusion with an imaginary diffusion constant occur do not necessarily lead to the totting-up of the observed effects but can, instead, result in a destructive interference. This is asymptotic for a new phase in physics, intimately related to the mathematics of complex functions. It describes diffusion as probability amplitude from one point to the next along the line. That is, if an electron has certain amplitude to be at one point, it will, a little later, have some amplitude to be at neighboring points. The imaginary coefficient i makes the behavior completely different from the ordinary diffusion equation such as the equation that describes gas spreading out along a thin tube – instead the real exponential solutions and the results are shown in complex waves. Physics, however, has already gone one stage beyond the complex numbers in order to describe weak and strong interaction in elementary particle physics (non-abelian gauge theory that uses "hyper-complex" numbers – multivectors, by working, for example, the $SU(2)$ theory of quantum flavor dynamics). Such hyper-complex mathematics of diffusion may be related to the realm of life yet too complex to solve but recently applied, at least, to the kinematics of the human knee. The complex diffusion problem can also be recalled in view of the substrate-bound *Maxwellian* understanding of light, deeply rooted in the world view of many physicists even today, as well as to *Steiner's* view of electricity as light in a 'submaterial' state [18].

d) *Practical aspects of heat flow – contact resistance and periodical outcome*

As a matter of interest we can begin this section by mentioning the incident described by *Schwartz* in 1805 when he experienced an unusual audio sound while an as-cast hot ingot of silver was placed on the cool iron anvil [12]. Later, it was closely studied by *Trevelyan* and *Faraday* who showed that any hot metal standing on two separated tips resonates with the cooling substrate (preferably with an amply different coefficient of heat expansion). Practically speaking, the metal is pushed up by one of its tip and gets back to another one, and so on, which thus endows an oscillation continuity.

No two solids will ever form a *perfect thermal contact* when they are pressed together and the usefulness of the electric resistance analogy is immediately apparent when looking into the interface of two conducting media. Since some roughness is always present, a typical plane contact will always include thermal impedance such as tiny air gaps, structural irregularities, etc. Heat transfer thus follows at least two parallel paths across such an interface.

We can treat the contact surface by placing an interfacial conductance, h_c , (in $[W/(m^2K)]$) in series with the conducting material on the either side. It accounts for both the contact material and the surface's mutual finish executed by a joining force (deformation), near-surface imperfections and interface temperature profile, $T = T(r)$ providing $R_{total} = (1/h_1 + 1/h_c + 1/h_2)/A$, where $h_{1,2}$ are the respective conductivity of materials on the both sides (i.e., $h_1 \approx \lambda_1/d_1$, d being the thickness). Some typical interfacial conductances for normal surface finishes and moderate contact pressures (up to 10 atm) provides average data for h_c (in $[W/m^2 K]$) as follows:

Steel/Cu (pressurized at 70 atm)	< 45 000
Cu/Cu	10 000 – 25 000
Al/Al	2 200 – 12 000
Graphite/metals	3 000 – 6 000
Ceramics/metals	1 500 – 8 000
Ceramics/ceramics	500 – 3 000
Steel/steel (evacuated)	100 – 500 $[W/m^2 K]$

A frequent task is to find the temperature distribution and heat flux for a sample holder granted as the long enough hollow cylinder with a fixed wall temperature – inside temperature T_i for radius r_i and outside T_o for r_o . For $T = T(r)$ we have $(1/r) \partial/\partial r (r\partial T/\partial r) = (1/a) (\partial T/\partial t)$ to provide general integration in the form $T = c_1 \ln r + c_2$. The solution gives $(T - T_i)/(T_o - T_i) = \ln(r/r_i)/\ln(r_o/r_i)$. It would be instructive to see what happens when the wall of the cylinder becomes very thin, or when (r_i/r_o) is close to unity. In this case $\ln(r_i/r_o) \approx (r - r_i)/r_i$ and the gradient has a simple linear profile $(T - T_i)/(T_o - T_i) \approx (r - r_i)/(r_o - r_i)$, the same solution that we would get for a planar wall. The heat flux falls off inversely with the radius.

We often want to transfer heat from the outside through composite resistances where we, again, can recognize *Ohm's Law* similarity and write the resulting thermal resistance in the form called the overall heat transfer coefficient, R_{therm} . It represents the series of actual thermal resistances in the same way as it is traditionally made for an electrical circuit with multiple electrical resistances. Recalling the preceding example of a convective boundary condition of a cylinder we can write for heat Q a simplified equation, $Q = R_{therm} s \Delta T t$, where $R_{therm} = 1/\{1/h + r_o \ln(r_o/r_i)/\lambda\}$ is given in $[W/(m^2K)]$ units and h is again the customary interfacial conductance.

The opposite approach would be a more detailed inspection of individual thermal processes taking place on the entire interface. Let us consider only two parallel thermal passes: one, most rapid solid conduction, carried out through the direct contacts and the other, so called interstitial heat transfer, which is much slower as intermediated through gas-filled interstices by convection, or even by radiation across evacuated gaps, as illustrated in Fig. 3. Surprisingly it may establish enormous temperature gradients along the interface – just assuming that the solid conduction takes place on one micron interface with one degree temperature difference then the resulting value for the term $\Delta T/\Delta x$ ascend to 10^4 K/m, which is comparable to the gradient produced on the wall of a high temperature furnace. It is clear that a series of such contacts arbitrary distributed along the interface give rise a community of heat sources that have a periodical resolution. The resulting heat wave is not planar and horizontally parallel to the conductive interface but has a sinuate profile. Further it is associated with the local volume changes due to the temperature dependency of expansion coefficient so that it is also the source for the above mentioned sound effect when

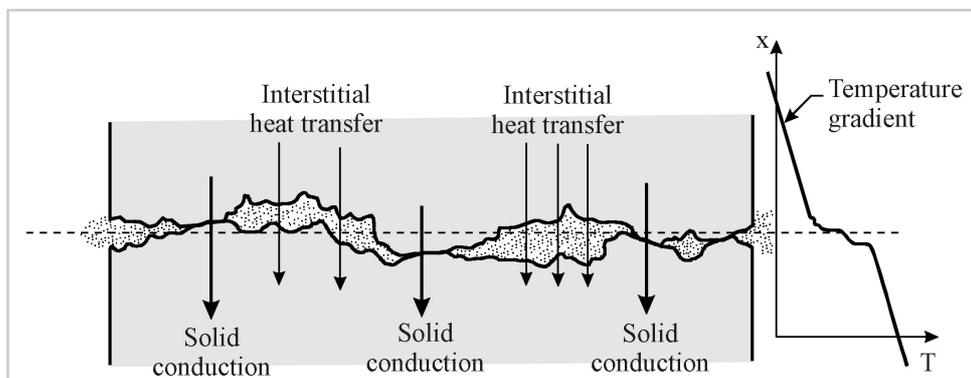


Fig. 5.3: Illustrative portrait showing the overall heat transfer from side to side of the two (macroscopically) well-linked solid bodies. The separation plane represents a thermal contact between two real (often-uneven) solid surfaces eligible, however, to create spot-high temperature gradients, which are located at the individually disassociated thermal junctions. Miniature contact places exhibit either the good (conduction – thick arrows) or poor (mixed connectivity – thin arrows) heat transfer. Possible effect of such uneven distribution of intimate thermal contacts is often overlooked. In view of always existing 'rough-touch-character' of most thermal contacts the possibility of an internal heat pulsation cannot be excluded even for the ordinary thermally-controlled experiments, which uses the miniaturized sample-sells that possess relatively large surfaces of their associated mechanical contacts. Even the opposite (retarding) performance may be anticipated when the poor-connective-sites execute the damping role for the externally introduced modes of thermal oscillation.

a hot ingot possessing jagged surface with tips is placed on a cold metallic plate. A thermally fluctuating interface is likely to be a very common feature of many reacting interfaces. It may furnish two solutions; a traditional solution, where the sinuous profile is extinguished by gradual retardation of thermal waves if the bulk (e.g. the sample cell) is large enough, or a less common solution, where such thermal fluctuations are enhanced and grown up by some processes, which multiply thermal effects (e.g. by befitting self-organization). This may occur even for special cases of thermophysical measurements when working in micro-dimensions (minia-

ture samples or very thin walls of sample holders), which are not capable to compensate for thermal fluctuation. Such a case is gradually manifested through routine observations by the detection of thermal noise. It may be superimposed by externally ordained temperature oscillations that would positively enhance the localized tendency to thermal vacillation as happens in the case of thermally modulated methods of thermoanalytical experimentation (see Chapter 12).

A periodical thermal source is, therefore, very important to analyze. It can act on a coupled body in two basic ways:

(i) when provided by an external (stationary) and large enough (unbounded) body of temperature, T , that is repeatedly changing in a particular manner, usually expressed according to the convenient goniometric function, $T(0,t) = A \cos \omega t$, where A stands for the (maximum) amplitude and ω is the angular frequency given by relation $\omega = 2\pi/T = 2\pi f$, where T is the period and f is the frequency,

(ii) when represented by an internal heat generator the heat production of which is again denoted by a goniometric function, usually understood as the time derivative of the previous *cosinus* (due to dT/dt), then $T(0,t) = B \sin \omega t$, where B stands for the product ωA . For example, the solution for temperature steady state assuming a simple infinite plate in the fixed environment of such periodical changes of temperature, $T_p = T_{p0} + T_{p_{max}} A \cos \omega t$, resolves in the analogous function, $T(x,t) = A(x) \cos(\omega t - \varphi_x)$, where φ_x represents the phase shift and $A(x) = f(\omega^2 \lambda)^{1/2}$ stands for a complex function, f , of angular frequency, ω , and heat conductivity, λ . There follows some important points:

- The resulting amplitude of oscillation, $A(x)$, decreases exponentially with the penetration depth, x , i.e., $A(x) \approx A \exp(-\omega x / 2\lambda^2)^{1/2}$.
- The transferred temperature oscillations are time delayed that is again proportional the penetration depth $(\omega x / 2\lambda^2)^{1/2}$.
- The penetration depth depends on the oscillation periodicity, i.e., the smaller period the lesser penetration. The ratio $A(x)/A$ equals to $\exp(-\omega x / 2\lambda^2)^{1/2}$ which make possible to estimate heat conductivity using $\lambda^2 = \omega x / \{2 \ln^2 A(x)/A\}$.

e) Warm-cool feeling

As was accentuated in chapter one, as the most decisive processes of our instinctive responsiveness, is the spontaneous sensation of warmth. So it would not be perceived unusual to also pay attention to the transient thermal properties that play an important role in our positive sensation of our clothes wrapping. In particular, it applies for flat textile fabrics, as there are involved not only the classical parameters like thermal capacity and thermal diffusivity, but also some transient thermal parameters, which describe the *warm-cool feeling* [23] or *thermal-contact feeling of fabrics*. It occurs during the short or periodical thermal contact of human skin (thermo-sensors) with any object of a different temperature.

On the market of thermo-physical instruments there even exist two measuring apparatuses that are commercially available, e.g., the Japanese '*THERMO-LABO*' instrument and the European '*ALAMBETA*' instrument, which can express the level of thermal-contact feeling in terms of the so called 'thermal absorptivity'. The generally accepted measuring methodology or reference values are, however, missing and the thermal-handle of fabrics, whose level strongly affects the clients when buying clothes for their clothing or not, is still evaluated subjectively.

The principle of an automated instrumentation relies on the application of a direct ultra thin (0.15 mm) heat flow sensor, which is attached to a metal block of constant temperature which differs from the sample temperature. When the measurement starts, the measuring head, containing the mentioned heat flow sensor, drops down and touches the surface plane of the measured sample, which is located on the instrument base under the measuring head. At this moment, the surface temperature of the sample suddenly changes (i.e., the boundary condition of first order is worked out), and the instrument computer registers the heat flow course. Simultaneously, a photoelectric sensor measures the sample thickness.

The computer display then shows the steady-state values for characteristics such as the thermal conductivity λ [$W/(mK)$], thermal resistance R [m^2K/W] and thickness of the sample s [mm], but also the transient (non-stationary) parameters like thermal diffusivity and so called thermal absorptivity b [$Ws^{1/2}/(m^2K)$]. Thus it characterizes the warm-cool feeling of textile fabrics during the first short contact of human skin with a fabric. It is defined by the equation $b = (\lambda \rho c)^{1/2}$, however, this parameter is depicted under some simplifying conditions of the level of heat flow q [W/m^2] which passes between the human skin of infinite thermal capacity and temperature T_1 . The textile fabric contact is idealized to a semi-infinite body of the finite thermal capacity and initial temperature, T_0 , using the equation, $q_{dyn} = b (T_1 - T_0) / (\pi \tau)^{1/2}$, which is valid just for the short initial time, τ , of thermal contact between the skin and fabric. For longer times, exceeding a few seconds (where the minimum time is given by the square of thickness s divided by 12,96 and also divided by thermal diffusivity, a), the heat flow, q , loses its dynamic (transient) character and its level sinks to the steady-state level given by the relation $q_{st} = (T_1 - T_0) / R = \lambda(T_1 - T_0) / h$. The higher the level of thermal absorptivity, the cooler the feeling it represents. Practical values of this parameter for dry textile fabrics range from 30 to 300 [$Ws^{1/2}/m^2K$]. It was approved that this parameter (which was formerly also used in civil and mechanical engineering) characterizes with good precision the transient thermal feeling which we get in the moment, when we put on the undergarment, shirts, gloves or other textile products. It was found, that 'grey' fabric always exhibits the highest thickness, highest thermal resistance (and consequently lowest thermal conductivity) and lowest thermal absorptivity (warmest contact feeling). During the subsequent stages of any chemical treatment, practically all the above mentioned thermophysiological properties

become worse. Singeing, for example, makes the outstanding superficial fibres shorter, which reduces the thermal-insulation air layer entrapped amongst the fibres, during any resin treatment the air is substituted by a polymer of higher thermal conductivity and capacity, etc.

Thermal contact sensation by means of some reliable measuring instrument opens new ways for the optimization of this relatively new fabrics-surface characteristic, which often presents a factor that influences the choice of cloth or garment by a customer, and whose method of objective assessment deserves an international standardization. Since the touch sensation strongly affects our choice, the objective assessment of this sensation turned out to be a very important subject in the last decade and became a part of generalized thermal analysis.

f) *Turbulent boundary layers*

We must be reminiscent, however, that besides the flow of heat, there also exist other fluxes such as that of fluid, solutions of salt, the viscous stresses or even the flux of electrons or light. These laws are commonly based on the conservation of momentum and additional hypotheses, the justification of which lies in the satisfactory comparison of deductions from these laws with experimental observations. Such comparisons between theory and observation are limited, particularly in respect to the more complex situations, which may arise when several different fluxes become alive simultaneously. It is conceivable and even probable, that such classical laws of heat conduction, diffusion, and momentum transfer must be altered to account for phenomena, which cannot be otherwise explained. In short, the state of our knowledge of macro- and micro-molecular transfer of properties is not complete.

For example, turbulence in a fluid medium can be viewed as a spectrum of coexisting vortices in which kinetic energy from the larger ones is dissipated to successively smaller ones until the very smallest of these vorticular 'whirls' are damped out by viscous shear stresses. It is best illustrated by clouds patterns where huge vortices of continental proportion feed smaller 'weather-making' vortices of the order of hundreds of kilometers in diameter. They further dissipate into vortices of cyclone and tornado proportions that yet disintegrate further to smaller whirls as they interact with the ground and its various protrusions. Interestingly the process continues right on down to millimeter and micro-scales. Practically we want to create a certain measure of the size of turbulent vortices ('length-scale'). This may be done experimentally by placing two velocity-measuring devices very close to one another in a turbulent flow field or using so called mixing length introduced by *Prandtl* as an average distance that a parcel of fluid moves between interactions. It bears a physical significance similar to that of the molecular mean free path. This mixing length, l , helps to define so called 'eddy diffusivity for momentum', ϵ_m . For the notations of the instantaneous vertical speed of the fluid parcel and the velocity fluctuation that increases in the y -direction when a fluid parcel moves downwards (+) into slower moving fluid, we obtain measurable definition of $\epsilon_m =$

$l^2 |\partial u / \partial y|$. This value can be useful to characterize the turbulent fluctuations in the boundary layer (friction velocity, viscous sublayer or buffer layer dependent to the *Reynold's* number (see also Chapter 13).

Alike the existence of a turbulent momentum boundary layer there is also a turbulent thermal boundary layer, which is characterized by inner and outer regions. In its inner part, turbulent mixing is increasingly weak and heat transport is controlled by heat conduction in the sublayer. Farther from the wall, a logarithmic temperature profile is found, and in the outermost parts of the boundary layer, turbulent mixing becomes the dominant mode of transport. The boundary layer ends where turbulence dies out and the uniform free-stream conditions prevail, with the result that the thermal and momentum boundary layer thickness is the same. *Fourier's* Law might likewise be modified for turbulent flows by introducing the local average of the turbulent temperature, T' , and the eddy diffusion of heat, ϵ_h , which suggests yet another definition, the turbulent *Prandtl* number, $Pr_t \equiv \epsilon_m / \epsilon_h$.

Knowing that the complex heat transfer coefficient, h_x , is a complex function (of k , x , c_p , u_{max}) and that the mean film temperature, $T_f = (T_w + T_\infty)/2$, the derivation can be based on the *Fourier's* Law again, $h_x = q / (T_w - T_\infty) = \lambda / (T_w - T_\infty) (\partial T / \partial y)_{y=0}$, certainly under certain simplifications such as the fact that a fluid is incompressible, pressure deviation does not affect thermodynamic properties, temperature variations in the flow do not change the value of k and the viscous stresses do not dissipate enough energy to warm the fluid significantly. By assuming the control volume, R_v , in a heat-flow and fluid-flow field we can write that the rate of internal energy increase in R_v is equal to the sum of the rate of internal energy and flow work out, net heat conduction rate out and the rate of heat generation, all related to R_v . It provides the so called 'material derivative', abbreviated as DT/Dt , which is treated in details in every fluid mechanics course and which represents the rate of change of the temperature of a fluid particle as it moves in a flow field. For the field velocity, u , and particle velocity, v^{\rightarrow} , it takes the energy differential form, $DT/Dt = \partial T / \partial t + v^{\rightarrow} \nabla T$, or in particular, $\partial T / \partial t + v_x \partial T / \partial x + v_y \partial T / \partial y = a(\partial^2 T / \partial x^2 + \partial^2 T / \partial y^2)$, which is even more common in its dimensionless form, when T is substituted by θ , which is equal to the ratio of instantaneous versus maximum gradients, $(T - T_w) / (T_\infty - T_w)$, where subscripts w and ∞ mean the wall boundary and infinity.

This is a subject sample when this specific field of heat transfer involves complex motions which can be seen, however, as a remote discipline of classical thermal analysis but which, nevertheless, takes part in any complex process of self-organization, and is to be treated later on.

g) *Special aspects of non-equilibrium heat transfer*

There is a vast amount of literature on heat conduction when counting with relaxation terms [24], which is trying to correct its paradoxical theoretical nature, i.e., the so-called absurdity of the propagation of a thermal signal with infinite speed. It follows from the solution of the heat and/or diffusion equation, which gives a definite

Table 5.I: Survey of methods of thermophysical measurements.

-
- 1) Sourceless methods (using external contacts)
 - a) Stationary
 - unrestricted
 - relative
 - b) Non-stationary
 - regular state
 - constant initial temperature
 - general thermal change
 - periodical thermal change
 - radiated waves
 - 2) Using an internal source
 - a) According to the shape of heat source
 - point
 - line
 - planary
 - volume
 - combined
 - b) According to the action of heat source
 - impulse
 - permanent action
 - periodical action
 - discretionary
-

construal of propagation for any time. This certainly contradicts the macroscopic observations and was one of the first incentives for the development of extended irreversible thermodynamics. Let us examine an isolated system, which is initially composed of two subsystems at different temperatures. At a given instant, they are put in thermal contact. Equilibrium thermodynamics theory predicts that the final equilibrium state will be that of equal temperatures. However, it does not give any information about the evolution from the initial to the final states, which could be either a pure relaxation or even an oscillatory approach. Though in the oscillatory case the heat could paradoxically flow from cold to hot regions in several time intervals, it is not in contradiction with the second law of thermodynamics because of its global nature. The problem becomes acute when one tries to give a local formulation of this second law in particular time and in local space, which is crucial in second sound experiments. It leads to the definition of the localized production of entropy, s' , and the formulation of an extended equation for the evolution of heat, $\mu q = \nabla \theta^{-1}$, to be compatible with the required positive definiteness of s' and positive values of the parameter μ , i.e., $\nabla \theta^{-1} - \alpha \theta^{-1} q' = \mu q$, where $\alpha = \tau/\lambda T$ and $\mu = (\lambda T^2)^{-1}$. For small values of heat flux, the contribution of multiple order of $(q q)$ to the absolute temperature, θ , can be neglected, so that q is taken equivalent to the local-equilibrium temperature, T . Then it provides the form of *Cattaneo* equation, $\tau q' = -(q + \lambda \nabla T)$.

It is important to realize that there is the generalized absolute temperature, θ , and not merely the local-equilibrium temperature, T , which is the relevant quantity appearing in the entropy flux and the evolution equation for the heat flux. Considering infinitesimally small ther-

mal disturbances around an equilibrium reference state, the values of θ and T become identical with each other up to the second-order corrections and the evolution equation of T is as follows,

$$\rho c \tau \partial^2 T / \partial t^2 + \rho c \partial T / \partial t = \nabla (\lambda \nabla T), \quad (5.3)$$

where, for simplicity, relaxation time, τ , and heat conductivity, λ , can be assumed constant. Joining the preceding equations together it results in a new hyperbolic equation of the telegrapher type, namely

$$\tau (\partial^2 T / \partial t^2) + \partial T / \partial t = a \Delta T. \quad (5.4)$$

Under high frequency perturbations (or pulses) the first-order term derivative is small compared with the two other terms and the equation becomes a wave equation whose solution is known in the literature as second sound (for, e.g., dielectric solids in low temperatures). There is several other contexts known, such as in the analysis of waves in thermoelastic media, fast explosions, etc.

In the case of suddenly heated materials (dielectric discharge, laser pulses, fast exotherms or even picosecond-irradiation-induced nuclear fusion) the associated energy transfer cannot be adequately described using the classical Fourier's Law. In order to study such special responses of the system subject to a general perturbation due to an energy supply term, $g(r,t)$, the energy balance equation (5.3) have to be extended and the right-hand side is replaced by $[g(r,t) + \tau \partial g(r,t) / \partial t] / \rho c$.

It is important to note that the time derivative of the energy supply term has no counterpart in the classical theory of heat. The difference between the classical and extended formalism follows. In the classical description, the response to heat perturbation is instantaneously felt in all space, because the term $\Delta T(x, t)$ is non-zero at any position in space for $t > 0$. In contrast, $\Delta T(x, t)$, derived upon the mathematical manipulation with the energy added equation (5.4), vanishes for $x > \sqrt{(\rho c / \lambda \tau)} m^2$, so that a perturbation front propagates with the speed $u \approx \sqrt{(\rho c / \lambda \tau)}$, while the positions beyond the front are unaltered by the action of pulse.

The description based on a generalized hyperbolic equation predicts the propagation of a front peak, which is absent in the classical parabolic model. It means that the latter underestimates the high temperature peak, which may be present in the wave front, which means that the distribution of thermal energy is altered. In the classical parabolic case it is scattered within the whole spatial region, whereas there is a sharp concentration of energy in the actual case of the hyperbolic solution. It has serious consequences in understanding the absolute non-equilibrium temperature, θ , which is continuous across the ideal wall between the system and thermometer, while their respective local-equilibrium temperatures, T 's, may be different. A more intuitive understanding may be achieved in viewing the situation where two hypothetical thermodynamic systems are thermally connected through an ideally connecting plate. One system is at equilibrium temperature, T , while the other is at a non-equilibrium

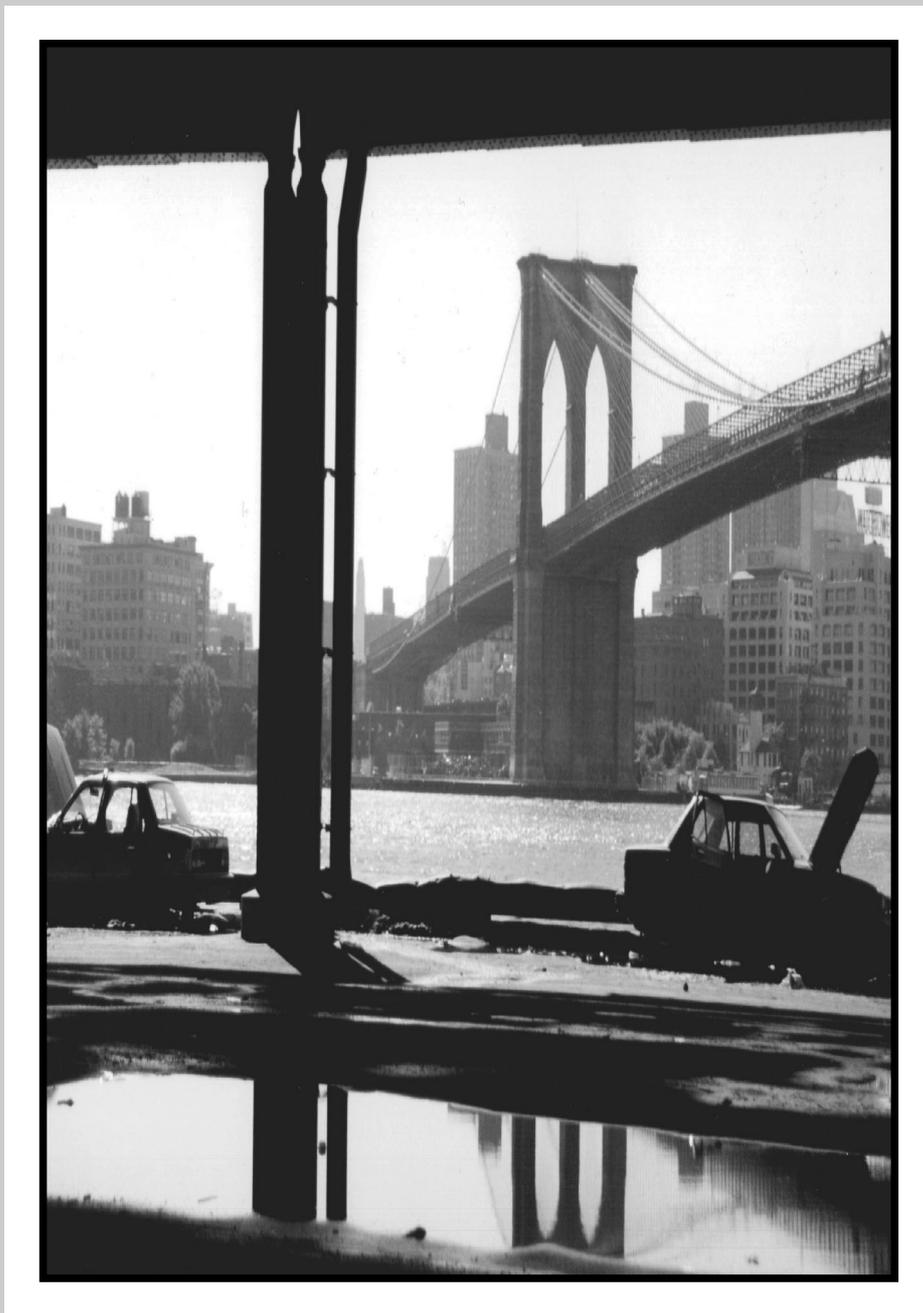
steady state under a high heat flux generated by a temperature difference across its system body. According to classical theory, no heat should flow from one system to another if equilibrated. However, a contrary flow is to emerge, which is proportional to the gradient of the non-equilibrium temperature, $\nabla\theta$, because one equilibrium side has $\theta_1 = T_1$ while the other $\theta = T(1 - \gamma q^2)$ where γ is proportional to $k^3 T^3$. It yields the disequality $\theta < T$. This

example corroborates the previous statements, according to which a thermometer indicates the generalized temperature: heat transfer between the two systems will take place until they have reached the same temperature, rather than the same local-like equilibrium. This idea provided an incidental basis to the definition of a "coldness" function assumed to depend on the empirical temperature and its time derivative.

¹ The difficulty with setting up the precise 'freezing' points was linked with the pervasive effect of water undercooling in its dependence on the environment and type of measurement, which variously effected the precise temperature determination of water solidification. As mentioned above, it was caused by the properties of solid ice, which is a more packed but lighter form of water, having the hexagonal structure, which shows evidence of distinctive incommensurability with the pentagonal-like symmetry of solidifying liquid water containing high number of fluid-like centers of ice-incommensurable icosahedrons and dodecahedrons, therefore capable of undercooling below the standard freezing point (now 0 °C). Therefore other complementary systems were searched that were based on every day practice such as that with salty water (experience with ice formation over sea) or mixtures of water with alcohol (freezing of wine).

² Perhaps, that is how 'irreversible heat flow' acquired its unpleasant moral connotation where the term 'dissipation' was taken synonymous to 'intemperate or vicious mode of living'. The natural behavior of heat entails a distinction between past and future or even illustrates extrapolation to an ultimate heat death of the Universe. Thus it is understandable that heat played a crucial role in the process of age estimation of the Earth. During the late 17th Century *Buffon* anticipated its age to be about 75 000 years accounting on laboratory experiments for the different cooling rates of different substances of various diameters and *Joly* extended it by three orders of magnitude measuring the ocean salinity and its inflow by rivers. *Leibnitz* in his '*Protogaea*' assumed that the outer surface of the molten proto-earth would solidify irregularly leaving the inner part still liquid. On the basis of *Fourier's* theory, *Thompson* tried to approximate how much energy could be stored in the Earth that was formed from a contracting cloud of interstellar dust that has since cooled and condensed, and he arrived to the age of about hundred millions of years. Impact of the additional energy received from radioactivity decay increased it by four times until radioactive chronology pushed the value up to the present estimate of 4.6 10⁹ years – quite a difference from the original statement of the Irish bishop *Ussher* (1654) who said that the biblical "let's be light" happened just on the 23rd March of the year 4004 BC.

³ Let us assume that the general force F , responsible for the movement of electric charge, is locally identical with the electric field intensity characterized by the electrostatic potential, V , (*Kirchoff's* conjecture) so that $F_v = -(\partial V/\partial v)$. *Ohm's* Law can be then formulated in the differential form as $i_v = -\gamma(\partial V/\partial v) = \gamma F_v$, where i_v and F_v are the local current density vector and the local electric field vector (i.e., the normal component of the current density flowing through the arbitrary chosen area element $d\Sigma$ in interior of the conductor) and parameter γ is the conductivity. The following theorem can, thus, be proved. If the electric current flows through a conductor in accordance with *Ohm's* Law there is, however, no net charge in its interior due to the neutrality condition. For the current flowing into the volume element $\{dx\ dy\ dz\}$ in the direction of the x -axis one can write, $j_{x1} = \gamma\ dy\ dz\ (\partial V/\partial x)_1$ with the difference $(j_{x2} - j_{x1}) = -\gamma(\partial^2 V/\partial x^2)_1\ dx\ dy\ dz$. The same equation should be valid also for the y and z directions. Taking into account the fact that the in the stationary state the sum of incoming and out coming currents in the volume element has to be zero (equation of continuity) we can find an equivalent to *Laplace's* equation indicating the absence of space charge, so that "in a homogeneous ohmic conductor, with prescribed potential difference on its terminals, the potential distribution inside the conductor is independent of parameter $\gamma \neq 0$, provided it remains finite". It was suggested to complete the purely electrostatic term γF_v , by a chemical (diffusion related) term, i.e., the force linearly depending on the gradient of the net charge concentration ρ , The *Ohm-Kirchoff's* Law can then be rewritten as $i_v = -\gamma \nabla(\varphi + \lambda^2 \rho/\epsilon)$ where φ and ϵ are respectively the electrostatic potential and permittivity, $\gamma \lambda^2/\epsilon$ has the same meaning as a diffusion constant, where λ is a length parameter added for the sake of homogeneity (with physical meaning of the screening, e.g., *Thomas-Fermi* screening length of about 10⁻¹¹ for metals giving corrections beyond the observation limits). For equilibrium, where $i_v \rightarrow 0$, the electrostatic and chemical terms are fully comparable throughout the whole volume and therefore they should offset each other, $\varphi/\lambda = \lambda \rho/\epsilon$, having a character of the boundary condition for the jump of normal electric field component across the space charge region of the thickness, λ . It becomes useful in explaining the low-temperature magneto-capacitance experiments useful in studying two-dimensional electron behavior where the quantum motion can be viewed as diffusive with a diffusion constant given by ratio of Planck's constant over the effective electron mass [see, e.g., J.J. Mareš., J. Křištofik., P. Hubík, *Physica E* 12(2002)340].



CHAPTER SIX

6. Thermodynamic principles

a) Aspects of chemical thermodynamics

The conventional field of a mathematical description of the system¹, Ω , defined as a physical and macroscopic object (see Fig. 6.1a) in which certain (phenomenologi-

cal) physical quantities (variables, *observables*) can be directly or indirectly measured, is traditionally acknowledged to constitute the entire domain of thermodynamics [24–35]. Perhaps, it is one of the most general theories developed for the direct application to physico-chemical systems, where attention focuses on the investigation of

thermal properties of materials based on the choice of certain parameters selected to represent the system. The basic concept involves the assumption of the existence of a stable, so-called ‘*equilibrium state*’, see Fig. 6.2., where each out-of-equilibrium situation of any system or sub-system evolves *reversibly* towards equilibrium, but not *vice versa*. The privilege of such reversible processes is that they can be described with the differential forms of linear equations while, on the contrary, irreversible transformations can be treated only by inequalities (and often as non-linearity). The equation of energy conservation in thermo-

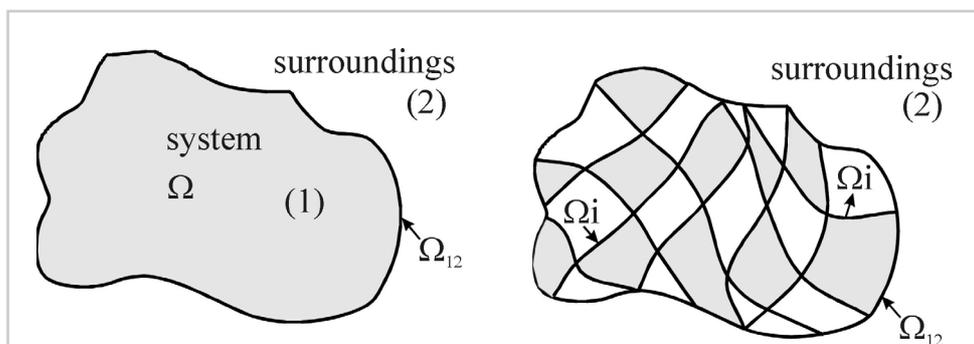


Fig. 6.1 (a): Circumscription of a basic thermodynamic system, Ω , with its central homogeneous interior (1) and the surface circumference, Ω_{12} , separating it from its outer periphery (called surroundings, 2). (b) A successively developed heterogeneous system (right), which subsists more complicated features, but is also more common in natural case as any variant of non-ideal homogeneous system. The interior is broken to smaller areas (grains or cells) separated by authentic interfaces, which properties are different from those of its yet homogeneous cores. Thoughtfully, we can also imagine such a (total) system, Ω , to consist of numerous (identical and additive) homogeneous subsystems, Ω_i 's, all being in good mutual (thermal and other) contact, which thus make possible to simply communicate the concept of an active (non-equilibrium) system under flow.

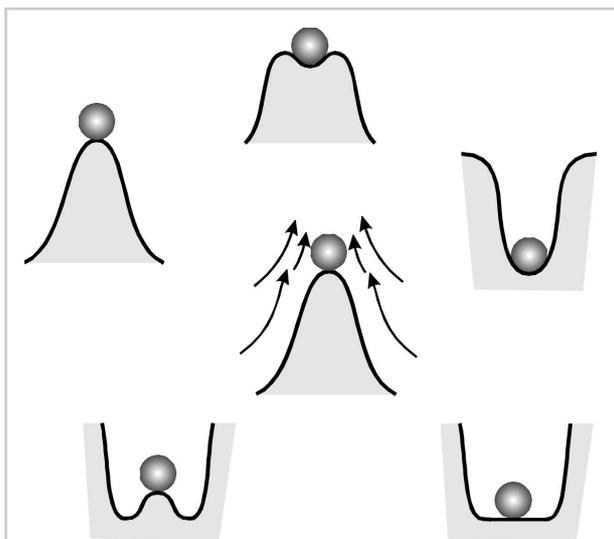


Fig. 6.2: Illustration of the mechanically anticipated stability of a system represented by the receptacle (energy-pitcher) with a movable ball showing (upper, clockwise) the stages of unstable, stable and metastable equilibrium. The especially implied case of dynamical stability of disequilibrium is shown in the middle – it is illustrated by a fountain-effect where the ball is held at the upper (highly unstable) position by the permanent action of force (such as stream of water, air or the other energy flow).

dynamics is traditionally a continuity equation, $dU = dQ - dW$. We understand it in such a way that within the domain, Ω , with its outer $1 \leftrightarrow 2$ boundary, Ω_{12} , there is the *internal energy* variation, dU , due to the fluxes of energy in two forms: *heat* across the interface Ω_{12} ($dQ > 0$ is incoming) and *mechanical work* delivered by Ω itself ($dW < 0$, if work is received). It is worth noting that this already includes several aspects of irreversibility [25,33]: i.e., the thermal flow, $\Delta \Sigma^{\text{flow}}$, from T_1 to T_2 (with $T_1 > T_2$) and the transformation of dW to dQ (at fixed T and P) are irreversible while the transformation dQ to dW (at fixed T and P) is factually impossible. It is clear that *disequilibrium* makes things moving. For instance, thermal discontinuity, $T_1 > T_2$, is needed to push the heat flow through the $T_1 \rightarrow T_2$ interface, but certainly not for the opposite $T_2 \rightarrow T_1$ or not even for T_1 equal T_2 . This argumentation coincides with the irreversibility of the reverse heat flux.

There are variables such as temperature, T , and pressure, P , which are identified with the *intensive, controllable field forces*, I ; i.e., they are the same for any subsystems (Ω_1 and Ω_2) and for any choice of Ω . There are also the *extensive variables* (X) like volume, V , and entropy, S , which have the character of *measurable deformations*. Namely for any choice of Ω_1 and Ω_2 it holds that $X_1 + X_2 = X$ (e.g., $V_1 + V_2 = V$, assuming no contribution from the interface Ω_{12} between Ω 's). Extension to further choice of the other matching variables to encompass the system description in a more complete (as well as com-

plex) way can be made, including, e.g., the magnetic field, \mathbf{H} , or mole number, n , paired with the magnetization, M , and chemical potential, μ . The above mentioned variables are considered to be the *state variables* and thus are defined by means of the internal energy, U , by its derivatives, e.g., $(\partial U/\partial S)_V = T = T(S, V)$ or $(\partial U/\partial V)_S = P = P(S, V)$. It yields the so-called *equations of the state*. In simple terms, for an ever present, multi-directional (*disordered*) motion (always associated with heat flow), U always associates with the product of T and S , while for an unidirectional (*ordered*) motion, U is moreover represented by other products, such as P and V , or \mathbf{H} and M , or n and μ . In addition, some distinct forms of *thermodynamic potentials*, Φ , (as the state functions, again) are established, traditionally named after the famous thermodynamists, such as *Gibbs*, G , or *Helmholtz*, F . This yields, for example, the renowned relations for entropy, i.e., $S = S(T, P, \mu) = -(\partial F/\partial T)_{V, n} = -(\partial G/\partial T)_{P, n} = (\partial F/\partial T)_{I, X}$.

What we are able to handle theoretically and compare to experiments are the *response functions* that are listed in Table 6.I. Their behavior is independent of the immense multiplicity of the underlying components, that is, the variety of their different physical-chemical properties, which arises from experimental discovery, not as a theoretical axiom and factually confirms the conceptual power of thermodynamics.

In view of a non-stationary character of near-equilibrium thermal analysis we have to distinguish three gradual stages of our thermodynamic description related to the intensive parameters [25,36] and here particularly related to temperature:

<i>(Classical)</i> <i>Equilibrium</i>	<i>Near-</i> <i>equilibrium</i>	<i>Non-</i> <i>equilibrium</i>
$I (dI \rightarrow 0)$	$I (\Delta I, dI/dt = \text{const})$	$I (dI/dt, d^2I/dt^2 \approx \text{const})$
$T (dT \rightarrow 0)$	$T (\Delta T, dT/dt = \text{const})$	$T (dT/dt, d^2T/dt^2 \approx \text{const})$

Classical thermodynamics of a closed system is thus the counterpart of dynamics of a specifically isolated system. The closed system defines and describes the energy-conserving approach to equilibrium, which is factually a ‘thermal death’. The counterpart in dynamics is the reality of external fields which give and take away energy or momentum to the system without being modified. Still further, we can consider thermodynamics of the open system with two thermal baths providing the possibility of thermal cycles. We may go on assuming several baths getting closer and closer to the description of a real multiplicity situation in nature.

Therefore, in classical thermodynamics (understood in the yet substandard notation of *thermostatistics*) we generally accept for processes the non-equality $dS \geq dQ/T$ accompanied by a statement to the effect that, although dS is a total differential, being completely determined by the states of system, dQ is not. This has the very important consequence that in an isolated system, $dQ = 0$, and entropy has to increase. In isolated systems, however, processes move towards equilibrium and the equilibrium state corresponds to maximum entropy. In true non-equilibrium thermodynamics, the local entropy follows the formalism of extended thermodynamics where gradients are included and small corrections to the local entropy appear due to flows, making $dS/dt \geq dQ/dt (1/T)$. The

Table 6.I: Temperature coefficients derived from the relationship between the generalized forces, I , and deformations, X .

Measurable Extensive, X ,	Controlled Intensive, I ,	dX/dI	dX/dT	dI/dT
Entropy, S ,	Temperature, T ,		Heat capacity $C_p = T(dS/dT)$	
Volume, V	Pressure, P ,	Compressibility $\phi = dV/dP/V$	T-expansion $\alpha_v = dV/dT/V$	P-coefficient $\beta_v = \alpha_v/\phi$
Magnetization, M ,	Mag. field, \mathbf{H} ,	Magnetic Susceptibility $\chi = dM/d\mathbf{H}$	Magnetocaloric coefficient $\alpha_M = dM/dT$	Thermal mag. susceptibility $d\mathbf{H}/dT = \alpha_M/\chi$
El.polarization, \mathbf{P} ,	Elec. field, \mathbf{E} ,	Dielectric Susceptibility $\chi_p = d\mathbf{P}/d\mathbf{E}$	Pyroelectric coefficient $p_p = d\mathbf{P}/dT$	Thermal dielec. susceptibility $d\mathbf{E}/dT = p_p/\chi_p$
Mech.deformation, ϵ ,	Mech.strain, σ ,	Elasticity Module $K_\epsilon = d\epsilon/d\sigma$	Therm.coef.of deformation $\alpha_\epsilon = d\epsilon/dT$	Therm.coef.of strain $K_{\sigma T} = d\sigma/dT$

local increase of entropy in continuous systems can be then defined using the local production of entropy density, $\sigma(r,t)$, cf. Chapter 15. For the total entropy change, dS , consisting of internal changes and contributions due to interaction with the surroundings (source, i) we can define the local production of entropy as $\sigma(r,t) \equiv d_i S/dt \geq 0$. Irreversible processes [29-34] obey the *Prigogine* evolution theorem on the minimum of the entropy production and $S = S^{\text{dis}} + \sum \text{source}$, where $\sum \text{source} > 0$.

We can produce disequilibrium operating from the outside at the expense of some external work, $\Delta W^{\text{ext}} > 0$ (using the Gibbs terminology) and once the system is taken away from its equilibrium we can consider ΔW^{ext} as $\Delta \Phi^{\text{max}}$, now understood as the maximum obtainable work. We can relate the ratio of ΔW^{ext} to $\Delta \sum \text{source} \{ = \Delta Q(1 - T_o/T) - (P - P_o) \Delta V \}$ as the inequality greater than zero. For $\Delta W^{\text{ext}} \rightarrow 0$ we can assume the ratio limit to catch the equality $\Delta \sum \text{source} / \Delta W^{\text{ext}} = 1/T = \partial S / \partial U$. It is important as it says that the arrow of thermodynamics goes in the direction of the increased entropy (or dissipated energy) that was embedded in the disequilibrium situation. This is another representation of the second law of thermodynamics as it leads us in a natural way to think in terms of vitality of disequilibrium. If there is no disequilibrium we must spend energy to create it. Nevertheless, if disequilibrium is already given, we may think of extracting energy from it. As a result, the ratio $\Delta \sum \text{source} / \Delta W^{\text{ext}}$ can be understood in terms of heat flow in view of the efficiency of *Carnot's* ideal conversion ($\eta = 1 - T_2/T_1$) to become $\Delta \sum \text{flow} / \Delta W^{\text{ideal}} = 1/T_2$. It comes up with a new content: before we talked of energy that was dissipated but here we point out the energy, which is actually extracted. Thermodynamics is thus a strange science because it teaches us at the same time both: *how both The Nature and our active artifact system behave.*

b) Effect of the rate of heating

For the standard thermal analysis examinations, the *heat exchange* Q' ($= dQ/dt$) between the sample and its surroundings, must be familiarized as a fundamental characteristic, which specifies the experimental conditions of all thermal measurements [24,36]. As such, it must be reflected by the fundamental quantities when defining our extended system, i.e., the principal quantities must be expressed as functions of time, $T=T(t)$, $P=P(t)$ or generally $I=I(t)$. Therefore a sufficient description of the sample environment in dynamic thermal analysis requires specification, not mere values of T or P and other I , but also particular inclusion of the time derivative of temperature, T' ($= dT/dt$), respecting thus the kind of dynamic environment (usually according to the kind of heating employed). Please, note that the apostrophe ($'$) signifies derivatives and the *italic* letters (I, T, Φ) functions as used further on.

Hence, the state of material can be characterized in terms of material (*constitutional*) functions [36] of the following type:

$$V = V(T, T', P), S = S(T, T', P),$$

or generally, $\Phi = \Phi(T, T', P)$. 6.1

Let us write the basic energy equation in forms of fluxes, $U' = Q' - PV'$ or as a general inequality relation, $0 \geq U' + TS' - PV'$, where primes represent the time derivatives. Substituting the general thermodynamic potential, Φ , the above inequality, eventually complemented with another pair of ($I \leftrightarrow X'$), is changed to, $0 \geq \Phi' + ST' - VP'$ (eventually added by $X \leftrightarrow I'$). Now we can substitute the partial derivatives from material relations, equation 6.1, into the inequality of the state function, $\Phi(T, T', P)$, or

$$0 \geq [\partial \Phi / \partial T + S] T' + [\partial \Phi / \partial P - V] P' + [\partial \Phi / \partial T'] T'' \quad 6.2$$

According to the permissibility rule, the above relation must hold for any allowed process and for all values T and P , and their derivatives, which can thus be chosen arbitrarily and independently. For $T=0$ and $P=0$, it is reduced to its last term, i.e., $0 \geq [\partial \Phi / \partial T'] T$, which can be solved for all T only if $[\partial \Phi / \partial T'] = 0$. Consequently, the state function $\Phi(T, T', P)$ cannot depend on T' and its form reduces to mere $\Phi(T, P)$. In the same way we can eliminate the second and any other term by accounting the pairs $T - P$, or generally $T - I$.

However, the analysis of the entropy term of the first term of eq.6.2 is more difficult [33,36] because it can be split into two parts, i.e., equilibrium related entropy, $S_{\text{eq}} = S(T, T'=0, P)$, and the complementary term, $S_i = S - S_{\text{eq}}$, or:

$$0 \geq [\partial \Phi / \partial T + S_{\text{eq}}] T' + [S - S_{\text{eq}}] T'' \quad 6.3$$

For the fixed values of T and P it takes the of an analytical relationship, $0 \geq aT' + b(T'')T'$, for the variable T' , with $b(T'')$ approaching zero if $T' \rightarrow 0$. Such an inequality can be satisfied for arbitrary T only if $a=0$ and if $b(T'')T' \geq 0$, i.e., if $\partial \Phi / \partial T = S_{\text{eq}}$ and $[S - S_{\text{eq}}] T' \leq 0$. The resultant relation represents the dissipation inequality. Provided the term $S = S(T, T', P)$ is negligible or, at least, sufficiently small. This is a portrayal of a *quasistatic process* for which the standard relationships of (equilibrium) thermodynamics are valid to an agreeable degree (not forgetting that *italic* V, S and Φ stand for the denomination of functions).

c) Thermal properties and measurable quantities

Changes in the thermal state of our system are, as a rule, accompanied by changes in nearly all macroscopic properties of the system and, vice versa, a change in a macroscopic property results in a change in thermal properties [25]. This fact underlines the fundamental importance of the logical structure of the mathematical description, which mutually connects all variables regardless if they are specified or not. In addition to the previously accounted basic pair of parameters, T - S and P - V , that are adjusted and controlled externally, we can enlarge the definition of experimental conditions by including other experimentally measurable quantities, X . We can choose them to represent the (instantaneous) state of individual samples under specific study, cf. Table 6.I. Such

variables must be readily available and it is obvious that they depend on the size and structure of material (so that they must have extensive character). For practical purposes we often use the function called *enthalpy*, $H = H(S, P)$, and we can write it as a function of controllable intensive parameters only, at least the basic pair T and P , so that $H = H(S, P) = H(S(T, P), P)$. Applying *Maxwell* transformations², e.g., $(\partial V/\partial S)_P = (\partial T/\partial P)_S$, we get

$$dH = (\partial H/\partial S)_P [(\partial S/\partial T)_P dT + (\partial S/\partial P)_T dP] = T [(\partial S/\partial T)_P dT + (\partial V/\partial T)_P dP] + V dP, \quad 6.4$$

which can be rearranged using coefficients shown in Table 6.I. In practical notions we introduce the coefficients of thermal capacity, C_p , and thermal expansion, α_v :

$$dH = C_p dT + V(1 - \alpha_v T) dP. \quad 6.5$$

If the system undergoes a certain change under the action of an external force field, F , then the work done, dW , by the system is given by the product of the generalized force and the component of the generalized deformation parallel to the direction of the acting force. It is obvious that the work resulting from the interactions of our system with its environment will be decisive for the thermodynamic description. Let us replace volume by magnetization, M , and pressure by magnetic field, H . Then $dU = TdS + HdM = dQ + HdM$, which is the most useful relationship describing the dependence between the thermal and magnetic changes in the material under study (cf. magnetocaloric effect, chapter 20). The corresponding Gibbs energy $G = G(T, H)$ is given by $dG = -SdT - MdH$ and the previous equation 6.5 acquires an additional term associated with magnetocaloric coefficient, α_M , i.e.,:

$$dH = C_p dT + V(1 - \alpha_v T) dP + (M + \alpha_M T) dH \quad 6.6$$

Similar approach can be applied to the systems, which exhibits electric field, E , paired with electric polarization, P , adding thus the term $(P + p_p T) dE$ for the pyroelectric coefficient of dielectric polarization, p_p . Mechanical deformation, ϵ , paired with mechanical strain-tension, σ , contributes the coefficient for mechano-elastic properties, α_ϵ , as $(\epsilon + \alpha_\epsilon T) d\sigma$. Chemical potential, μ , paired with mole number, n , adds the term $(n + K_{nT} T) d\mu$ for the coefficient of chemical activity, K_{nT} .

By using all pairs of variables involved, we can continue to obtain the generalized function, Φ , already termed as the general thermodynamic potential, which is suitable for description of any open system, even if all external force fields are concerned. Although a thermophysical experiment does not often involve all these variables, this function is advantageous to localize all possible interrelations derived above as well as to provide an illustrative description for generalized experimental conditions of a broadly controlled thermal experiment, e.g.,

$$d\Phi = -S dT + V dP + \sum_i \mu_i dn_i - M dH + P dE + \epsilon d\sigma + \text{any other } (X \leftrightarrow dI) \quad 6.7$$

d) Chemical reactions

The course of a chemical reaction, which takes place in a homogeneous (continuous) system can be described by a pair of new quantities: extensive chemical variable, ξ , denoted as the *thermodynamic extent of reaction* (and corresponding to the amount of reactant), and intensive chemical variable, A , called the *affinity* and having a significance similar to the chemical potential (i.e., $\xi A \Leftrightarrow n \mu$). The significance of ξ follows from the definition equation $d\xi = dn_i/v_i$, expressing an infinitesimal change in the amount, n_i , due to the chemical reaction, if n_i is the *stoichiometric coefficient* of the i -th component. If the temperature and pressure are constant, the expression for $n_i (= v_i \xi)$ yields the equation for the Gibbs energy in the form of a summation over all components, i , $\Delta G_r = \sum_i \mu_i v_i = (dG/d\xi)_{T,P}$. This quantity becomes zero at equilibrium and is negative for all spontaneous processes.

The difference between the chemical potentials of the i -th component in the given system, μ_i , and in a chosen initial state, μ_i^o , is proportional to the logarithm of the *activity*, a_i , of the i -th component, i.e., to a sort of the actual ratio of thermodynamic pressures. It thus follows that $\mu_i - \mu_i^o = RT \ln a_i$ and on further substitution the *reaction isotherm* is obtained:

$$\Delta G_r = \sum_i v_i \mu_i^o + RT \ln \prod_i a_i^{v_i} = \Delta G_r^o + RT \ln \prod_i a_i^{v_i} \quad 6.8$$

where \prod denotes the product and a_i is given by the ratio of so-called *thermodynamic fugacities* (ideally approximated as p_i/p_o). The value of the *standard change in the Gibbs energy*, ΔG_r^o , then describes a finite change in G connected with the conversion of initial substances into the products according to the given stoichiometry (when $\xi = 1$). It permits the calculation of the *equilibrium constant*, $K_a = \prod_i a_i^{v_i}$ and the associated equilibrium composition if $\Delta G_r^o = -RT \ln K_a$.

Chemical reaction is accompanied by a change of enthalpy and, on a change in the extent of reaction, ξ , in the system; the values of both G and H of the system change too. If the relationship, $G = H - TS$, is applied in the form of $H = G - T(\partial G/\partial T)_{P,\xi}$ and when assuming that the quantity $(\partial G/\partial \xi)_{P,T}$ is zero at equilibrium, then

$$(dH/d\xi)_{T,P} = -T \partial/\partial T (\partial G/\partial \xi)_{P,v(\text{eq})} = -T \partial/\partial T (\sum_i v_i \mu_i)_{P,\text{eq}} \quad 6.9$$

is obtained. The equilibrium value of $(dH/d\xi)_{T,P}$ is termed the *reaction enthalpy*, ΔH_r , which is positive for *endothermic* and negative for *exothermic* reaction. The *standard reaction enthalpy*, ΔH_r^o is the quantity provided by a process that proceeds quantitatively according to a stoichiometric equation from the initial standard state to the final standard state of the products.

It is convenient to tabulate the values of ΔH_r^o and ΔG_r^o for the reaction producing compounds from the elements in the most stable modification at the given reference temperature, $T^o (\cong 298 \text{ K})$, and standard pressure, $P^o (\cong 0.1 \text{ MPa})$. Tabulated values of G 's and H 's relate to one

mole of the compound formed and are zero for all elements at any temperature.

The overall change in the enthalpy is given by the difference in the enthalpies of the products and of the initial substances (so-called *Hess' Law*). The temperature dependence is given by the *Kirchhoff Law*, i.e., upon integrating the relationship of $(\partial\Delta H^\circ/\partial T) = \Delta C_p$ in the form

$$\Delta H_{T,r}^\circ = \Delta H_{\theta,r}^\circ + \int_{\theta}^T \Delta C_{p,r}^\circ dT \quad 6.10$$

where the $\Delta H_{\theta,r}^\circ$ value is determined from the tabulated enthalpy of formation, mostly for the temperature $\theta = 298$ K. For $\Delta G_{T,r}^\circ$ it holds analogously that

$$[\partial(\Delta G_{T,r}^\circ/T)/\partial T]_p = (\Delta H_{T,r}^\circ)/T^2 \quad 6.11$$

and the integration and substitution provides

$$\Delta G_{T,r}^\circ = \Delta H_{\theta,r}^\circ - T \int_{\theta}^T (1/T^2) [\int_{\theta}^T \Delta C_p] dT + T \Delta G_{\theta,r}^\circ \quad 6.12$$

where the integration constant, $\Delta G_{\theta,r}^\circ$, is again obtained by substituting known values of $\Delta G_{298,r}^\circ$. On substituting the analytical form for C_p ($\cong a_0 + a_1T + a_2/T^2$) the calculation attains practical importance. Similarly the equilibrium constant, K , can be evaluated and the effect of a change in T on K is determined by the sign of ΔH_r° – if positive the degree of conversion increases with increasing temperature (endothermic reactions) and vice versa.

e) *Estimation and simulation of thermodynamic data for inorganic compounds*

Until recently, the researchers were restricted for using only experimental methods for thermodynamic data determination, C_p and ΔH_{298}° , which is one of the most important thermochemical information. A parallel development of semi-, quasi- and strictly- empirical methods of thermodynamic calculations has been found essential in assisting us to obtain 'fast insight' to the thermodynamic outfit [35]. This was substantiated by difficulties inherent in receiving reliable data through the experiment as well as by their relative inaccuracy, expensiveness and, last but not least, lengthiness.

For the case of condensed substances we would like to review in brief the most important estimations [37–39] first concentrating our attention to the standard molar heat capacities, C_{pm}° of solid mixed oxides, recently reviewed by *Leitner et al* [37] where almost 400 valuable quantities are presented. They reconsidered the most widely used *Neumann-Kopp* rule [37,39] and compared it with the contribution methods based on both the atomic an ionic contributions and the structural and simple-oxides contributions. The selected values of heat capacities given in [J/K mol] for solid binary oxides at 298.15 K are given together with some anionic contributions to heat capacities as shown in the following Table 6.II. (as based on data published in ref. [37]).

The estimation of standard enthalpies of formation, ΔH_{298}° , is attempted to review in more details. The in-

herent data, however, are presented in such a way as to follow the original figures given in ref. [38] and, therefore, the previously operated (and now unc customary) units of [kcal/mol] are retained in order to uphold the inherent constants published in the original papers.

Mendeleev's half-sum rule

Numerical value of a physico-chemical property of a compound is equal to the arithmetical mean from the values of the neighboring compounds in the row of the atomic table. Compared compounds may have common anions (e.g., CdBr_2 and HgBr_2) or cations (e.g., CdCl_2 and CdI_2).

Electronegativities

For ionic and metallic compounds the following formulae can be used, $\Delta H_{298}^\circ = -23.066 Z (\epsilon_A - \epsilon_B)^2$, where ϵ_A and ϵ_B are the tabulated electronegativities. The number of valence bonds can be substituted for Z , which is approximately given by the equality $Z = \eta_c B_c = \eta_a B_a$ where η_c and η_a are the number of cations and B_a and B_c are the valence of cation or anion. When applied to metalloids, some ambiguity is involved because of the valence uncertainty so that the method should be based on the elements exhibiting stable valence or the valence should be tailored. For instance, for MgAg it is expedient to assume the average group value of 1.5 and for MgTl to assume the hypothetical Tl^{2+} with $\epsilon_{\text{Tl}(3)} \cong 1.9$, which exhibits rather good correlation between experimental (–12.0) and calculated (–11.53) values. For complex compounds another modification is applicable assuming the constancy of ratio $\Delta H_{298}^\circ / \{27(\epsilon_A - \epsilon_B)\} = K_e$, which makes possible to estimate the average value of K_e as well as the average values of mean ϵ_A and ϵ_B . For example, for the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ the value of K_e is 11.13, and Z is 14 (related to the number of oxygens, i.e., 2×7), the mean ϵ_A is 3.44 and ϵ_B is 1.34 (assuming the average of Y^{3+} , Ba^{2+} and Cu^{2+}). Calculated ΔH_{298}° equals to –687.7, which correlates well with the experimentally obtained value of –649.7 kcal/mol (cf. Chapter 19).

Quasi-additive method

For the *Born-Haber* thermochemical cycle it follows that $\Delta H_{298}^\circ = \eta_c J_c - \eta_a J_a - n i_c i_a$ where η_c and η_a are respective charges of cations and anions, and n is the number of atoms in the formal unit (molecule) of compounds [40]. The parameters J_c , J_a , i_c and i_a are tabulated in ref. [37,38].

Cell model

Enthalpy of the A_{1-x}B_x phase, which forms two metals A and B , can be calculated from the tabulated values of electronegativities, ϵ , atomic volumes, V , and electronic densities on the boundaries of the so-called '*Wigner-Seitz*' cell, ζ_{ws} . It brings into play the equation, $\Delta H_{298}^\circ = 2 f(x) \{ (1-x) V_A^{2/3} + x V_B^{2/3} \} \{ -P (\Delta\epsilon)^2 + Q (\Delta\zeta_{ws}^{1/3}) \} / \{ 1/(\zeta_{ws(A)}^{1/3}) + 1/(\zeta_{ws(B)}^{1/3}) \}$, where P and Q are the model constants and $f(x)$ is the complex function of atomic con-

Table 6.II: Selected values of heat capacities of solid binary oxides and some related anionic contributions (all given at 298.15 K, after [37,38]).

Oxide	Phase	$C_{pm}^{\circ}(298)/$ ($J \cdot K^{-1} \cdot mol^{-1}$)	Oxide	Phase	$C_{pm}^{\circ}(298)/$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Ag ₂ O	SOL	66.32	Mn ₂ O ₃	SOL	99.04
Al ₂ O ₃	SOL	79.01	MnO	SOL	44.76
(AlO ₂)	anion 1-	47.40	MnO ₂	SOL	54.42
(AlO ₃)	anion 3-	67.73	MoO ₂	SOL	55.99
B ₂ O ₃	SOL	62.98	MoO ₃	SOL	75.14
(BO ₂)	anion 1-	40.30	Mn ₃ O ₄	TETRA	140.53
(BO ₃)	anion 3-	52.00	(MnO ₄)	anion 1-	91.10
(B ₄ O ₇)	anion 2-	134.26	(MnO ₄)	anion 2-	86.80
BaO	SOL	47.06	(MnO ₄)	anion 3-	97.50
BeO	SOL-A	24.98	Na ₂ O	SOL-A	68.56
Bi ₂ O ₃	SOL-A	112.13	Nb ₂ O ₅	SOL	132.13
CaO	SOL	42.42	Nd ₂ O ₃	SOL-A	111.34
CdO	SOL	44.16	NiO	SOL-A	44.29
Ce ₂ O ₃	SOL	117.05	PbO	RED	45.74
CeO ₂	SOL	61.53	Pb ₃ O ₄	SOL	154.94
CoO	SOL	55.22	Pr ₂ O ₃	SOL	116.63
Co ₃ O ₄	SOL	123.42	Rh ₂ O ₃	SOL	89.12
Cr ₂ O ₃	SOL	114.26	Sc ₂ O ₃	SOL	93.94
CrO ₃	SOL	79.12	SiO ₂	QUARTZ(L)	44.42
Cr ₃ O ₄	SOL	135.64	(SiO ₃)	anion 2-	69.30
(CrO ₂)	anion 1-	52.40	(SiO ₄)	anion 4-	73.50
(CrO ₃)	anion 3-	84.90	(Si ₂ O ₅)	anion 2-	103.80
(CrO ₄)	anion 2-	86.40	Sm ₂ O ₃	SOL-A	115.82
(Cr ₄ O ₇)	anion 2-	166.50	SrO	SOL	45.15
Cs ₂ O	SOL	75.90	Ta ₂ O ₅	SOL	131.48
Cu ₂ O	SOL	62.47	TeO ₂	SOL	63.88
CuO	SOL	42.26	TeO ₃	SOL	71.47
Dy ₂ O ₃	SOL-A	116.26	TiO ₂	RUTILE	55.10
Er ₂ O ₃	SOL	108.49	(TiO ₃)	anion 2-	71.90
Eu ₂ O ₃	CUBIC	124.68	(TiO ₄)	anion 4-	85.90
Fe ₂ O ₃	SOL-A	104.77	(Ti ₂ O ₅)	anion 2-	120.80
Fe ₃ O ₄	SOL	151.78	Tl ₂ O ₃	SOL	105.46
FeO	SOL	48.04	Tm ₂ O ₃	SOL-A	116.72
(FeO ₂)	anion 1-	59.70	UO ₂	SOL	63.59
Ga ₂ O ₃	SOL	93.86	UO ₃	SOL	81.19
Gd ₂ O ₃	CUBIC	105.51	V ₂ O ₅	SOL	127.37
GeO ₂	HEXAGONAL	51.95	(VO ₃)	anion 1-	70.90
(GeO ₃)	anion 2-	68.20	(VO ₄)	anion 3-	87.74
HfO ₂	SOL-A	60.26	(V ₂ O ₇)	anion 4-	158.90
(HfO ₃)	anion 2-	78.47	WO ₃	SOL-A	72.80
HgO	SOL	43.89	(WO ₄)	anion 2-	89.70
Ho ₂ O ₃	SOL	114.96	(W ₂ O ₇)	anion 2-	161.30
K ₂ O	SOL	84.53	Y ₂ O ₃	SOL-A	102.51
La ₂ O ₃	SOL	108.78	Yb ₂ O ₃	SOL-A	115.36
Li ₂ O	SOL	54.25	ZnO	SOL	41.07
Lu ₂ O ₃	SOL	101.76	ZrO ₂	SOL-A	56.21
MgO	SOL	37.26	(ZrO ₃)	anion 2-	73.40

Table 6. III: Selected values of electronegativity, ϵ , boundary electronic densities, ζ_{ws} and atomic volumes, V for some elements (after [38]).

Element	ϵ	$\zeta_{ws}^{1/3}$	$V^{2/3}$	Element	ϵ	$\zeta_{ws}^{1/3}$	$V^{2/3}$
Ag	4.45	1.39	4.8	Al	4.20	1.39	4.6
Au	5.15	1.57	4.8	Ba	2.32	0.81	11.3
Be	4.2	1.6	2.9	Bi	4.15	1.16	7.2
Ca	2.55	0.91	8.8	Cd	4.05	1.24	5.5
Co	5.10	1.75	3.5	Cr	4.65	1.73	3.7
Cs	1.95	0.55	16.8	Cs	5.55	1.89	4.2
Cu	4.55	1.47	3.7	Fe	4.93	1.77	3.7
Ga	4.10	1.31	5.2	Ge	4.55	1.37	4.6
Hf	3.55	1.43	5.6	Hg	4.2	1.24	5.8
In	3.90	1.17	6.3	Ir	5.55	1.83	4.2
K	2.25	0.65	12.8	La	3.05	1.09	8.0
Li	2.85	0.98	5.5	Mg	3.45	1.17	5.8
Mn	4.45	1.61	3.8	Mo	4.65	1.77	4.4
Na	2.70	0.82	8.3	Nb	4.0	1.62	4.9
Ni	5.20	1.75	3.5	Pb	4.1	1.15	6.9
Pd	5.6	1.65	4.3	Pt	5.65	1.78	4.4
Rb	2.10	0.60	14.6	Re	5.5	1.9	4.3
Rh	5.4	1.76	4.1	Ru	5.55	1.97	4.1
Sb	4.4	1.25	6.8	Sc	3.25	1.27	5.1
Si	4.7	1.5	4.2	Sn	4.15	1.24	6.4
Sr	2.40	0.84	10.2	Ta	4.05	1.63	4.9
Tc	5.3	1.81	4.2	Th	3.3	1.28	7.3
Ti	3.65	1.47	4.8	Tl	3.9	1.12	6.6
U	4.05	1.56	5.6	V	4.25	1.64	4.1
W	4.8	1.81	4.5	Y	3.20	1.21	7.3
Zn	4.10	1.32	4.4	Zr	3.40	1.39	5.8

centrations (C_A and C_B) and surface concentrations (C_A^s and C_B^s) of atoms of A and B, respectively. The function $f(x)$ is further specified as $C_A^s \cdot C_B^s \{ 1 + 8 (C_A^s \cdot C_B^s)^2 \}$, where $C_A^s = (1-x) V_A^{2/3} / \{ (1-x) V_A^{2/3} + x V_B^{2/3} \}$ and $C_B^s = x V_B^{2/3} / \{ (1-x) V_A^{2/3} + x V_B^{2/3} \}$. The value Q/P is constant for every group or family of binary compounds and can be derived from the key experimental values of ΔH_{298}° . In the following Table 6.III, the main model parameters are listed to assist the direct estimation (after [38]).

Increment method

The effective charges of atoms in molecules and ions are used through the equation, $\Delta H_{298}^\circ = E_{c.l.} + \Delta H_c^\circ + \Delta H_a^\circ$, where the terms on the right hand side are the energy of crystal lattice and the enthalpies of the formation of cation and anion, respectively. It further depends on the *Madelung* constant, effective charges and distances between ions in the crystal lattice as shown in detail in ref. [41]. It has been modified by equation, $\Delta H_{298}^\circ = n_a a + n_c c + (2 n_c)^2 + n_a^2$, where n_a and n_c stand respectively for the number of anions and cations and a and c are constants [42]. Another modification [43] employs equation, $\Delta H_{298}^\circ = (n_A + n_B)(x_A - x_B)^2 + n_A Y_A + n_B Y_B + n_L (w_B/w_A)$, where n_L is the number of bonds, n_A and n_B are the corresponding number of anions and cations (with other parameters tabulated in the related references).

Average contribution

If the electronegativity of the central cation is about 1.9 then it is possible to use the data of simple oxides to calculate the complete value by applying the rule, which shows that the contribution made by oxides is equal to (-7) if m represents the number of oxygens in the compound. The standard enthalpy of complex oxide from elements is then given by $\Delta H_{298}^\circ = \sum_i (\Delta H_{298}^\circ)_i - 7 m$. It was generalized to nitrides as $\Delta H_{298}^\circ = \sum_i n_i (\Delta H_{298}^\circ)_i + H_A$, where H_A is the standard formation enthalpy based on simple components (in kcal/mol, again).

Comparison methods

Such evaluation is based on the comparison of values of the selected property in two analogous rows taken for similar compounds under the same conditions. For example, $\Delta H_{298}^\circ(\text{II}) = a \cdot \Delta H_{298}^\circ(\text{I}) + b$, where (I) and (II) represent the changes of formation enthalpy from elements of similar compounds of the two given rows, I and II. The constants, a and b , associate to a simple relation, $\Delta H_{298}^\circ = aP + b$, where P can stand for any thermodynamic property. It can be further generalized to $\Delta H_{298}^\circ/Z = a \log n + b$, where z stands for the valency of cation or anion in the compound, n is the atomic number in the system of cations and anions, and a and b are the coefficients, again, specific for the given group of compounds.

Empirical dependence of the standard enthalpy of formation by the so-called 'Linearization Approximation Rule'

For the double oxides in the system AO-BO, a linear correlation [44,45] between standard enthalpies of formation of the double compounds (produced along the AO – BO junction) has been observed. The value $\Delta H_{cc}^{\circ}(A_xB_yO_z)$ equals to $x_{AO} \Delta_f H^{\circ}(AO) + x_{BO} \Delta_f H^{\circ}(BO)$, where x_{AO} is the molar fraction of component oxides and $\Delta_f H^{\circ}$ is the standard enthalpy of formation of the component oxide from the elements. In most cases so far investigated [41], the value of $\Delta_f H^{\circ}(AO)$ is bigger than $\Delta_f H^{\circ}(BO)$ so that the graphical dependence exhibits a minimum and its both branches can be approximated by linear equations of the form, $\Delta H_{cc}^{\circ} = a + b \Delta_f H^{\circ}$. For practical calculation of the constants, a and b, the linear regression was used with constrains of the following type, $\Delta H_{cc}^{\circ} = 0$, if either $x_{AO} = 1$ or $x_{BO} = 1$. The average deviation (approved for 121 various compounds within 35 investigated systems, including CaO with SiO₂, TiO₂, Al₂O₃ or B₂O₃) stayed below 10 % when comparing the experimentally

a very important and crucial object, which is called the *interface*, and which is accompanied by its surface area, A. The area stands as a new extensive quantity, which is responsible for the separation phenomena, and which is indispensable for the definition of all *heterogeneous* systems, see Fig. 1b. The internal energy, $U = U(S, V, A, n)$, holds in analogy to the previous definitions and the corresponding intensive parameter is the surface Gibbs energy, γ , ($= \partial U / \partial A$), which has the meaning of a *tension*. According to the depth of study, such a new pair of variables, $A \leftrightarrow \gamma$, can further be supplemented by another pair, $\varpi \leftrightarrow \phi$, where ϖ is the curvature of the interface and ϕ is the surface curvature coefficient. The existence of both these new pairs of variables indicates the thermodynamic instability of phases (1) and (2) in the vicinity of their separating interface. It yields the natural *tendency to contract the interface area and decrease the surface curvature*.

Changes of interface characteristics enable a certain nominalization of the contact energy, which is in the centre of thermodynamic descriptions of any heterogeneous

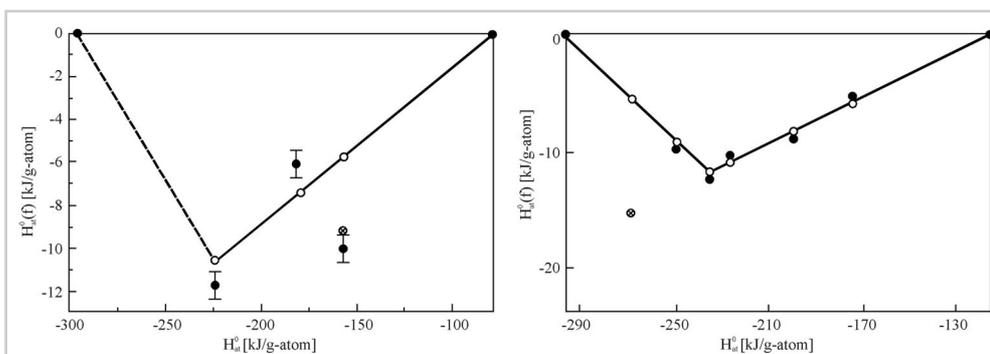


Fig. 6.3: Application of the linear approximation rule (abbreviated as LAR, see open circles) for the revision and correction of the published standards enthalpies of formation (solid circles) from simple oxides ($H_a^{\circ}(f)_j$) yet given in the outmoded units of kJ (g atom)⁻¹ (to pledge the original notation of authors [44]) for some double oxides in the systems:

(a) SrO-Bi₂O₃ (given in the atomic ratios Sr:Bi:O). 1 – 1:0:1; 2 – 6:2:9; 3 – 3;2;6; 3 – 2;2;5; 4 – 18;22;51; 6 – 6;14;27; 7 – 1;4;7 and 8 – 0;2;3. and

(b) SrO-CuO (given in the atomic ratios Sr:Cu:O) 1 – 1:0:1; 2 – 1:1:2; 3 – 2:1:3; 4 – 14;13;41; 5 – 0:1:1. For more details see Chapter 19.

located and theoretically estimated data. For example, for the Ca₁-X₂-O₄ compound with X = Si, it is respectively 18.9-16.4; for X = Ti, it is 13.4-14.8; for X = Al, it is 3.69-3.55, and for X = B, it is 17.6-16.0, all given in the units of kJ/(g-atom), see Fig. 6.3.

f) Heterogeneous systems, nucleation and the effect of surface energy

If the test system contains two or more phases, cf. Fig. 1b, then these phases separates a phase *boundary*, which has properties different from those of the bulk phases it separates. It is evident that the structure and composition of this separating layer must be not only at a variance with that of both phases but must also implement certain transitional characteristics in order to match the differences of both phases it divide. Therefore, the boundary is

systems putting on display the phase separating interfaces. A direct consequence is the famous *Laplace* formulae, $P^{(1)} - P^{(2)} = (1/r^{(1)} - 1/r^{(2)})\gamma$, which states that the equilibrium tension, P, between the phases (1) and (2), is affected by the curvature of the interfaces, i.e., by the difference in radii $r^{(1)}$ and $r^{(2)}$ that is, more or less, mechanically maintained at the equilibrium. It can be modified for a spherical particle of the phase (1) with the radius, $r^{(1)}$, located in the phase (2), so that $P^{(1)} - P^{(2)} = 2\gamma/r^{(1)}$. By introducing chemical potentials, μ , the relation converts to conventional, $\mu^{(1)} - \mu^{(2)} = 2\gamma V/r^{(1)}$, where V is the partial molar volume and γ is the interfacial energy. With a multi-component system, this equation can be written separately for each component, i (on introducing the subscripts, i), which may result in the formation of concentration gradients across the interface layers during the formation and growth of a new phase.

Another consequence is the well-established form of the *Kelvin* equation, $\log(p/p_0) = 2\gamma V^{(2)}/(RT r^{(1)})$, which explains a lower pressure of vapors of the liquid with a concave meniscus, $r^{(1)}$, in small pores. This effect is responsible for early condensation phenomena (or local melting of porous materials) or for overheating of a liquid during boiling (as a result of the necessary formation of bubbles with a greater internal pressure than the equi-

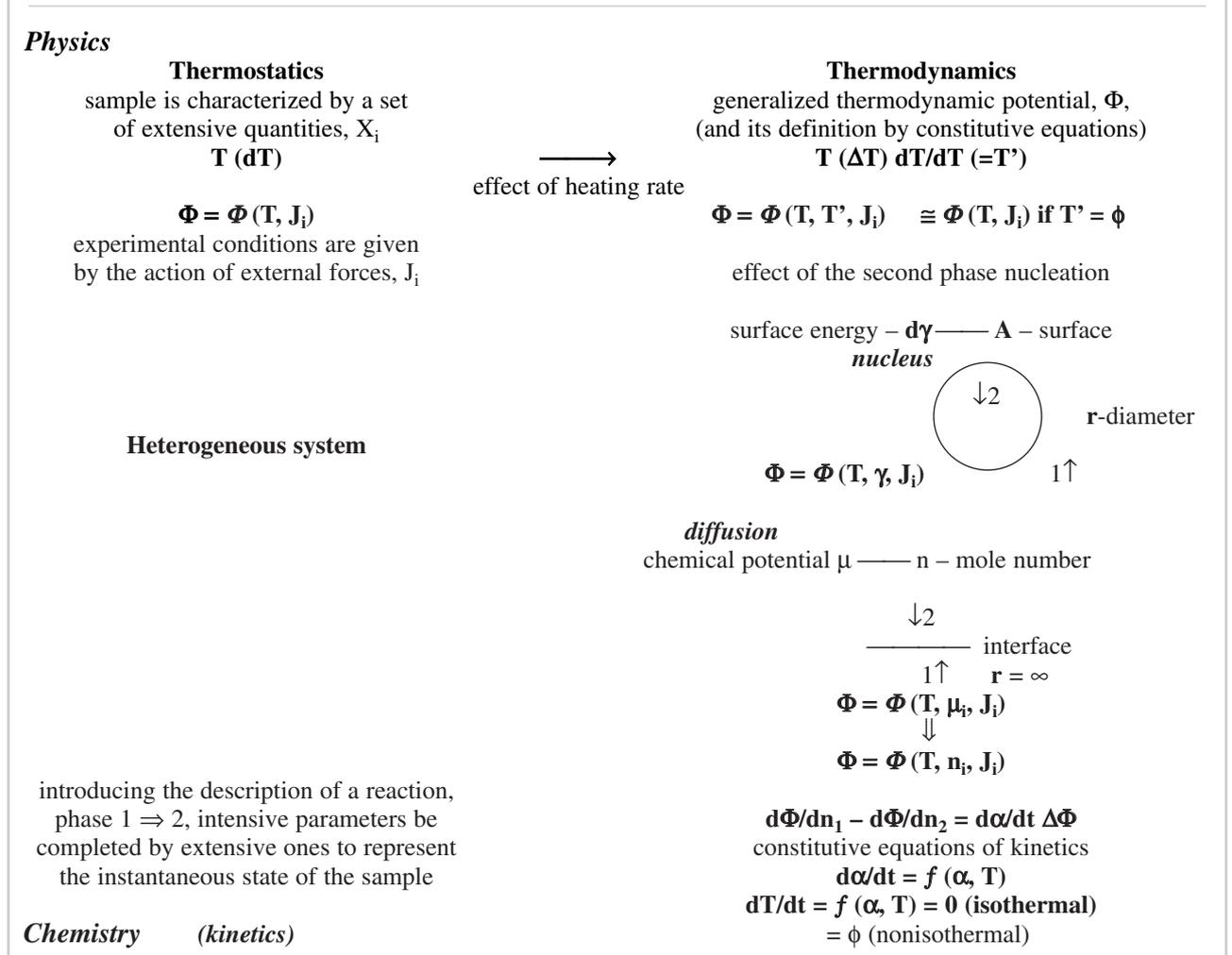
librium one above the liquid). An analogous equation holds for the growth of crystal faces during solidification, i.e., $\log(p/p^{(sp)}) = 2\gamma V^{(s)}/(RTh)$, where h is the longitudinal growth of the given crystalline face. When an apparent pressure ($p^{(ap)}$) inside the crystal is considered instead of the original partial pressure (p), it discriminates smaller pressure for larger crystals and results in the spontaneous growth of greater and disappearance of smaller crystals. With common anisotropic behavior of crystals, it is worth mentioning that the surface energy depends on the crystal orientation which, according to the *Wulff Law*, leads to the faster growth in directions characterized by greater, γ , according to the ratios, $\gamma_1/h_1 = \gamma_2/h_2 = \dots$, where h_1 is the perpendicular distance from the *Wulff* coordinate system center of the crystalline phase.

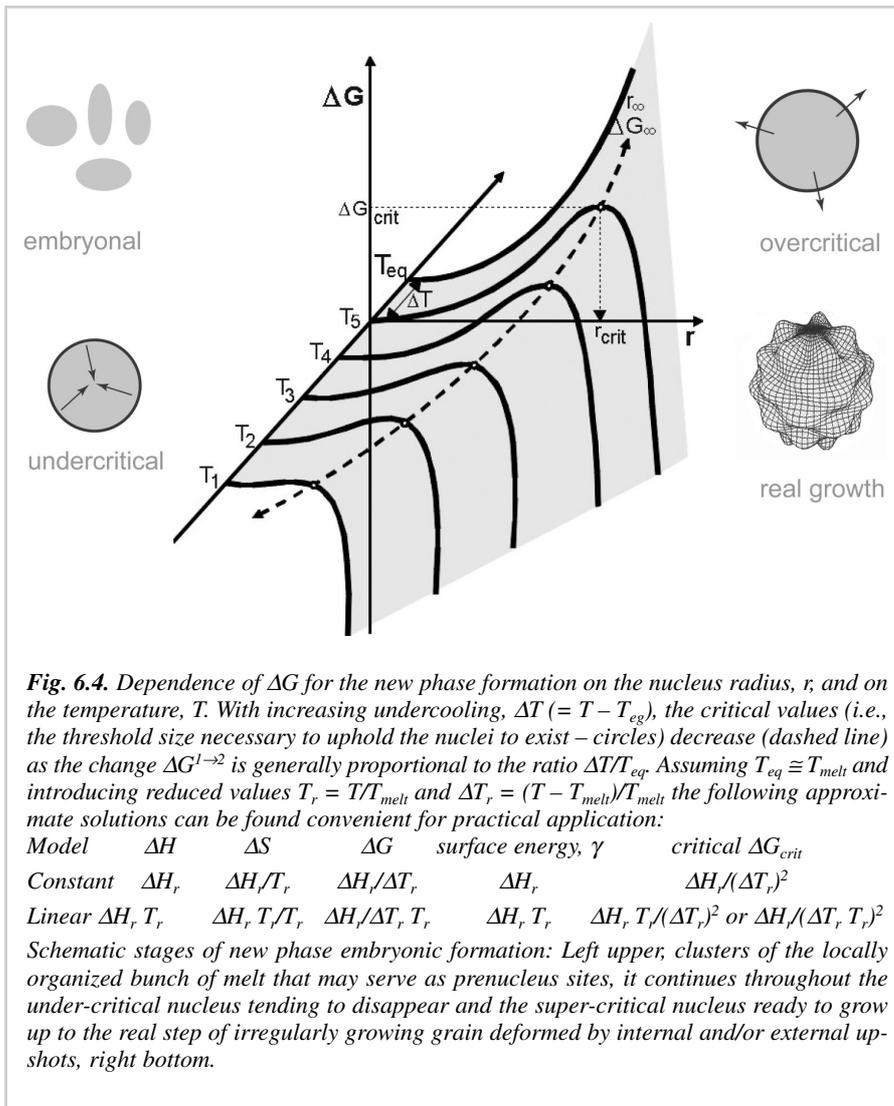
The surface energy can also decrease because of the segregation of various components into the interface layer, whether by concentration of admixtures relocated from the main phase, or by adsorption from the surroundings. In accordance with the formulation of the general potential, Φ , the following relation can be written for the interface in a multicomponent system at equilibrium:

$$\sum_i \mu_i dn_i - SdT + A d\gamma = \Phi = 0, \text{ or, } d\gamma = - \sum_i \Gamma_i d\mu_i + s^{(2)} dT, \quad 6.13$$

where $\Gamma_i = n_i^{(2)}/A$ and $s^{(2)} = S/A$ are important experimentally measurable coefficients often employed in adsorption measurements, i.e., $G_i = \partial\gamma/\partial\mu_i$, as the specific surface adsorption and, $s^{(2)} = \partial\gamma/\partial T$, as the specific molar entropy. A practical example is the *Gibbs* adsorption isotherm, $\Gamma_i = - C_2 d\gamma/(RTdC_2)$, which describes the concentration enrichment of the surface layer, where C_2 is the admixture concentration in the main bulk phase. This can also become important with polycrystalline solids, because the surface layer of individual microcrystalline grains can contain a rather different concentration of admixtures than that coexisting in the main parent phase, similarly to the gradients developed by temperature non-equilibration (see next Chapter 7). Owing to the variation of experimental conditions, the resulting precipitates may thus exhibit different physical properties due to the differently inbuilt gradients, which can manifest themselves, for example, in the measurements of variability of the total electric resistance of such polycrystalline samples.

Table 6.VI: Illustrative development of a thermodynamic description in connection with the effect of real heating, heterogeneity and the transfer to the adjacent field of kinetics.





It is clear that heterogeneous systems, which are more common in nature, exhibit supplementary intricacy of the resultant properties, as compared to homogeneous systems. In the contradiction with the often idealized (but less frequent) homogeneous systems, heterogeneous systems must include the action of inherent interfaces, which makes the description more convoluted, see Table 6.IV. A specific but generally challenged problem is the existence of boundaries, which are spherically separating each particle of the newly formed second phases within the matrix phase. Such an interlayer interface is factually performing the elementary role of a *disturbance* within the system continuity (i.e., true homogeneity defects). Within any homogeneous system, any interface must be first created, which process accompanies a particular course of the new phase formation called *nucleation*. The *surface energy* plays, again, a decisive role because it factually acts contrary to the spontaneous process of transition proceeding from the initial (homogeneous, mother) phase (1) into the newly produced, but regionally separated, phase (2). In the bulk, this is accompanied by a definite decrease of Gibbs energy, $\Delta G_v^{1 \rightarrow 2}$. Disregarding

the energy of mixing, the Gibbs energy of a spherical nuclei with volume, r^3 , is negative, but is compensated for the positive surface energy, γ , which is dependent on, r^2 , and which value predominates for all small nuclei at $r < r_{crit}$. The resultant dependence, see Fig. 6.4., thus exhibits maximum for a critical nuclei radius, r_{crit} , proportional to the simple ratio $\gamma/\Delta G_v^{1 \rightarrow 2}$, with the critical energy barrier, $\Delta G_{crit}^{1 \rightarrow 2}$, and amounting to the powered ratio 3:2 for the ration, $\gamma^3/(\Delta G_v^{1 \rightarrow 2})^2$. For the equilibrium temperature, T_{eq} , (where $\Delta G_v^{1 \rightarrow 2} \rightarrow 0$ and $\Delta G_{crit}^{1 \rightarrow 2} \rightarrow \infty$) follows that the nucleation of a new phase is thermodynamically impossible (even if athermal nucleation can occur owing to implicated fluctuations). Nucleation can thus happen only under distinct non-equilibrium conditions, i.e., during a definite change of undercooling (or reverse supersaturation). Further on, at given thermodynamic conditions³, all nuclei with $r < r_{crit}$ are unstable and have a definite tendency to disintegrate and disappear. Only nuclei with $r > r_{crit}$ are predisposed to grow spontaneously, see Fig. 6.4. A more detailed portrayal is given in the following Chapter 8 in connection with the description of kinetic phase diagrams, cf. Fig. 7.7.

The surface free energy can be approximated by a function of the latent heat and molar volume, v , so that $\gamma = 0.065 \Delta H_f v^{2/3}$, where ΔH_f is the enthalpy of melting. The free energy difference between the liquid and solid phase is proportional to the temperature of melting, T_m , i.e., $\Delta G = \Delta H_f (T_m - T)/T_m$, assuming that the associated ΔC_p approaches zero. Afterwards we can obtain an approximate equation for the excess Gibbs energy of the critical nucleus formation, $\Delta G_{crit}^{1 \rightarrow 2} = (16/3)\pi(0.065)^3 \Delta H_f T_m^2/(T_m - T)^2$. The critical temperature, T_o , where the nucleation frequency of the metastable phase (*) is equal to that of the stable phase, is linked to the ratios of enthalpies, $R = \Delta H_f^*/\Delta H_f$, which must be less than unity. If this is satisfied, then $T_o = [T_{mr} - \sqrt{(RT_{mr})}]/[T_r - \sqrt{(RT_{mr})}]$ where T_{mr} and T_r are the reduced temperatures, T_m^*/T_m , and, T/T_m , respectively. A schematic illustration of the stable and metastable Gibbs energies versus temperature is shown in Fig. 6.6a. We may generally expect that the nucleation frequency of the metastable phase is larger than that for the stable phase if (and only if) the undercooling (or equally, but less likely, supersaturation) is large enough.

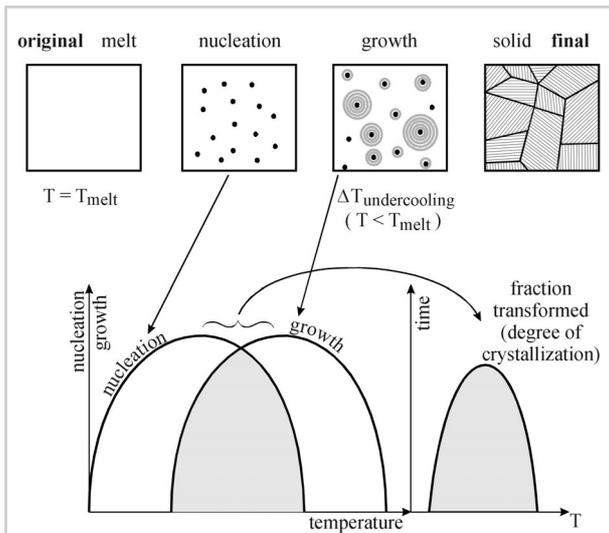


Fig. 6.5: Inclusive diagram of the mutually overlapping patterns of nucleation and growth showing that if nucleation curve goes first before the growth curve (left), the overall crystallization process (right) is straightforward (upper) towards the formation of solid crystalline product upon cooling. However, if their sequence is opposite the crystallization becomes difficult because for the early process of growth there are no nuclei available to seed the growth, which favors greater undercooling. The cooperative position of the curves, and the degree of their mutual overlapping, then determines the feasibility of overall processing, e.g., the ease of crystallization and/or opposite process of vitrification, for the latter the nucleation curve should be delayed behind the growth curve as much as possible.

molecularly rough interface of the metastable phase experienced in the case of doped Fe-C alloy, cf. Fig. 6.6.

g) Effect of perturbations and features of a rational approach

Every system bears certain degree of fluctuations around its equilibrium state, i.e., is subjected to *perturbations*, δ . In the case of entropy⁴, its instantaneous state, S , differs from the equilibrium state, S_{eq} . It can be conveniently depicted by using an extrapolation series $\delta S + \delta^2 S/2 + \dots$ etc.. The resulting difference can then be specified on the basis of internal energy, U , such as $(S - S_{eq}) = \Delta S = (1/T_1 - 1/T_2) dU + [\partial/\partial U_1(1/T_1) + \partial/\partial U_2(1/T_2)](\partial U)^2/2$. The first term on the right-hand side vanishes at the instant of equilibrium (i.e., $\delta S \rightarrow 0$ because $T_1 = T_2$) and the second term must be negative because $C_V(\delta T)^2/2T^2 = \delta^2 S > 0$. Such an average state is stable against thermal fluctuations because of the positive value of heat capacity, C_V . In a non-equilibrium stationary state, however, (see Chapter 15) the thermodynamic forces (F) and the corresponding flows of energy, \mathbf{j}_E , and matter, \mathbf{j}_M , do not disappear but, on contrary, gain important status. Hence the first entropy variation is non-zero, $\delta S \neq 0$, and the second variation, $\delta^2 S$, of a given elementary volume (locally in equilibrium) has a definite value because the complex integrand has negative sign. Thus the term $d/dt(\delta^2 S) = \sum_M dF_M dj_M > 0$ (simplified at the near-equilibrium conditions as $\sum_M F_M j_M > 0$) must be positive if the non-equilibrium stationary state is stable. As shown above, the classical description has been undoubtedly useful; nevertheless, it has some drawbacks both from the

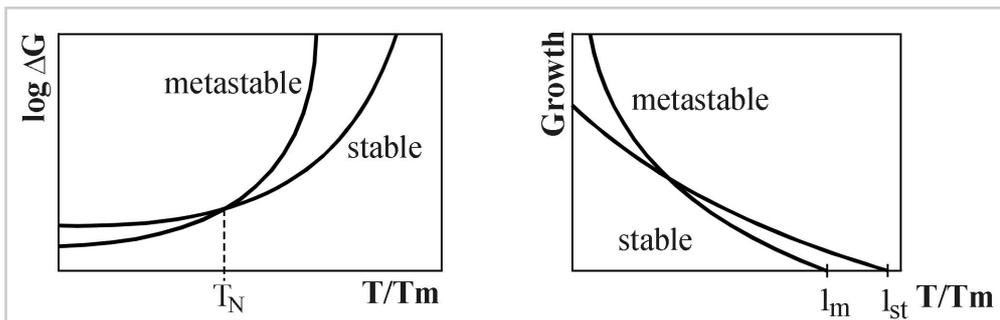


Fig. 6.6: Relationship of logarithmic representation of the change of Gibbs energies (a) for the inherent stable and metastable phases characterized by the values $T_{mr} = 0.8$ and $T_r = 0.5$. Hypothetical relation of growth rate versus reduced temperature assuming the validity of power law with the exponents $m=1.4$ and 2.0 characterizing the stable and metastable phases, respectively.

There are just few systematic studies of the total growth rate. In general, the growth rate, G , can be expressed as a function of undercooling, ΔT_{under} , employing, again, a common form of the power law, $G = G_0 (\Delta T_{under})^m$, with the numerical constants of G_0 and m falling between 1 and 2 without having any particular physical meaning. However, when m of the metastable phase is larger than that of the stable phase, the growth rate of the metastable phase is larger. This effect is sometime associated with the morphology of the interface, such as the faceted solid-liquid interface of the stable phase or the

fundamental and practical points of view. It is based on the macro- and/or local-equilibrium hypothesis, which may be too restrictive for a wider class of phenomena where other variables, not found in equilibrium, may influence the thermodynamic equations in the situations taking place when we get out of equilibrium. The concept is consistent with the limiting case of linear and

instantaneous relations between fluxes and forces, which, however, becomes unsatisfactory under extreme conditions of high frequencies and fast non-linear changes (explosions). Then the need arises to introduce the second derivatives ($''$), such as $\Phi = \Phi(T, T', T'', P, \dots)$ and the general thermodynamic potential, F , is can be no longer assumed via a simple linear relation but takes up a new, non-stationary form

$$\Phi = -ST' + VP' + (\partial\Phi/\partial T)T''_{T', P} + (\partial F/\partial T')T''_{T', P} \tag{6.14}$$

where all state variables become dependent on the temperature derivatives.

It is worth mentioning that an advanced formalism was introduced by *Coleman and Truesdel* [46,47] in the form known as *rational thermodynamics*, which is particularly focused on providing objectives for derivation of more general constitutive equations. We can consider the absolute temperature and entropy as the primitive concepts without stressing their precise physical interpretation. We can assume that materials have a memory, i.e., the behavior of a system at a given instant of time is determined not only by the instantaneous values of characteristic parameters at the present time, but also by their past time (history). The local-equilibrium hypothesis is not always satisfactory⁵ as to specify unambiguously the behavior of the system because the stationary or pseudo-stationary constitutive equations are too stringent. The general expressions describing the balance of mass, momentum and energy are retained, but are extended by a specific rate of energy supply leading to the disparity known as the *Clausius-Duhem* fundamental inequality, $-\rho (G' + ST') - \nabla T (q/T) \geq 0$, where ρ and q are production of entropy and of heat, ∇ stays for gradients and prime for time derivatives.

There are some points of its rationality worth mentioning:

- i) The principle of equipresence, which asserts that all variables, which are present in one constitutive equation; must be a priori present in all other constitutive equations.
- ii) The principle of memory, or heredity, which dictates that current effects depend not only on the present causes but also on the past grounds. The set of variables, x , is no longer formed by the variables of the present time but by their whole history, i.e., $x = f(t - t_0)$.
- iii) The principle of local action, which establishes that the behavior of a given material point (subsystem, cf. Fig. 6.1.) should only be influenced by its immediate neighborhood, i.e., higher-order space derivatives should be omitted.
- iv) The principle of material frame-indifference, which is necessary to assure the notion of objectivity, i.e., two reference observers moving with respect to each other must possess the same results (usually satisfied by the Euclidean transformation).

¹ One of the most widespread concepts in various fields (physics, society and/or mind) is the notion of 'state'. In fact, there is no physical definition of what is the state alone and we can only assume that a system under question must possess its own identity connected to a set of its properties, qualities, internal and external interactions, laws, etc. This 'identity' can then be called the state and the description of state is then made upon this set of chosen properties, which must be generally interchangeable when another same system is defined. Thermodynamics, as one of the most frequent users of the notion of state, is presented as a method of the description and study of various systems, which uses somehow a heterogeneous mixture of abstract variables occasionally defined on different scales (cf. Chapter 1). It is because thermodynamic concept involves an energetic communication between macro- and micro- levels. For example the heat is an energy transfer to the hidden disordered molecular modes, which makes troublesome to co-define the packaging value of internal energy when including processes at macroscopic level such as the mechanical work (of coordinated molecular motion as whole). Another important portrayal attitude is the understanding of thermodynamic variables as averaged quantities and the assignment of such variables to individual parts that may be composed together to form other parts. Such problems, inspected from both view of thermal physics and philosophy, is splendidly dealt with by *Holeček* in his book "Averaging in Continuum Thermomechanics" (ZČU Plzeň, in print).

² From the cross-derivatives $d^2\Phi/dTdV$ and $d^2\Phi/dVdT$, which must be equal to each other, we can derive one of a group of useful thermodynamic interaction, called *Maxwell* relations. It follows that $(\partial V/\partial S)_P \equiv V \leftarrow_S P = S \rightarrow_P T \equiv (\partial T/\partial P)_S$, which is not at all obvious.

³ Some other, often hidden but ingrained minima in the textbook plot of Gibbs energy versus nucleus size can come into view when the studied system is subjected to a more detailed analysis. Besides the demonstrative minimum, which is conventionally linked with the formation of nuclei critical radius, r_{crit} (thus expressing certain optimal ratio between the relatively expanding bulk over its squeezing surface, $r_{crit} \sim r^3/r^2$) some other minima can be confined with certain, well-organised clusters often existing within the melt below r_{crit} . Such ordered agglomerations, forming in chalcogenide melts surprisingly stable embryo, can persist quite larger overheating acting thus as prenucleus sites. Another clusters' arrangement remaining within the liquid state can, however, possesses an incommensurable structure with respect to the stable nucleus structure thus blocking the entire process of spontaneous nucleation. This is the above-discussed case of liquid water near freezing where pentagonal embryos formed in cold water prevent the formation of stable hexagonal nuclei of ice necessary for timely solidification thus responsible for large undercooling. Similarly, the additional local minima of Gibbs energy can be created during the actual course of nuclei growth above r_{crit} . The formation of irregular shapes due to the preferential growth of certain crystal faces, surface incorporation of defects or otherwise fluctuating interface, cf. Fig. 15.1, often cause this anomaly on the ideally postulated thermodynamic course. In most cases of justifiable growth the development of crystal shape is likewise controlled by the interface response to the complex interactions of heat, mass or pressure fluxes along and across the reaction boundary creating thus localities of preferential growth, which often yields fractal morphological patterns regularly experienced in dendrite structures, see Chapter 15.

⁴ The classical thermodynamics adhered for long on the definition of equilibrium value of the entropy. Let us mention, for example, the pioneering work by *Planck* in his discarded 1879 dissertation, citing "in every natural process the sum of the entropies of all

bodies involved in the process increases". Even this, seemingly understandable characterization, was then rejected and even *Kirchhoff* stated that "the concept of entropy, the magnitude of which was measurable only by means of a reversible process and hence was definable only for such, could not legitimately be applied to irreversible processes". Later, in the linear non-equilibrium thermodynamics, it was overcome by the local definition of multiple neighboring equilibrium states, which, however, was criticized for it is approximately calculus. In the subsequent rational thermodynamics, it is different because it, factually, is not thermodynamics in its proper meaning but rather thermo-mechanics of continuum. For that reason it first formulates constitutive equations, including material's memory, transport equations, etc., and then combine them with the balance equations of mass, impact and energy to produce differential equations of the state (such as the 2nd *Fick* or *Navier-Stokes* Laws). Consequently rational thermodynamic enabled to construct the concept of absolute temperature and entropy under non-equilibrium conditions bringing into play only the primitive quantities of work, heat and empirical temperature confirming thus the existence of these parameters, T and S, even far away from the traditional equilibrium. The internal structure, however, became complex, having many entropies and exhibiting non-validity of *Gibbs* Laws, which may disable precise entropy determination, which, however, does not degrade its 'entropical' value, at all. [I. Samohýl "Thermodynamics of Irreversible Processes in Fluid Mixtures", Teubner, Leipzig 1987, or P. Šilhavý "Mechanics and Thermodynamics of Continuous Media" Springer, Berlin 1997)

- ⁵ A special attention requires second-order transitions, which are associated with symmetry breaking of the system's Lagrangian, and thus with the appearance of fractured congruity coordinates. Phase transitions are, therefore, central and fundamental aspects of the thermodynamic formalism, directly coupled to the existence of so called basic thermodynamic coordinates (K.G. Wilson, Phys. rev. B4 (1971) 3174 & 3184). Unlike other branches of physics, thermodynamics in its standard postulation approach (e.g., H. Cullen "Thermodynamics" Wiley, New York 1960) does not provide numerical predictions. For example, it does not evaluate the specific heat or compressibility of a system, instead, it predicts that apparently unrelated quantities are equal, such as $\{(1/T)(dQ/dP)_T\} = - (dV/dT)_P$, or that two coupled linear irreversible processes satisfy the *Onsager* theorem ($L_{12} = L_{21}$). Recent development in many-body theory and field theory in the interpretation of phase transitions and in the general theory of symmetry can provide another attitude applicable to a new conceptual basis of thermodynamics. In the middle of seventies *Cullen* suggested that 'thermodynamics is the study of those properties of macroscopic matter that follows from the symmetry properties of physical laws, mediated through the statistics of large systems' (H. Cullen, Foundation of Physics 4 (1974) 423). In this respect we can quote that every continuous transformation under which the Lagrangian of a given system remains invariant implies the existence of a conserved function (of the microcoordinates and their derivatives). That is that all continuous symmetry of a system implies a conservation theorem and vice versa (L. Tisza "Generalized Thermodynamics" MIT Press, Cambridge 1966). The most primitive class of symmetries is the class of *continuous space-time transformations*, which assigns the invariance of physical laws under time translation implying thus the conservation of energy, spatial translation the conservation of momentum and rotational symmetry the conservation of angular momentum. Another important area of symmetry considerations centers on the concept of so called '*broken symmetries*' (P.W. Anderson, Science 177 (1972) 393). Though each and every system may exhibit the full symmetry of its Lagrangian, due to the characteristics of relative infinity of large systems such entirety may 'condense' into states of lower symmetries exhibiting thus the indispensable commitment of '*macroscopic order parameters*'. The breaking of the symmetry establishes also a multiplicity of ground states (or a sort of 'vacuums') related by the transformations of the broken symmetry group. The prototypes of associated variables are the electric and/or dipole moments, or even volume because a gas has no intrinsic value of the volume so that the translation symmetry of space must be broken by the solid system, which contains the gas. It is a convenient happenstance that a conventional 'simple systems', often exemplified in elementary thermodynamics, have one prototype of each of the three characteristic classes of thermodynamic coordinates: (i) coordinates conserved by the continuous space-time symmetries (internal energy, U), (j) coordinates conserved by other symmetry principles (mole number, N) and (ij) non-conserved (broken) symmetry coordinates (volume, V). Worth mentioning is also the associated mechanisms of irreversibility, or better the entropy increase, which are *dynamical*, and which lie outside the scope of standard thermodynamics. Notwithstanding, the entropy-maximum property of equilibrium states is hardly understandable unless linked with these dynamical considerations. The equal *a priori* probability of states is already in the form of a symmetry principle because entropy depends symmetrically on all permissible states. The particular function ($S \cong \log W$) is determined completely then by symmetry over the set of states and by the requirement of extensivity. Consequently it can be shown that a full thermodynamic (heat) theory can be formulated with the heat, Q, being totally absent. Nonetheless, familiar central formulas, such as $dS = dQ/T$, remains lawful although dQ does not acquire to have the significance of energy.



CHAPTER SEVEN

7. Equilibrium and kinetic phase diagrams, nucleation and growth, glasses

a) Equilibria and generalized Clapeyron equations

In the chemistry of solids, data on the chemical composition, i.e., the concentration expressed in mole fraction, $N_i = n_i/n$, are most often used. If some components are part of the surroundings (a partially open system), the component (i) can be divided into conservative and volatile. In most real cases, the studied system consists of several (at least two) phases (j), denoted by exponents s_1, s_2, \dots (solid phase) or l_1, l_2, \dots (liquid phase), etc.. Generalized function, Φ , termed the general thermodynamic potential, can be of practical use when the effect of external force fields is assumed. Although a thermophysical experiment involving all these variables is not encountered in practice, this function is advantageous for finding necessary interrelationships, as already shown by the relation $\Phi = U - TS + PV - \sum \mu_i n_i - I \Leftrightarrow X$.

If the existence of two components A and B with the mole fractions N_A and N_B (or also concentrations) is considered, then we have to restore to chemical potentials, μ , so that

$$\Phi^A(T, I, \mu_A, \mu_B) = \Phi^B(T, I, \mu_A, \mu_B). \quad 7.1$$

The number of phases can be at most four, which however, leaves no degree of freedom to the system behavior (i.e., coexistence at the isolated points only). Through analytical expression needed to separate μ 's, we obtain

$$(dT/\mu_A)_I = (N_A^{s_1} N_B^{s_2} - N_A^{s_2} N_B^{s_1}) / (S^{s_2} N_B^{s_1} - S^{s_1} N_B^{s_2}). \quad 7.2$$

Analogous expression holds for the case of $(dI/\mu_A)_T$, i.e., when S is replaced by the corresponding extensive quantity, X. The denominator is always positive and because μ increases with the increasing concentration, the above ratio depends solely on the sign of the numerator, i.e., on the ratio of the mole fractions. If $N_A^{s_2} > N_A^{s_1}$, the concentration of component A is greater in phase s_2 than in phase s_1 and the temperature of this binary mixture increases with increasing concentration of A. The same reasoning can be applied for the behavior of component B.

Thermoanalytical methods often solve questions connected with the study of oxidation and dissociation processes. When working under certain oxidizing atmosphere, given either by p_{O_2} or chiefly defined by the powers, y, of ratios of CO/CO_2 or H_2/H_2O in the form of the standard equation $\Delta G_o = -RT \ln(p_{CO} p_{CO_2})^y$ we arrive for simple reactions at approximately linear functions. This attracted considerable attention in the fifties when applied to the description of equilibrium states for competing metal-oxide or oxide-oxide reactions, often known as *Jefferson monograms* [25,28,48]. It was of service even recently when refining reactions to take place in the copper sesquioxide systems necessary to care for the preparative methods in ceramic superconductors [49], see Fig. 7.3. (details are supplied in Chapter 19).

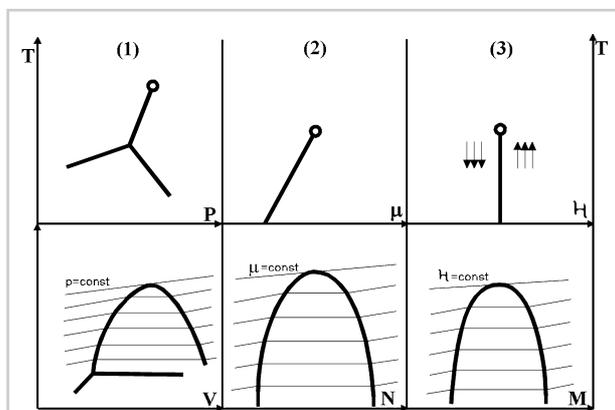


Fig. 7.1. Graphical illustration of the formation of critical points (circles) on the temperature dependencies for the three selected systems and chosen pairs of the associated intensive and extensive parameters. (1) liquid and gases (pressure), (2) solid solutions (chemical potential) and (3) magnetic systems (magnetic field).

In a single-component system ($i = 1$) containing one component, n, only, three different phases can coexist in equilibrium, i.e., $\Phi^g = \Phi^l = \Phi^s$. If only one intensive variable, I, is considered in addition to T, it can be solved for all three phases, g, l and s, at the isolated points (T, I) called *triple points* [45]. For two phases, the solution can be found in the form of functions $T = T(I)$, see Fig. 1., i.e., for liquids, T - P, hypothetical solutions, T - μ , dielectrics, T - E, mechanoelastics, T - σ , and, T - H, ferromagnetics (cf. Fig. 7.2.). Particular solutions yield the well-known Clapeyron equations, shown in the previous Table 6.I. [24].

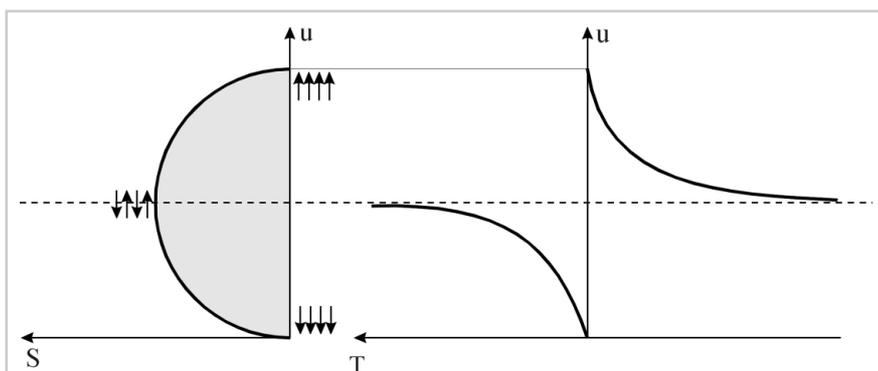


Fig. 7.2. Some curiosity symptom for a possible uncertainty in the temperature behavior of a hypothetical system, which passes from one ordered state (aligned arrows) to another one (opposite alignment) through a disordered state (alternated arrows). Here in the middle, the entropy turns out to reach maximum so that the temperature, $T = dS/dU$, apparently passes through the infinitesimal singularity [for more details see, e.g., M. Marvan "Negative Absolute Temperatures" Teubner, Leipzig 1967].

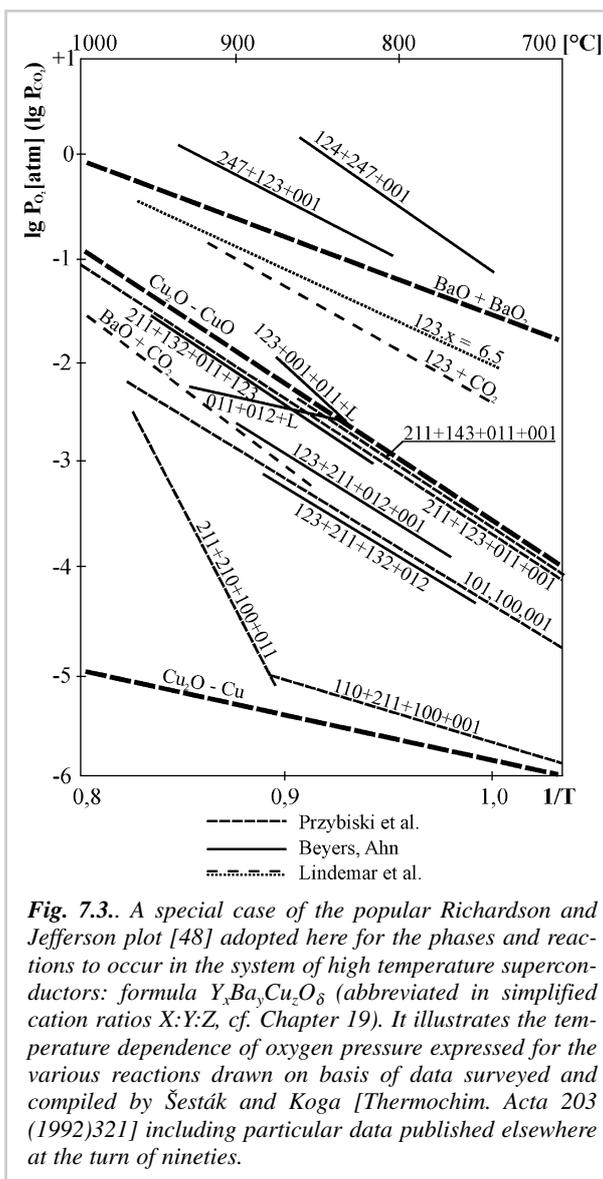


Fig. 7.3. A special case of the popular Richardson and Jefferson plot [48] adopted here for the phases and reactions to occur in the system of high temperature superconductors: formula $Y_xBa_yCu_zO_\delta$ (abbreviated in simplified cation ratios X:Y:Z, cf. Chapter 19). It illustrates the temperature dependence of oxygen pressure expressed for the various reactions drawn on basis of data surveyed and compiled by Šesták and Koga [Thermochim. Acta 203 (1992)321] including particular data published elsewhere at the turn of nineties.

Such a classical approach towards the calculation of chemical equilibrium based on the construction of a stability condition for each independent chemical reaction is rather awkward for the entire computation of equilibrium of complex systems containing a greater number of species. The earliest non-stoichiometric algorithm based on the minimization of Gibbs energy on the set of points satisfying mass balance was initially proposed for homogeneous systems in [50,51] and survived in [52]. The first approximations to equilibrium compositions [51–54] played important role, which often assumes the convex behavior of Gibbs energy function and the total system immiscibility.

Among many others let me mention the algorithm developed under the Czech domestic teamwork [55], which applied simple premises, such as the Gibbs energy is a linear function of the number of moles, the mixing effects are removed by neglecting higher logarithmic terms of the Gibbs energy function, etc. It provided bases for a practical elaboration of the computer controlled evaluation

and guided the establishment of databases, called “MSE-THERMO” [56], which has become a serious partner to many other valuable ready-to-use programs broadly available in the literature.

b) Ideal and real solid solutions, phase diagrams

In the classical thermodynamic description of a system in chemical equilibrium, the given phase areas in the phase diagrams represent the phase zones of minima of the Gibbs energy, whereas the phase coexistence is given by the Gibbs phase rule [57–60]. To construct a phase diagram it requires mapping all available phases and locating their phase boundaries which, unfortunately, is not possible by mere measurement of temperature and/or concentration changes of the Gibbs potential. Equilibrium phase diagram, however, cannot say anything about the reaction, which transforms one phase to another, nor about the composition or the structure of phases occurring under conditions different from those that make equilibrium possible. In general, under the conditions of phase equilibria, when the chemical potential, μ , of the liquid phase (for each component) is equal to that of the solid phase, stable coexistence of both phases occur, which is also the base of any theoretical description. Further step shown in the next paragraphs is the indispensable awareness that there is not enough driving force concealed in their equilibrium difference ($\Delta\mu = 0$) necessary to carry on any change.

Important basis to understand phase diagrams is the analysis of thermal behavior of the formation of solid solutions (ss). This process is accompanied by a change in the Gibbs energy, ΔG_{mix}^s , called the partial molar Gibbs energy of mixing (assuming that $\Delta G \equiv (1 - N_B)\mu_A + N_B\mu_B$, when $N_A + N_B = 1$). Its value is considered as the difference in the chemical potentials of component A in the solid solution and in the standard state of solid pure component, i.e., $\Delta\mu_A^s = \Delta G_{mix}^s - N_B(\partial\Delta G_{mix}^s/\partial N_B)$. In the graphical representation, expressing the dependence of the Gibbs energy on the composition, it represents the common tangent for the solid phases, s1 and s2.

The derived character of the phase diagrams is primarily determined by the behavior of the ΔG_{mix}^s dependence, which is customarily shown as a subject of chemical potentials between the standard (o) and actual states, as $\Delta G_{mix}^s = N_A(\mu_A - \mu_A^o) + N_B(\mu_B - \mu_B^o)$, but it can be conveniently expressed by the simplified set of equations

$$\Delta G_{mix}^s = \Delta H_{mix}^s - T \Delta S_{mix}^s = \Delta G_{mix}^{ex} + \Delta G_{mix}^{id} \quad 7.3a$$

$$\Delta G_{mix}^{ex} = \Delta H_{mix}^{ex} - T \Delta S_{mix}^{ex} = RT (N_A \ln \gamma_A + N_B \ln \gamma_B) \quad 7.3b$$

$$\Delta G_{mix}^{id} = -T \Delta S_{mix}^{id} = RT (N_A \ln N_A + N_B \ln N_B) \quad 7.3c$$

The term with superscript (id) expresses the ideal contribution from the molar Gibbs energy of mixing while that with (ex) represents its excess contribution. The extent of non-ideality of the system is thus conveyed showing the degree of interactions between the mixed components, A and B, which in the solution interact through forces other than those in the original state of pure components. It may result in certain absorption or libe-

ration of heat on the real process of mixing. It is most advantageous to introduce the *activity coefficient*, γ , and the activity of component, i , is then determined by the product of mole fraction and the activity coefficient, $a_i = N_i \gamma_i$. Whereas the mole fraction can be directly measured, certain assumptions must be made to determine the activity coefficients. For an ideal solution, $\gamma = 1$, and the mixture behaves ideally, i.e., there is no heat effect of mixing ($\Delta H_{\text{mix}} = 0$). The literature contains many empirical and semiempirical equations [61,62] for expressing the real activity coefficients in dependence on the solution composition, which consistent description is a key problem for separation processes. It, however, fall beyond the capacity of this book. Most common is the single-parameter description based on the so-called *regular behavior* [63] of solutions (when $\Delta H_{\text{mix}}^{\text{ex}} \gg T \Delta S_{\text{mix}}^{\text{ex}}$), i.e.,

$$\Delta G_{\text{mix}}^{\text{ex}} = \Omega N_A N_B = \Omega N_A (1 - N_A). \quad 7.4$$

where Ω is a temperature-independent (strictly regular) or temperature-dependent (modified) interaction parameter. It is evident that for a constant Ω value, the dependence is symmetrical at $N = 0.5$. However, in the study of solid solutions an asymmetrical dependencies are most frequently accoutered when introducing the simplest linear dependence in the form $\Omega = \Omega_0 (1 + \Omega_1 N)$, often called *quasiregular model* [25,62,63]. These descriptions are suitable for spherical-like molecular mixtures of metals.

For more geometrically complicated molecules of polymers and silicates we have to take up another model suitable for *athermal solutions*, where $T \Delta S_{\text{mix}}^{\text{ex}}$ is assumed to have a greater effect than $\Delta H_{\text{mix}}^{\text{ex}}$. Another specific case of the specific solid-state network are ionic (so called *Tyemkin*) solutions [64], which require the integration of energetically unequal sites allocation in the above mentioned concept of regular solutions. This is usually true for oxides where, for example, energetically disparate tetrahedral and octahedral sites are occupies on

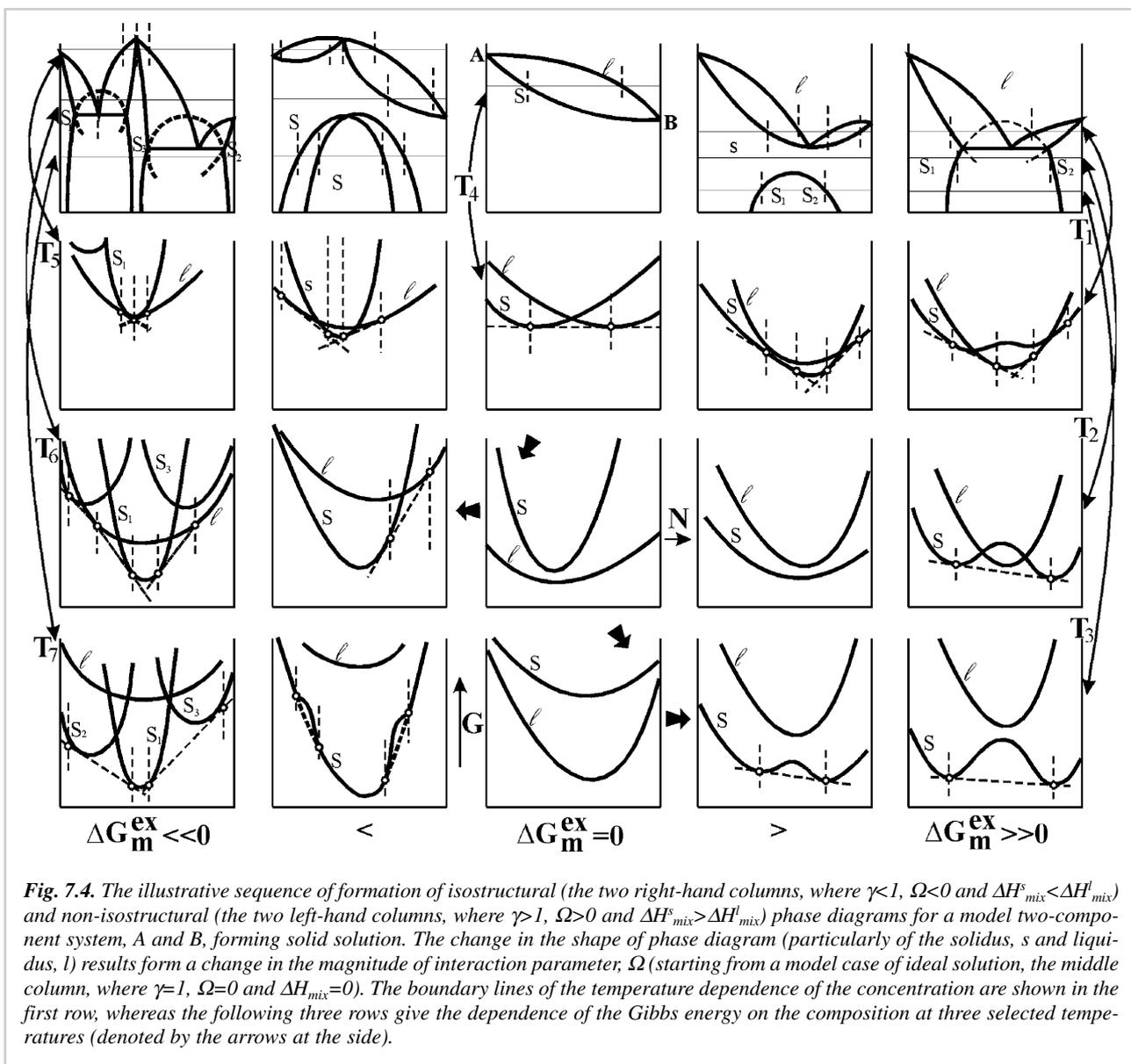


Fig. 7.4. The illustrative sequence of formation of isostructural (the two right-hand columns, where $\gamma < 1$, $\Omega < 0$ and $\Delta H_{\text{mix}}^s < \Delta H_{\text{mix}}^l$) and non-isostructural (the two left-hand columns, where $\gamma > 1$, $\Omega > 0$ and $\Delta H_{\text{mix}}^s > \Delta H_{\text{mix}}^l$) phase diagrams for a model two-component system, A and B, forming solid solution. The change in the shape of phase diagram (particularly of the solidus, s and liquidus, l) results from a change in the magnitude of interaction parameter, Ω (starting from a model case of ideal solution, the middle column, where $\gamma = 1$, $\Omega = 0$ and $\Delta H_{\text{mix}} = 0$). The boundary lines of the temperature dependence of the concentration are shown in the first row, whereas the following three rows give the dependence of the Gibbs energy on the composition at three selected temperatures (denoted by the arrows at the side).

different levels by species (ions), so that the ordinary terms must be read as a summation of individual species allocation. Another specification may bring on thermal or concentration dependent, Ω , such as *quasi-subregular* models, where $\Omega = \Omega_o (1 - \Omega_T)$ or $= \Omega'_o (1 - \Omega_N)$ [25].

The most important minute is the impact of ΔG 's on the shape of the phase diagram, see Fig. 7.4., which accounts the relative position of the Gibbs energy function curves for the liquid and solid phases, and the contribution from the individual ΔG 's terms and, finally, the shape of the functional dependence of the molar Gibbs energy of mixing on the composition and thus also on the resultant shape of the $\Delta G = \Delta G'(N)$ function. It follows that in a hypothetical diagram of the G vs N dependence the lowest curve represents the most stable phase at a given temperature. Therefore, for temperatures above the melting points of all the phases involved, the lowest curve corresponds to the liquid phase, whereas for temperatures well below the melting points, the lowest curve corresponds to the solid phase. If the two curves intersect, a two-phase region is involved and the most stable composition of two coexisting phases is given by abscissas of the points of contact of the curves with the common tangent. If $\Delta G_{\text{mix}}^{\text{ex}}$ is negative, than the resultant ΔG function is also negative, because the term $\Delta G_{\text{mix}}^{\text{id}} = -T\Delta S_{\text{mix}}$ is also negative. On the other hand, if $\Delta G_{\text{mix}}^{\text{ex}}$ is positive, the situation is more complicated because of the opposite effect from $T\Delta S_{\text{mix}}$ term, the value of which predominates, especially with increasing temperature. Therefore there are two basic cases: first the mixing of the components A and B is accompanied by a positive enthalpy change, ΔH_{mix} , which is actually contributing to an increase in ΔG_{mix} . It results from a stronger interactions in pure components A and B, i.e., A with A and B with B, in solution. The eutectic point is lower than the melting points of pure components. As the interactions in the solid state are much stronger than in the liquid, the solid solutions have a tendency to decrease the number of interactions by a separation process, i.e., by clustering phases richer in components A or in component B. On the contrary, if mixing of components accompanied by a negative enthalpy change, that further decreases the ΔG_{mix} value, the interactions between the unequal components predominates and the solution AB is more stable than the components A and B. Therefore the eutectic temperature is higher than the melting points of A and B. In solid solutions clustering again is advantageous but now through the enrichment of AB pairs at the expense of AA and BB.

Important guide in better orientation in possible phase boundary shifts is the effect of pressure, see Fig. 7.5., which well illustrates various shapes of most frequent binary phase diagrams.

For ternary diagrams the relationship is analogous but more complex when including three components A, B and C and the adequate sets of three equations [25, 57–60]. Most numerical procedures results in the determination of *conodes*, i.e., lines connecting the equilibrium compositions, the terminal points of these conodes and the regions thus formed are then analogous to the previously described binary diagrams. A detailed explana-

tion falls, however, beyond the simple illustrative intention of this chapter.

c) Nucleation phenomena and phase transitions

Any process of a phase transition (necessarily creating system's heterogeneity) does not take place simultaneously within the whole (homogeneous) system, but proceeds only at certain energetically favorable sites, called *nuclei* (cf. preceding section 6.6). We can envisage the newly created face (interface) to stick between the parent and second (different) phases as an '*imperfection*' of the system homogeneity, representing thus a definite kind of *defects*. Nucleation phenomena, i.e., formation (due to fluctuations) of a distinct domains (embryos, clusters) of a new (more stable) phase within the parent (original, matrix) phase, are thus important for all types of the first-order phase transitions. It includes reorientation processes, compositional perturbations as well as the defect clustering (such as cavity-cracks nucleation under stress or irradiation of reactor walls or the development of diseases when a malady embryo overgrow the self-healing, etc.). Therefore the *nucleation* can be seen as a general appearance responsible for the formation processes throughout the universe, where the clusters of several atoms, molecules or other species are formed as the consequence of the fluctuation of thermodynamic quantities. As a rule, the small clusters are unstable due to their high surface-to-volume ratio but some clusters may bring themselves to a critical size, a threshold beyond which they are ready to step into a spontaneous growth.

The metastable state of the undercooled liquid (corresponding to $T < T_{\text{eq}}$) can differ from the state of stable liquid ($T > T_{\text{eq}}$) by its composition and structure. There can be found complexes or clusters of the prearranged symmetry (often met in the systems of organic polymers, common in some inorganics like chalcogenides and already noted for liquid water near freezing, cf. the appendix of Chapter 3), which can either facilitate or aggravate the solidification course. The nucleation can occur in the volume (balk) of the homogeneous melt (called *homogeneous nucleation*) or it can be activated by impurities, such as defects, faults, stress sites, etc., acting as foreign surfaces (yielding *heterogeneous nucleation* particularly connected with these inhomogeneities). In principle, both processes are of the same character although heterogeneous nucleation starts at lower supersaturations in comparison with the homogeneous case because the formation work of the critical cluster is lowered.

Such a decrease of $\Delta G_v^{1 \rightarrow 2}$ is usually depicted by a correcting multiplication factor, proportional to $(2 + \cos \theta)(1 - \cos \theta)^2$, where θ is the contact (adhesion, wetting) angle of the nucleus visualized in the form of an apex on a flat foreign surface of given inhomogeneity. However, only the angles over 100° have a substantial effect on the process of nucleation and they can be expected when the interface energy between the impurity and the growing nucleus is small, chiefly occurring with isomorphous or otherwise similar crystallographic arrangements. Practically the critical cluster size is usually less than 10^{-8} m and that is why the nucleation on surfaces with radius of

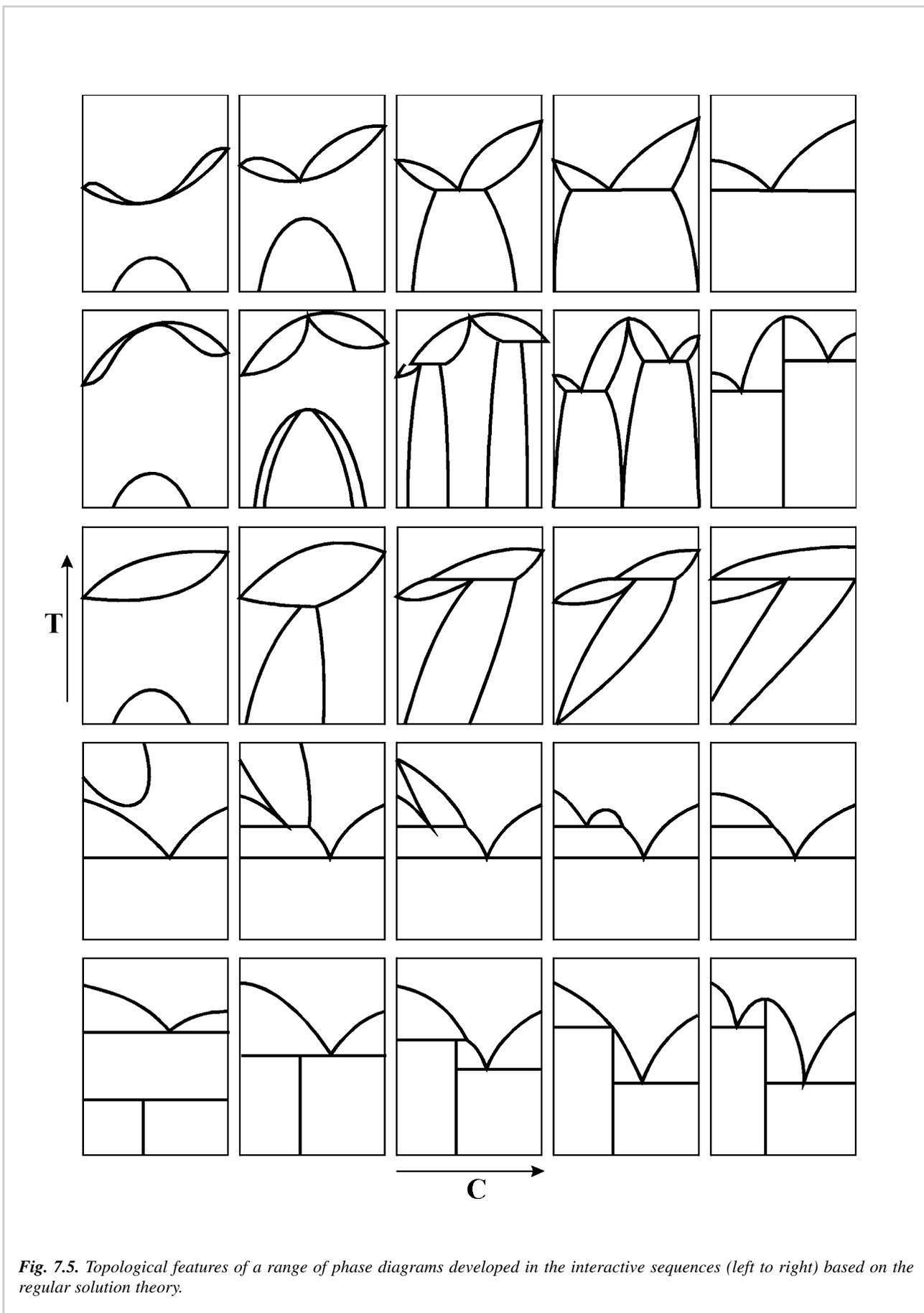


Fig. 7.5. Topological features of a range of phase diagrams developed in the interactive sequences (left to right) based on the regular solution theory.

curvature larger than 10^{-7} is considered as a true nucleation on the plane surface. In fact, we are usually unable to establish correctly such associated physical parameters, like number of pre-crystallization centers, value of interfacial energy or allied formation work of the critical cluster) and that is why the homogeneous nucleation theory has been put on more detailed grounds than heterogeneous. Moreover, homogeneous nucleation becomes usually more intensive (thus overwhelming heterogeneous nucleation) at any higher undercooling, which represents most actual cases under workable studies.

In general, the fluctuation formation of the embryonal crowd-together is connected with the work that is required for the cluster creation, $\Delta G_n(T)$, and it is given for the most common liquid-solid phase transition by:

$$\Delta G_n(T) = -n \Delta\mu(T) + A_n \gamma(T) + \Delta G_E \quad 7.5$$

where $\Delta\mu(T)$, n , A_n , $\gamma(T)$ and ΔG_E are, respectively, the temperature dependent supersaturation (i.e. the difference between the chemical potentials of the parent and crystal phases), number of molecules in cluster, the surface of a cluster (of n molecules, which equal to $\zeta n^{2/3}$, where ζ is a geometrical factor depending on the shape of the cluster), the temperature dependent interfacial energy per unit area and the Gibbs energy change due to external fields. If we know the nucleation work we can qualitatively determine the probability, P_n , for the formation of a given cluster according to $P_n \approx \exp\{\Delta G_n(T)/k_B T$, where k_B is the Boltzmann constant.

From the conditions of the extreme (*) in $\Delta G_n(T)$ $\{d\Delta G_n(T)/dn\} = 0$ it follows that $n^* = \{2\zeta \gamma/3 \Delta\mu(T)\}^3$ and $\Delta G^* = 4 \zeta^3 \gamma^3 / 27 \{\Delta\mu(T)\}^2$ showing that both the critical cluster size, n^* , and the activation energy of nucleation, ΔG^* , decreases with decreasing supersaturation sensitive to temperature. The term ΔG_E can be affected, for example, by the polarization energy, P , connected with the formation of a nucleus with antiparallel orientation of its polarization with respect to the external electric field, E . It adds the multiple of P , E and σ , which leads to a decrease in the overall energy of the system. A more general contribution of elastic tension, σ , tends to deform a nucleus that is usually formed under ever-present matrix strain (e.g., due to the different volumes of parent and crystal phases). It become evident for any miss-shaped spheroid, with flattened radius, r_f and thickness, 2δ , for which the deformation energy holds proportional to $r_f^2 \sigma (\delta\sigma/r_f)$. The term $(\delta\sigma/r_f)$ has the significance of the elastic Gibbs energy. In correlation, the classical studies by Nabarro [65] are worth mentioning as he calculated the tension in a unit volume for cases when the entire strain is connected within the mother phase. He assumed various shapes of nuclei in the form of function, (σ/r_f) , where for a spheroid it equals one, for needles it is much greater than one and, on contrary, for discs it becomes much lower than one. Although the mechanoelastic energy is minimal for thin disks, their surface is relatively larger compared with their volume and thus the optimal nucleation shape is attained for flattened spheroids. There can be found further contribution to ΔG^* , such as the internal

motion of the clusters which is sometimes included, but it becomes meaningful only for the nucleation of vapor. Equally important is the introduction of the concept of solid solutions, which brings complication associated with another parameter on which the nucleation becomes dependent. Namely it is the concentration, affecting simultaneous processes of redistribution of components, reconstruction of lattice and the redistribution of components between phases and particularly across the phase interface, which is balancing the composition inside each phase. The nucleation work become three-dimensional functions of n and C_s , exhibiting a saddle point, see Fig. 7.6., i.e., the point at which the curvature of the surface is negative in one direction and positive in the perpendicular direction, $(\partial\Delta G/\partial n = 0$ and $\partial\Delta G/\partial C_s = 0$ with associated ΔG^* and C_s^*) [66,67].

The main objective of nucleation (experimental) acquaintance is the determination of the nucleation rate, which is the number of supercritical stable embryos formed in the unit volume per unit of time. Another objective is the transient time, τ , (otherwise called induction, incubation or delay time or even time lag), which is associated with the system crystallization ability and which non-stationarity arises from the time-dependent distribution functions and flows. It is extremely short and hardly detectable at the phase transition from the vapor to liquid. For the liquid-solid phase transitions it may differ by many orders of magnitude, for metals as low as 10^{-10} but for glasses up to 10^2 – 10^4 . Any nucleation theory is suffering from difficulty to define appropriately the clusters and from the lack of knowledge of their basic thermodynamic properties, namely those of interfaces. Therefore necessary approximations are introduced as follows:

- restricted degrees of freedom of the system relevant for the clustering process,
- neglecting memory effects (so called ‘Markovian’ assumption),

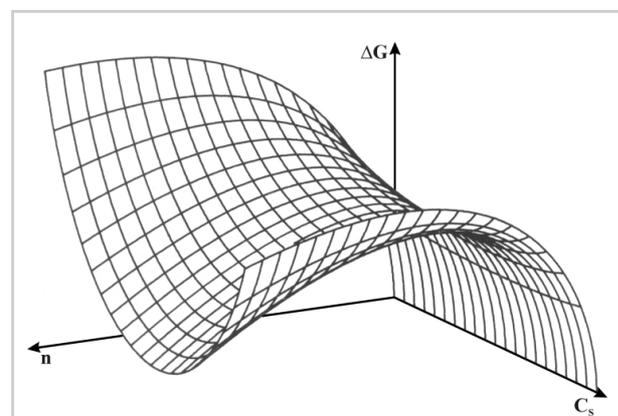


Fig. 7.6. Three-dimensional view of the nucleation work, ΔG , needed for the new phase formation of a spherical crystal grown from an undercooled binary, ideal solid-solution as a function of the concentration, C_s , of the solid phase and the number of atoms, n , in the growing nucleus. The melting points of the pure components were assumed to be 1300 and 1250 K. The initial concentration and temperature was chosen at 0.5 and 800 K, respectively..

- ignoring interactions between clusters,
- disregarding segregation or coalescence of larger clusters (rate equations linear with respect to the cluster concentration) and
- final summations being substituted by integration.

The detailed description of various theories is shown elsewhere [66-68].

d) Kinetic phase diagrams

The theory of phase equilibrium and the development of experimental methods used for such investigations gave the impetus to the extensive physico-chemical program aimed at the compilation, tabulation and interpretation of phase diagrams of substances in practically all the fields of natural science and technology. It started by the construction of basic metallurgical phase diagram of the system Fe-C, whose first version was completed in the middle of nineteenth Century. The theoretical foundation of thermodynamic analysis of the metastable equilibrium occurring

due to martensitic transformation was laid in late thirties of the twentieth Century when transformation of austenite to martensite was calculated for the given content of carbon (to include strain energy of the crystal network rearrangement, interfacial energy, undercooling, as well as under the use of activities instead concentration). It changed the classical view to 'true equilibrium' approach by admitting that the shape of experimentally determined phase diagrams can be affected by the 'degree of equilibration' moved during the experiment itself. The best example is the phase diagram of $\text{SiO}_2 - \text{Al}_2\text{O}_3$ continuously studied almost for hundred years. The interpretation of its high alumina regions varied from the experiment to experiment according to the duration of the system annealing (from hours to weeks) and was indicated as having both the incongruent and congruent melting point. Other disparity were reported in the composition range of mullite solid solution, etc.

It can be generalized that the resulting data can be prejudiced by the experimentalists' view on what is appro-

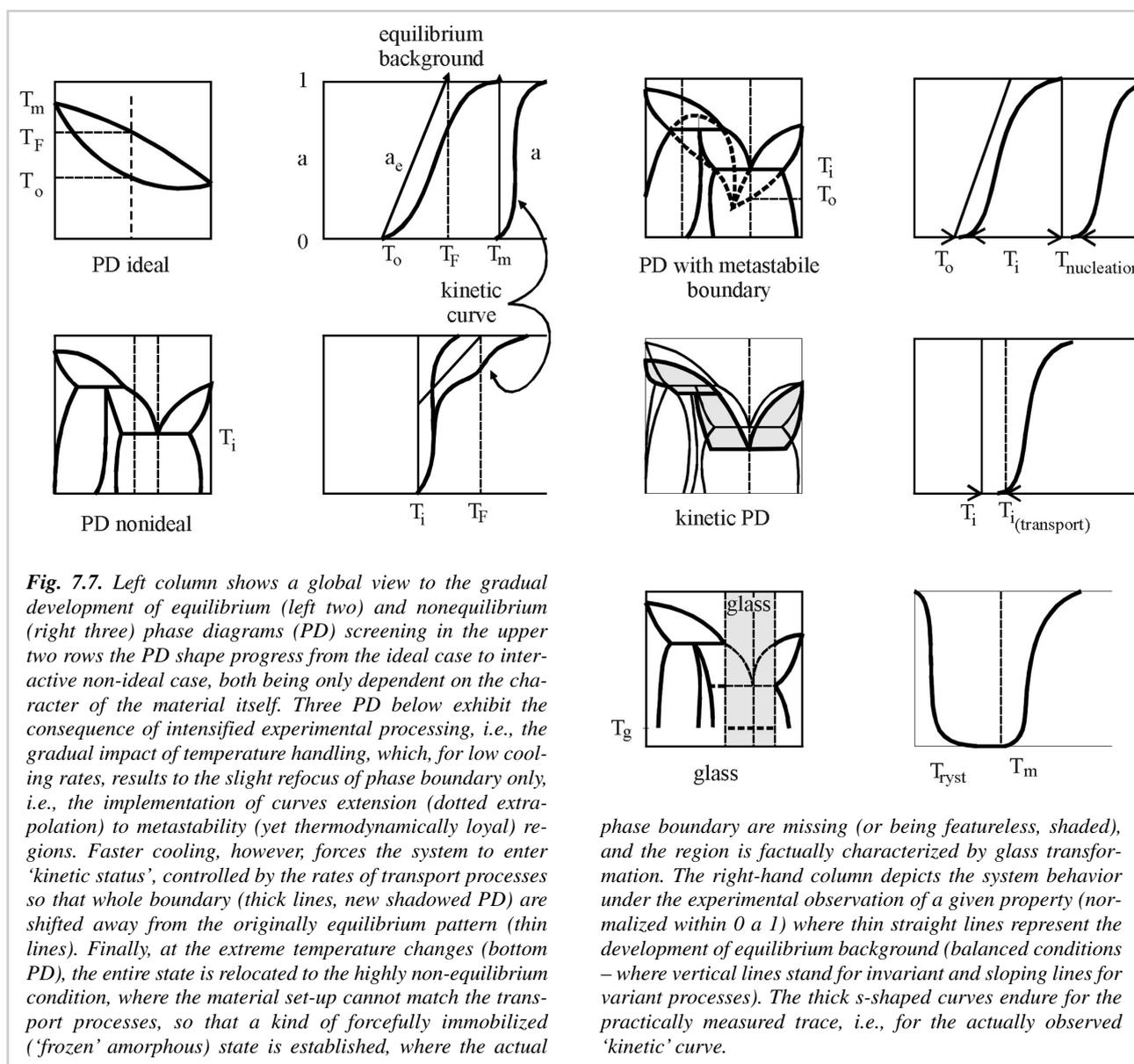


Fig. 7.7. Left column shows a global view to the gradual development of equilibrium (left two) and nonequilibrium (right three) phase diagrams (PD) screening in the upper two rows the PD shape progress from the ideal case to interactive non-ideal case, both being only dependent on the character of the material itself. Three PD below exhibit the consequence of intensified experimental processing, i.e., the gradual impact of temperature handling, which, for low cooling rates, results to the slight refocus of phase boundary only, i.e., the implementation of curves extension (dotted extrapolation) to metastability (yet thermodynamically loyal) regions. Faster cooling, however, forces the system to enter 'kinetic status', controlled by the rates of transport processes so that whole boundary (thick lines, new shadowed PD) are shifted away from the originally equilibrium pattern (thin lines). Finally, at the extreme temperature changes (bottom PD), the entire state is relocated to the highly non-equilibrium condition, where the material set-up cannot match the transport processes, so that a kind of forcefully immobilized ('frozen' amorphous) state is established, where the actual

phase boundary are missing (or being featureless, shaded), and the region is factually characterized by glass transformation. The right-hand column depicts the system behavior under the experimental observation of a given property (normalized within 0 a 1) where thin straight lines represent the development of equilibrium background (balanced conditions – where vertical lines stand for invariant and sloping lines for variant processes). The thick s-shaped curves endure for the practically measured trace, i.e., for the actually observed 'kinetic' curve.

appropriate experimental arrangement and adequate processing of the system resonance in order to attain equilibration in the reasonable time and, in fact, a really true equilibrium is ideally achievable only during almost limitless ‘geological-like’ processes. Actually available rates of experimental measurements fall, however, within the boundary area of so-called ‘thermodynamically imposed’ (somehow extreme) conditions. The introduction of real conditions to the existing thermodynamic description must refer to the state of local equilibrium, whether the rates of changes of state (macroscopic variables) are comparable with the rates of elementary (molecular) processes, which determine the state of the system at the microscopic level. It is often related to the ratio of $\Delta T/\Delta t \ll \langle T \rangle/\tau_T$ and/or $\Delta T/\Delta x \ll \langle T \rangle/\lambda$ where ΔT is the variation of temperature at macroscopic level during the time interval, Δt , (or over the distance, Δx), where τ_T is the matching period of the elementary thermal motion of molecules or their mean free path, λ , at the given average temperature, $\langle T \rangle$.

As already noticed, any new phase can be formed only under certain non-equilibrium conditions of a definite driving force, $\Delta\mu > 0$, and *at the minute of absolute equilibrium no new phase can ever originate*. The conditions of particular points at which the phase transformation takes place are further determined by the transport of heat (energy) and mass. For the probability of formation, P_{cs} , of the first critical nucleus, concentration C_{sol} , in a small time interval, $\Delta\tau$, holds within the framework of linear approximation, $P_{cs} = p(T, C_{sol}, C_{liq}) \Delta\tau$, where $p(T, C_{sol}, C_{liq})$ is the probability density equal to the product between the kinetic coefficient of homogeneous nucleation, K_n , and the unit time probabilities of a cluster realization ($p_1 \sim$ concentration difference), and its transition from liquid to solid phase ($p_2 \sim$ formation work). Thus we must study the temperature and concentration distribution in the system and their time changes in connection with the initial state and boundary conditions. So there arises a question how to correctly interpret the experimentally determined phase diagrams which do not fully comply with equilibrium conditions [66-68], the divergence being dependent on the proximity to the actually applied and thermodynamically required conditions. In determining the phase boundaries one can find experimental factors of different value and order, cf. Fig. 7.7.:

- arising from the nature of the material under study,
- associated with physico-chemical processes of the actual preparation of a representative sample from raw input materials,
- affected by the entire experimental set up and
- dependent on the kinetics of the phase transition (time hindrances of the new phase formation).

Hence it follows that the phase diagrams can generally fall into three, equally important, all-purpose groups regarding their practical validity and applicability. There are those having the effectiveness of unalterable relevance in order of :

- scientific age (suitable for tabulation of equilibrium data),
- livelihood (good enough for scientific generation in the sequence of years and useful to prepare materials durable long enough to be defined as stable) and

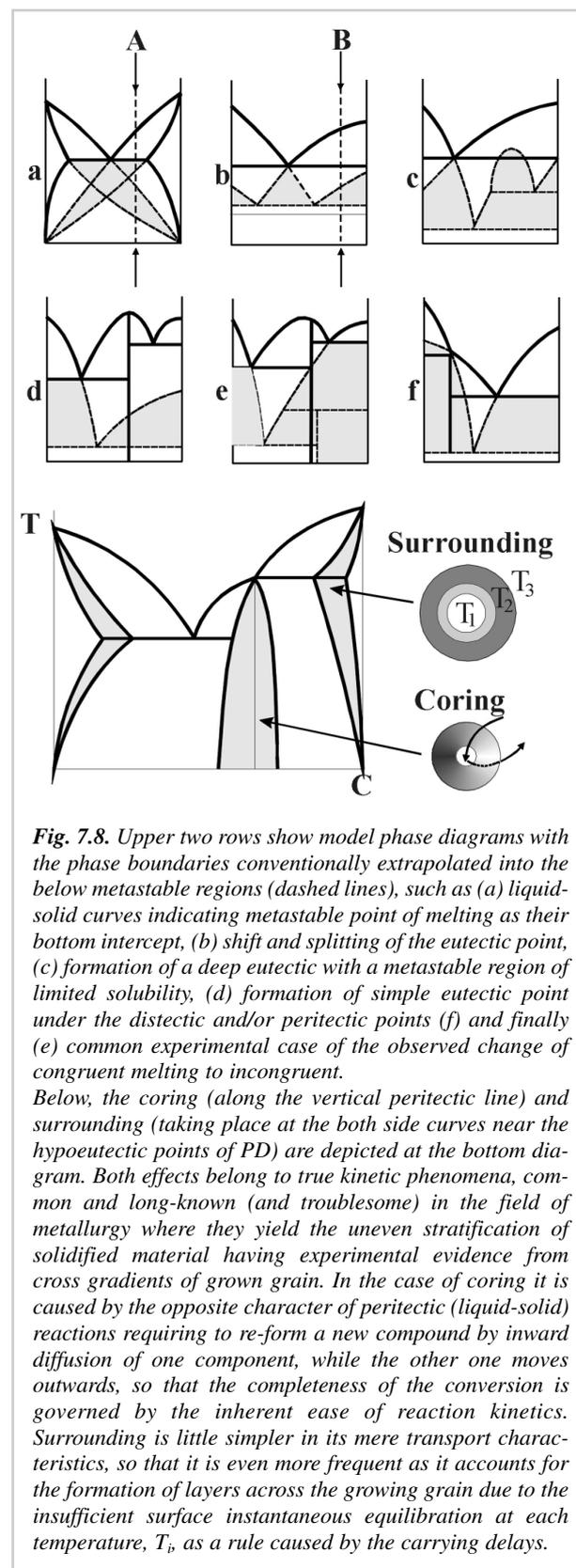


Fig. 7.8. Upper two rows show model phase diagrams with the phase boundaries conventionally extrapolated into the below metastable regions (dashed lines), such as (a) liquid-solid curves indicating metastable point of melting as their bottom intercept, (b) shift and splitting of the eutectic point, (c) formation of a deep eutectic with a metastable region of limited solubility, (d) formation of simple eutectic point under the distectic and/or peritectic points (f) and finally (e) common experimental case of the observed change of congruent melting to incongruent.

Below, the coring (along the vertical peritectic line) and surrounding (taking place at the both side curves near the hypoeutectic points of PD) are depicted at the bottom diagram. Both effects belong to true kinetic phenomena, common and long-known (and troublesome) in the field of metallurgy where they yield the uneven stratification of solidified material having experimental evidence from cross gradients of grown grain. In the case of coring it is caused by the opposite character of peritectic (liquid-solid) reactions requiring to re-form a new compound by inward diffusion of one component, while the other one moves outwards, so that the completeness of the conversion is governed by the inherent ease of reaction kinetics. Surrounding is little simpler in its mere transport characteristics, so that it is even more frequent as it accounts for the formation of layers across the growing grain due to the insufficient surface instantaneous equilibration at each temperature, T_i , as a rule caused by the carrying delays.

- for a given instant and experimental purpose (respecting particularity of a given arrangement and functionality to get ready-to-use materials of unusual properties to last for a certain limited period).

The latter requires deeper knowledge of metastable and unstable phase equilibria, which would also promote the application of the thermodynamics of irreversible processes in new branches of science and technology and may bring about the discoveries of new phases and of the yet unknown properties.

Current metallurgy bears the first accounts of the consequences of non-equilibrium solidification, i.e., phenomena known as ‘*coring*’ and ‘*surroundings*’, indubitably to occur in the vicinity of all characteristic (invariant) points [69,70], see Fig. 7.8. In the first case of coring, the melt under solidification does not encompass sufficient time to follow equilibration process along the balanced curve of solidus, which is caused by insufficient mass transport towards the phase interface. The precipitated grains, whose centers are closer to the equilibrium composition than their core-layers grown later, are the typical result. In the second case of surroundings, the originally precipitated phase starts to react with the remaining melt on reaching the peritectic temperature to form a new peritectic phase. It requires the atoms of one component to diffuse out from the melt to reach the phase interface. The thicker is the layer to cross, the slower the diffusion proceeds, particularly if the atoms of the second component must diffuse in the opposite direction through the solid layers to counterpart the reaction. This, evidently, must imply certain non-equilibrium conditions of the solidification and the gradual modification of the phase ‘equilibrium’ composition. Supplementary elimination of such non-equilibrium concentration gradients is usually accomplished by subsequent thermal treatment to allow equilibrating rearrangement. Similar phenomena are often encountered when single crystals are grown from foreign melts, their concentration gradients being dependent on the concentration changes in the matrix melt. These gradients can be again removed by specific thermal treatment or by melt agitation.

There is increased interest in more detailed mathematical analysis, description and synthesis of such ‘dynamic-like’ phase diagrams, which we coined the name ‘*kinetic phase diagrams*’ [66], cf. again Fig. 7.7. First, the *Gibbs* energies must be assumed for metastable phases, which occurs at higher energy levels and non-

equilibrium concentrations, because the *kinetic hindrance of nucleation* makes centers, suitable for the new phase growth, unattainable. For the practical use, metastable boundaries can be simply predicted by a straightforward extrapolation of the coexistence lines for the stable states into these non-equilibrium metastable regions, usually down to lower temperatures, Fig. 7.8. Alternatively, the preliminary shapes of metastable lines can be estimated from a superposition of two corresponding (usually simple-eutectic) phase diagrams. This is of considerable importance for all dynamic methods (from instrumental thermal analysis to laboratory quenching methods) to attain a correct interpretation of the phases on basis of observed effects (cf. Fig. 11.7).

For a system that cannot follow the experimentally enforced (usually strong) changes, even by establishing the previously discussed metastable phase equilibria due to backward nucleation, the boundary lines shift almost

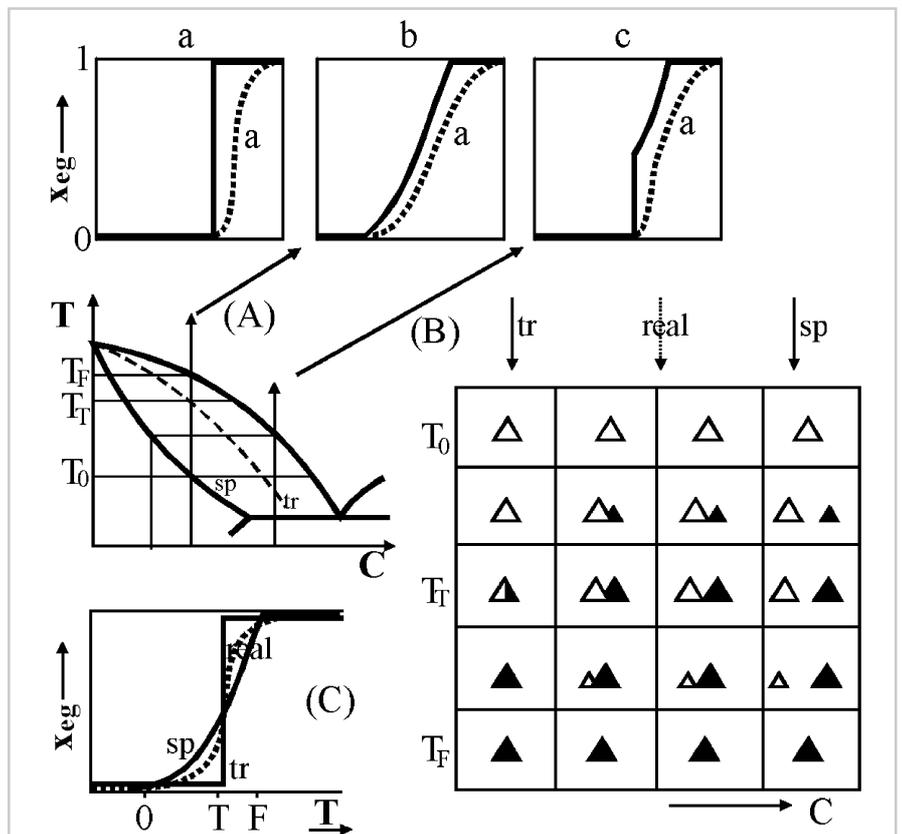


Fig. 7.9. Illustration of a hypothetical multiparametr (mixed) process obtained by assuming a competition of following reactions: an invariant phase transformation (*tr*) and variant phase separation (*sp*). Upper row shows the equilibrium background (solid line) and kinetic curve (dashed line, where *a* denotes the normalized progress of transformation) for classical cases of invariant (vertical), variant (sloped) and shared (combined) reactions connected in this diagram through arrows to the actual compositional cuts in a binary phase diagram. While (A) gives characteristics of transformation in the standard interval T_0 to T_F , (B) is an uncommon schematic representation of the possible sequences of the system states, where the open triangles denote the initial (disappearing) phase and the black triangles the resultant (appearing) phase. The left column in the right block shows the normal case of an authentic transformation while the right column stands for the extreme linked case of variant phase separation. Bottom curves correspond to the equilibrium (*tr* and *sp*) and real degrees of completeness of the overall process (Courtesy of P. Holba, Praha, Czechia).

freely along both the concentration and temperature axes. Thereby the regions of unstable phases are formed to be described in terms of the *kinetics of the physical-chemical processes* (especially fluxes of mass and heat). Such a truly kinetic phase diagram is fully dependent upon the experimental conditions applied (cooling rate, sample geometry, external fields, measuring conditions) and can portray materials, which state become fixed at room temperature by suitable freeze-in techniques. It is best treated mathematically in the case of a stationary process conditioning (e.g., *Focker-Planck* equation, Monte-Carlo methods or stochastic process theory [66]). It is complicated by the introduction of local cooling rates and degrees of undercooling in bulk and at interfaces and a mathematical solution requires very complicated joint solution of the equations for heat and mass transfer under given boundary conditions as well as that for the internal kinetics associated with phase transition on the solidification front. Evaluation yields interesting dependences between the undercooling, concentration, linear growth rate and cooling rate, see the following Table 7.I.

e) Aspects of invariant and variant processes

The passageway of a system through the phase diagram (cf. Fig. 7.7 again.) is best defined at the *invariant points*, where the system has no degree of freedom and where an ideal phase transition should occur at a single temperature. This, however, is real only with completely pure compounds or for systems with well-defined eutectic compositions. Taking a hypothetical phase diagram, which represents the dependence of the composition on temperature, the principal kinds of *equilibrium passage* through the phase boundaries can be distinguished on basis of the so called *equilibrium advancement of transformation*, λ_{eq} [78]. Using the relation for Z , as the *particularly measured property* (such as concentration, volume, mass, magnetization, etc.), we can normalize the equilibrium advancement within the standard interval from zero to one, i.e.,

$$\lambda_{eq} = (Z_{FT} - Z_o)/(Z_{F\infty} - Z_o) \quad 7.6$$

where Z_o , Z_{FT} and $Z_{F\infty}$ are respectively the limiting values of measured property at the final (index, F) and initial state (o), instantaneous (T) observed for given tempera-

ture, T, as well as its ultimate value (F_∞) measured at definitive temperature (T_∞). It is evident that λ_{eq} must be a function of temperature alone, as it actually expresses the shift of equilibrium with changing temperature. It, certainly, is attained only if assuming a completed equilibration at any given moment (ideally assured by infinitely slow heating). According to the shape of the $\lambda_{eq} = \lambda_{eq}(T)$ dependence, we can expect three types of dependence, see Fig. 7.9.

For the process with the stable initial states, we can distinguish *invariant* process, where λ_{eq} changes in sudden break from 0 to 1, while when the change proceeds gradually over a certain temperature interval, from T_o to T_F , we talk about the *variant* process of a continual character. If the transformation consists of both, the stepwise (invariant) and continuous (variant) changes, we deal with the so-called *combined* process [78]. It is necessary to stress out again that these three types of changes are valid only under ideal accession to phase transition whereas under real experimental conditions a certain temperature distribution (broadening) is always presented due to the inherent temperature gradient or other types of fluctuations possibly involved (concentration). Its practical use is best illustrated on the hypothetical sections through a phase diagram, exemplified in Fig. 7.9. For pure components, eutectics and distectic compositions, it exhibits invariant character while for two-phase regions it shows invariant course, which accounts the coexistence of two components. Under peritectic regions its change exhibits a combined character. Certainly it is valid only for processes with a stable initial state, not accounting yet the highly non-equilibrated states of metastable and unstable disequilibria.

In some cases the situation gets mixed up by inclusion the simultaneous effect of *phase separation*, β , which becomes actual due to the diffusionless or nucleation-free progression of a transition. It is seldom appreciated within current kinetic models because it is not only complicated mathematically but also particularly plagued by the experimental difficulty in the parallel determination of numerical data of both α and β . The possible interdependence is also illustrated in Fig. 7.9. again.

f) Thermodynamics of non-equilibrium glass transition

Special cases of non-equilibrium phase transitions are so-called '*kinetically enforced*' transformations, which

Table 7.I: Quantitative dependences of the growth parameters on the kinetic properties of solidification.

Change of values	T_f	ΔT	C_{liq}	$\Delta \sim C_{liq} - C_{solid}$	growth rate
Increase of values					
Cooling rate	intensive				
$10^3 \rightarrow 10^6$ K/s	increase	increase	increase	decrease	increase
Diffusion coeff.					
$10^{-7} \rightarrow 10^{-3}$ m ² /s	decrease	increase	increase	decrease	increase
Kinetic const.	increase	decrease			
$10^6 \rightarrow 10^1$ 1/s	to equil.	to zero	decrease	increase	increase

where T_f , ΔT , C_{liq} , $\Delta \sim C_{liq} - C_{solid}$ and growth rate G are respectively the temperature on the solidification front, undercooling, concentration of the liquid phase, concentration difference on the solidification front, and the growth rate of solid phase formation.

are best represented by the *glass transformation*, abbreviated as T_g . If we measure some macroscopic property, Z , of a system, which does not undergo easy crystallization during its solidification, then its temperature dependence exhibits a characteristic change in the passage region from an undercooled, yet fluid, melt to highly viscous, rigid substance (solid). This rather broad process of glass transition is often characterized by single temperature, T_g . This process accounts for the course of liquid *vitrification* and the resulting solid is called *glass*. Though this transformation exhibits most of the typical features of a second-order phase transition according to the *Ehrenfest* classification, it is *not a true* second-order phase transition due to the inherent irreversibility.

Let us employ the state function of affinity, A , defined previously in the preceding Chapter 5, together with the parameter, ζ , analogous to the above mentioned order parameter [71]. For an undercooled liquid (subscript, A), $\zeta = 0$, and for a glassy state (subscript, ζ), ordering arrives at constant value. For a second-order phase transition at T_E , it would hold that $(d\zeta/dT)_E = 0$, i.e., illustrated by the shift to the dashed line in Fig. 7.10. However, because ζ also changes to $(\zeta + d\zeta)$ for a glass, the equilibrium can be written as, liquid $\leftarrow dV_{E,A}(P,T) = dV_{E,\zeta}(P,T,\zeta) \rightarrow$ glass, so that it holds

$$-\Xi_A dP + \alpha_A dT = -\Xi_\zeta dP + \alpha_\zeta dT + (dV/d\zeta)_{T,P} d\zeta \quad 7.7$$

from which it follows that $\Delta\Xi_A V = (dV/d\zeta)_{T,P}^2 / (dA/d\zeta)$, $\Delta\alpha_V V = (dV/d\zeta)_{T,P} (dS/d\zeta)_{T,P} / (dA/d\zeta)_{T,P}$ and $\Delta C_p/T = (dS/d\zeta)_{T,P}^2 / (dA/d\zeta)_{T,P}$ where $\Delta\alpha_V$ is the difference between the expansions of the equilibrium undercooled liquid and that of frozen glass (the same valid for the difference in volume compressibility, $\Delta\Xi_A$ and heat capacity, ΔC_p). In practice, it follows that the classical form of

Ehrenfest equation is supplemented by another term dependent on the degree of ordering, which states that if the properties of an undercooled liquid would be known, the properties of the glass close to this state can be derived, i.e., $\Delta(\Xi C_V/\alpha_V)\Delta(1/\alpha_V) = \Delta(C_p/\alpha_V)\Delta(\Xi/\alpha_V)$, where T_o is the thermodynamic limit of glass transformation at $T_g \rightarrow T_f$.

The degree of irreversibility, π , can also be settled on the basis of a modified *Ehrenfest* relation established from statistical thermodynamics [72], or

$$\pi = \Delta C_p \Delta\Xi (T_g V_g \Delta\alpha_V)^2 \quad 7.8$$

where π denotes a ratio number to follow the concept of free volume, V_f , that decreases to a minimum at the glass transformation point and which is close unity for a single ordering parameter. For more ordering parameters it exceeds unity, which may lead to a concept of several T_g values as a result of gradual freezing of the regions characterized by the individual ordering parameters.

Geometrically, this means that the thermodynamic surface, which corresponds to the liquid, is formed by the set of characteristic lines of single-parameterized glass characterized by the constant, ζ . The shape of the surface at constant ζ in the vicinity of the equilibrium point is thus determined by two independent parameters, specifying the slope and fixing the curvature radius. Unfortunately, all the coefficients remain numerically undefined unless ζ is completely specified. To solve more complicated systems arising from penetration framework of multiple glasses, several ordering parameters (sub-systems) must be introduced. A number of workers tried to approach this problem by introducing experimentally measurable, the so-called *fictional temperature*, T_f [73,74], which are sensitively dependent to the cooling rates applied, experimental conditions, etc.. If a glass is annealed at a temperature close above T_g , an equilibrium-like value, corresponding to the state of undercooled liquid, is routinely reached at this temperature T_f . It can be geometrically resolved for any point on the cooling curve as the temperature corresponding to the intercept of the straight line passing through this point and parallel with heating line, with the equilibrium curve of the undercooled liquid. The temperature coefficient at the temperature $T^\#$ is then given by $(dT_f/dT)_{T^\#} = [(dZ/dT) - (dZ/dT)_g]_{T^\#} / [(dZ/dT)_{eq} - (dZ/dT)_g]_{T_f} = (C_p - C_{pg}) / (C_{pe} - C_{pg})$. The structural relaxation can be likewise described by using the parameter, ζ , upon the combination of above equation with the relationship $(dZ/dt)_T = (dZ/d\zeta)_T (d\zeta/dt)_T$ that yields

$$(dT_f/dT)_T = \{ [(dZ/d\zeta)_T (d\zeta/dt)_{eq}] / [(dZ/dT)_{eq} - (dZ/dt)_g] \} [(T_f - T) / \tau] \quad 7.9$$

where τ is the *relaxation time* corresponding to the given degree of ordering, which bears mostly an exponential form. It was also shown that many transport properties, Z , such as diffusion coefficient, viscosity or electric conductance of undercooled liquids obey a general *Fulcher* equation [75]

$$Z = Z_o T^{1/2} \exp [a_z / (T - T_o)]. \quad 7.10$$

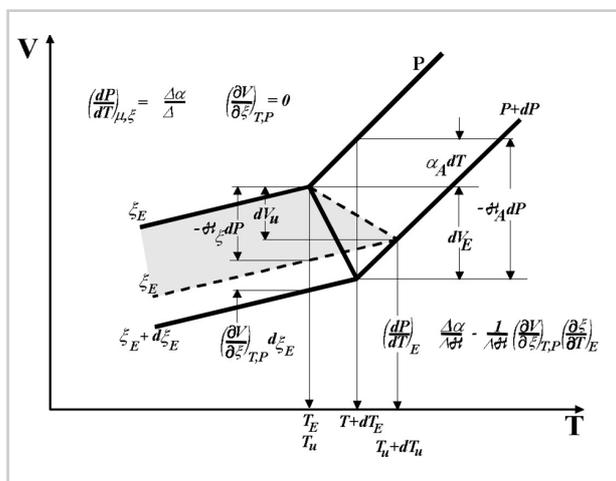


Fig. 7.10. Graphical representation of the Ehrenfest relationship for an ideal 2nd-order transition (point E) designated by the upper solid line and the middle dashed line, compared with glass transformation (point U, ordering parameter ξ) denoted by solid lines in the volume versus temperature diagram, where Δ denotes the change of volume compressibility, Ξ , volume expansion, α_v , and heat capacity, C_p .

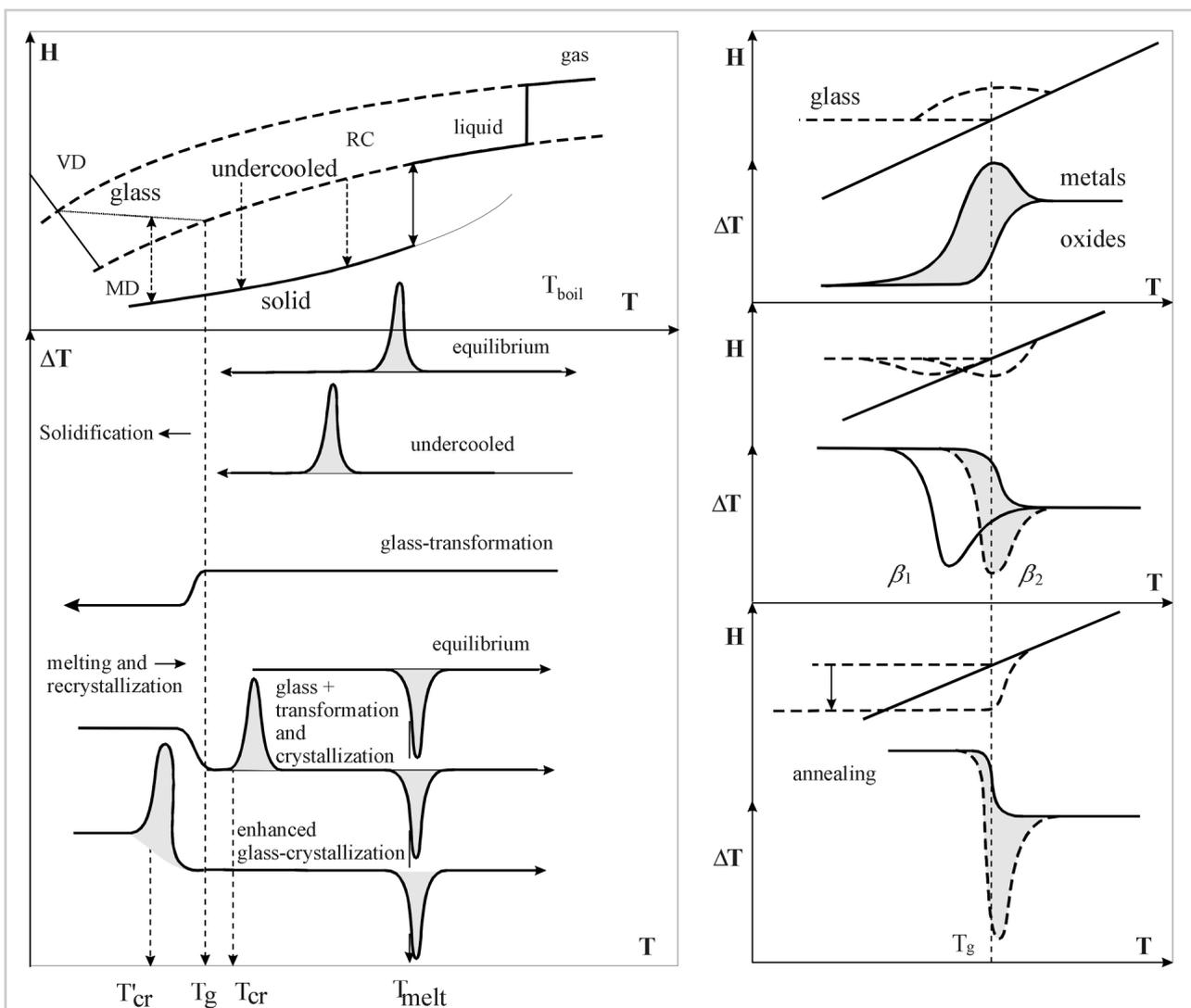


Fig. 7.11. Left: a schematic diagram of enthalpy, H , versus temperature, T , (upper) and its derivative ($dH/dT \equiv \Delta T$, bottom), which is accessible and thus also characteristic in its actual form upon the reconstruction of DTA/DSC recording. In particular, the solid, dashed and dotted lines indicate the stable (gas, liquid, solid), metastable (undercooled) and unstable (glassy) states. Rapid cooling of the melt (RC) can result in equilibrium and non-equilibrium (instantaneous and delayed, characterized by peak) solidification and, in extreme, also glass formation (characterized by stepwise T_g , which on reheating exhibits exothermic recrystallization below T_m). On the other hand, an amorphous solid can also be formed either by deposition of vapor (VD) against a cooled substrate (thin line) or by other means of disintegration (e.g., intensive grinding, high-energy disordering) of the crystalline state (moving vertically to meet the dotted line of glass). Reheating such an unstable amorphous solid often results in the early crystallization, which overlaps (or even precedes) T_g region and thus remain often unobserved. The position points are serviceable in the determination of some characteristics, such as the reduced temperature (T_g/T_m) or the Hrubý glass-forming coefficient $(T_c - T_g)/(T_m - T_g)$. On the right-hand side the enlarged part of a hypothetical glass transformation region is shown in more detail and for several characteristic cases. These are: cooling different sorts of materials (upper), reheating identical samples at two different rates (middle) and reheating after the sample prior reheating (often isothermal annealing, bottom).

In general, when a glass is equilibrated at a certain temperature, T_o , and then subjected to a temperature down-jump, $\Delta T = T_o - T$, one practically observes an instantaneous change of structure related properties due to vibrational contributions, which is followed by a slow approach to their equilibrium values corresponding the temperature, T . This structure consolidation is usually monitored by volume or enthalpy relaxation experiments and can be described by means of relative departures, δ_v or δ_H , respectively understood as $\{\delta_Z = (Z - Z_\infty)/Z_\infty\}$.

Initial departure from equilibrium can be related to the magnitude of the temperature jump and follows $\delta_v = \Delta\alpha \Delta T$ and/or $\delta_H = \Delta C_p \Delta T$ where $\Delta\alpha$ and ΔC_p are the differences of the thermal expansion coefficient and heat capacity between the liquid during its equilibrium-adjacent undercooling and the as-quenched glassy liquid (solid). An attempt to compare both volume and enthalpy relaxation rates was made by Hutchinson [76] using the inflections slopes of $\delta_v(t)$ and $\delta_H(t)$ data sets plotted on the logarithmic time scale. Seemingly this data are not

fully comparable quantities because $\Delta\alpha$ and ΔC_p may be different for various materials. *Málek* [77] recently showed that the volume and enthalpy relaxation rates can be compared on the basis of time dependence of the fictive temperatures, $T_f(t)$, obtained using relations $T_f(t) = T + \delta_v / \Delta\alpha$ and/or $= T + \delta_H / \Delta C_p$. It keeps relation to the fictive relaxation rate $r_f = - (dT_f / d \log t)$, identifiable as the inflectional slope of the stabilization period.

g) Use of temperature-enthalpy diagrams for a better understanding of transition processes in glasses

It is worth noting again that *glasses* are obtained by a suitable rapid cooling of melts (which process exhibits a certain degree of reproducibility) while *amorphous solids* are often reached by an effective (often unrepeatable) disordering process. Certainly, there can be further classification according to the glass origin, distinguishing thus liquid glassy crystals, etc., characterized by their own glass formation due to the specific arrestment of certain molecular movements. The non-crystalline state thus attained is in a constrained (unstable) thermodynamic state, which tends to be transformed to the nearest, more stable state on a suitable impact of energy-bringing warmth (reheating). The suppression of nucleation is the most important factor for any process of melts vitrification, itself important in such diverse fields as metglasses or cryobiology trying to achieve non-crystalline state for apparently non-glass-forming alloys or intra- and extra-cellular vitreous solutions needed for cryopreservation. Characteristic processes worthy of specific note, are the sequence of relaxation-nucleation-crystallization phenomena responsible for the transition of metastable liquid state to the non-crystalline state of glass and reverse process to attain back the crystalline state. Such processes are always accompanied by a change of the content of system enthalpy, which in all cases is sensitively detectable by thermometric and calorimetric measurements.

A most customary plot can be found in the form of enthalpy versus temperature [25,78], which can be easily derived using an ordinary lever rule from a concentration section of a conventional phase diagram, see the preceding section 6.6. The temperature derivative ($d\Delta H/dT$) of this function resembles the DTA/DSC traces (for DTA see the subsequent Chapter 11), each thermal effect, either peak or step, corresponding to the individual transformation is exhibited by the step and/or break in the related H vs. T plot [79], cf. Fig. 7.11. Such diagrams well illustrate possible routes of achieving a non-crystalline state. It shows the glass ordinarily prepared by liquid freeze-in via metastable state of the undercooled liquid (RC). Another state of amorphous solid can be prepared by the methods of intensive disintegration (milling) applied on the crystalline state of solids, which results in submicron grain-sized assemblage (MD, upwards from solid along the dotted line). Deposition from the gaseous state (VD, to thin sloped line) can be another source for amorphous solids. In the latter cases, however, the glass transformation is accelerated upon heating and its characteristic region turns out so early that is usually overlapped by coexisting crystallization, which can be only distinguished

through the careful detection of the baseline separation, which always occurs due to the change of heat capacity. Such cases exist in oxide glasses but are even more enhanced in non-crystalline chalcogenides. For most metallic glasses, however, there is so negligible change of C_p between the glassy and crystalline states so that the enthalpy record does not often show the expected baseline displacement, which even makes it difficult to locate T_g at all.

During any heat treatment of an as-quenched glass, relaxation processes can take place within the short or medium range of its network ordering, which covers *topological* movements of constitutional species, *compositional* rearrangements (when neighboring atoms can exchange their position) and *diffusional* reorganization connected with relaxation of structural defects and gradients. Such processes are typical during all types of annealing (such as isothermal, flush or slow heating) taking place below and/or around T_g and can consequently affect the glass transformation region. After the glassy state undergoes the glass transformation, which may be multiple due to the existence of two (phase-separated, interpenetrated) glasses, it is followed by precipitation of the closest, usually metastable, crystalline phase (dot-and-dashed lines in Fig. 7.12.). Considering a more complex case, for example the existence of a second metastable phase, the sequences of processes became multiplied since the metastable phase is probably produced first to precipitate latter into a more stable phase or catalyzing another simultaneous or subsequent crystallization of the second phase. It may provide a complex pattern of heat effects, the sequence of which is difficult to analyze; nevertheless, it is always helped by means of this hypothetical itemization.

Hrubý [80] attempted to give a more practical significance to glass-forming tendencies using easily available values of the characteristic temperatures determined conveniently by DTA/DSC for reheating of the already prepared glassy sample. The so-called *Hrubý* coefficient, K_{gl} , is then given by the ratio of differences $K_{gl} = (T_{cryst} - T_g) / (T_{melt} - T_{cryst})$. The greater the value of K_{gl} the better the glass-forming ability is approached. Despite the strong dependence of K_{gl} upon the method of glass preparation and measurement this coefficient exhibits a more sensitive interrelation to the glass formation peculiarities than a simple ratio T_g/T_{melt} . Best utilization of K_{gl} is in the comparison of glass-forming ability of different materials under different conditions and thermal treatments [81] cf. Fig. 7.11. again, but, regrettably, it is only assured by the entire use of material prepared beforehand.

The mechanical beginning and pre-treatment of glassy samples affect thermal measurements. The bulk and powdered sample can yield different enthalpy recordings and their identity can be best verified by the measurements where their properties are directly compared. For example, we can use such a DTA set-up where the reference sample is replaced by either of them, i.e., the powder-filled cell is compensated against the cell with the in-cast glass. Powdered sample may initiate surface-controlled crystallization at lower temperatures whilst the

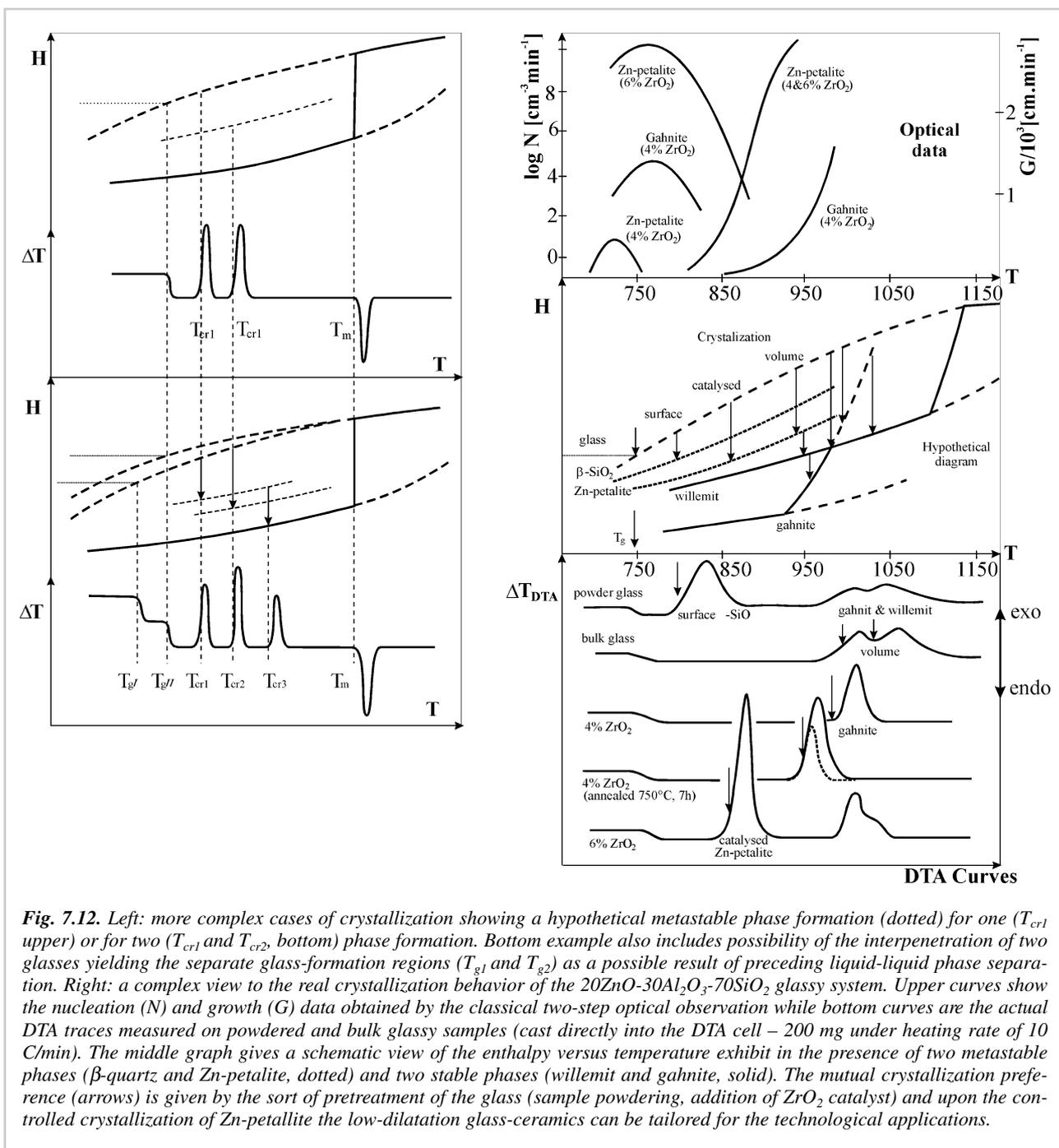


Fig. 7.12. Left: more complex cases of crystallization showing a hypothetical metastable phase formation (dotted) for one (T_{cr1} upper) or for two (T_{cr1} and T_{cr2} , bottom) phase formation. Bottom example also includes possibility of the interpenetration of two glasses yielding the separate glass-formation regions (T_{g1} and T_{g2}) as a possible result of preceding liquid-liquid phase separation. Right: a complex view to the real crystallization behavior of the $20ZnO-30Al_2O_3-70SiO_2$ glassy system. Upper curves show the nucleation (N) and growth (G) data obtained by the classical two-step optical observation while bottom curves are the actual DTA traces measured on powdered and bulk glassy samples (cast directly into the DTA cell – 200 mg under heating rate of 10 C/min). The middle graph gives a schematic view of the enthalpy versus temperature exhibit in the presence of two metastable phases (β -quartz and Zn-petalite, dotted) and two stable phases (willemit and gahnite, solid). The mutual crystallization preference (arrows) is given by the sort of pretreatment of the glass (sample powdering, addition of ZrO_2 catalyst) and upon the controlled crystallization of Zn-petalite the low-dilatation glass-ceramics can be tailored for the technological applications.

temperature region for the growth of nuclei in bulk glass is surface-independent and can be controlled by the sample gradual pulverization [82], cf. Fig. 7.12 b. Thus for larger particles, the absolute number of surface ready-to-grow nuclei is smaller, owing to the relatively smaller surface area in the particle assembly resulting in predominant growth of nuclei in bulk. With decreasing particle size the relative number of surface nucleation sites gradually increases, becoming responsible for a better-shaped thermal effect. The particle-size-independent formation energy can be explained on the basis of the critical nucleus size being a function of the curved surface [82]. Concave and convex curvature decreases and increases,

respectively, the work of nucleus formation depending on the shape of glassy particles. It often assumed that as-quenched glass has an amount of accessible nuclei equal to the sum of a constant number of quenched-in nuclei and that, depending on the consequent time-temperature heat treatment, the difference between the apex temperatures of enthalpy effects for the as-quenched and purposefully nucleated glass ($T_{apex} - T_{apex}^0$) becomes proportional to the number of the nuclei formed during the thermal treatment. A characteristic nucleation curve can then be obtained by simple plotting ($T_{apex} - T_{apex}^0$) against temperature (or just using DTA-DSC peak width at its half maximum, for details see next volume).

- ¹ Worth noting is an innovative thermodynamic concept for the description of partially open systems, which was introduced by *Holba* [Czech. J. Phys. 42 (1992) 549]. His original models take the advantage of the separation of components into two distinct categories: frees (shared) and conservative (fixed) and then suggests an adequate way of their description and analysis. Quasimolar fractions and quasimolar quotients are used to describe macroscopic composition of the system and quasimolar thermodynamic quantities are established to substitute molar quantities (otherwise customarily employed in closed systems). New thermodynamic potential, called hyperfree energy is introduced through *Lagendre* transformation to specify the equilibrium condition of such partially open systems. To assemble this hyperfree energy function, shortened thermodynamic quantities and quasimolar phase fractions are used, which makes also possible to derive a new form of Clapeyron-like equation. Such modified thermodynamics is suitable for better analysis of the behavior of complex systems with a volatile component studied under the condition of dynamic atmosphere as is, for example, the decomposition of oxides in air.
- ² The following case of scabrousness is often shown to illustrate possible curiosity existing under the radical application of temperature definitions. Let us take in account the given example of a system, which possesses magnetic spins that can be progressively reversed to the opposite direction. In a graphical sketch we can visualize such effect on the dependence of the system entropy on its energy, see Fig. 7.2. For either ordered state the entropy attains minimum while for the intermediate state it is maximal. The derivative dS/dU gives in fact reciprocal temperature and on its explicit drawing it provides two curves with undefined onset. The inequality $dU/dT > 0$ is, however, always satisfied. One special property of such a spin system is inquisitive display of 'negative absolute temperatures' so that the system can lose its internal energy by the spin-lattice interactions, which causes its temperature to decrease. For restoring the ordered spin arrangement, the system has to be contacted by a reservoir of higher 'negative absolute temperature'. This contact gives rise to a positive heat exchange, which reestablishes the spin system. We have two possibilities to interpret the effect caused by the spin-lattice interaction: (i) as a heat exchange between the spin system and the lattice as reservoir of positive absolute temperatures or (j) as a power exchange between the spin system and its vicinity. Both these physically equivalent possibilities belong to different diagrams. For spin system of 'negative absolute temperatures' there exist either: (i) the modified heat conducting processes, which satisfies the classical Carnot theorem or (j) the modified Kelvin processes, in which such a cyclic process is allowed, which only consumes heat from one reservoir. As spin calorimetry experiments show, the relation of thermal equilibrium between equilibrium systems induces a division of these systems into the classes of equivalence not only for the systems of positive absolute temperatures but also in the extraordinary region of negative absolute temperatures, and also between the reservoirs of different signs of temperature. Therefore empirical temperatures are well defined independently of the existence of reversible processes [W.G. Protector "Negative absolute temperatures", *Scientific American* 239 (1978) 78 and W. Muschik "Thermodynamic algebra, second law and Clausius' inequality at negative absolute temperatures" *J. Non-equil. Thermodyn.* 14 (1989) 173].
- ³ This description provides just a certain simplified access to the extensive field of glasses. Interestingly the topic of glass transition seemed clear in the seventies, i.e., viscosity increases with shortage of free volume, and molecular cooperativity must help to save fluidity at low temperatures. Consequently an unexpected and previously hidden complexity emanated, which persists until now. Namely, it was the mysterious crossover region of dynamic glass transition at medium viscosity and two independent courses of a nontrivial high-temperature process above and a cooperative process below the crossover providing a central question whether there are any common medium, such as the spatial-temporal pattern of some dynamic heterogeneity. Certainly this is the composite subject of specialized monographs published within various field series, such as the book by I. Gutzow, J. Schmelzer "The Vitreous State: thermodynamics, structure, rheology and crystallography" Springer, Berlin 1995, or the more detailed subject book by E. Donth "The Glass Transition: relaxation dynamics in liquids and disordered materials", Springer, Berlin 2001 or even the one which is in course of preparation by B. Hlaváček, J. Šesták „Thermal Science of Glassy State: microdynamics and microstructure of isotropic amorphous materials“ (to be published, Praha 2005). For more details the interested reader is regarded to see the Chapter 14.
- ⁴ The standard observations, based on measuring crystallographic characteristics and the amount of crystalline phases, such as typical XRD, are capable to detect the crystalline phase down to about 2–4 % within the glassy matrix. Indeed, we are not assuming here the detectability of minimum crystal size (peak broadening), nor we account for a specialized diffraction measurement at low diffraction angles. The critical amount of crystalline phase in the glassy sample became, however, the crucial question how to relevantly define the limit of 'true glassiness'. There appeared several proposals but the generally accepted figure is 10^{-6} vol. % (less common 10^{-3}), of crystallites to exist in glass not yet disturbing its glassy characteristics. The appropriateness of this value, however, is difficult to authorize. Nevertheless, the entire proof of the presence of glassy state is possible only on the basis of thermal measurements, i.e., upon the direct detection of glass transformation, which is the only characteristic for the glassy state alone without accounting for the interference of crystal counterparts.



CHAPTER EIGHT

8. Thermal physics of the process dynamics

a) Phase transitions and their order

The equality equation given in the preceding Chapter 7 (equation 8.1) can be used for the description of *phase transition*, i.e., the point where the potential, Φ , have the same values on both sides of the boundary between the phases 1 and 2 in question. Such a system must not only be in thermal, concentration and mechanical equilibrium, but must also meet further conditions of electromagnetic equilibrium. In other words, a continuous change in temperature must be accompanied by continuous changes in the other intensive parameters, I . However, the conditions for such a thermodynamic equilibrium place no further limitations on changes in the derivatives of Φ with respect to I , which can have various values in different phases. These phases must differ at least in one value of a certain physical quantity characterizing some property such as the volume, concentration, magnetization or also the specific heat, magnetic susceptibility, etc.

The discontinuity in the first derivatives of function Φ thus appears as the most suitable for an idealized classification of phase transitions [25,83]. The characteristic value of a variable, at which a phase transition occurs, is termed the *phase transition point* (T_{eq} , I_{eq}). The changes in the derivatives can be then expressed according to *Ehrenfest* classification and give the limit for the *first-order phase transitions*:

$$\begin{aligned} \Delta(T) &= (\partial\Phi^1/\partial T) - (\partial\Phi^2/\partial T) \neq 0 \Rightarrow \Delta S \ (\Delta H) \neq 0, \text{ at } T_{eq}, \\ \Delta(I) &= (\partial\Phi^1/\partial I) - (\partial\Phi^2/\partial I) \neq 0 \Rightarrow \Delta X \neq 0, \text{ at } I_{eq}. \end{aligned} \quad 8.1$$

From the viewpoint of thermoanalytical measurements in which the temperature is the principal parameter, a *certain amount of heat is absorbed and/or liberated* during the transition. For T_{eq} it holds that $\Delta H - T\Delta S = 0$, where ΔH is the latent heat of the phase transition, which must be supplied for one mole of a substance to pass from the phase 1 to phase 2. In the endothermic process, $\Delta H > 0$, and the heat is absorbed on passage 1 \rightarrow 2 while in the exothermic process, $\Delta H < 0$, and the heat is liberated. The set of equations specified in the previous Table 6.I. then enables monitoring of the effect of a change in the external field parameters (T and I) of the process, on the basis of a step change in measurable extensive quantities of the material under study.

Another limiting case is attained when $\Delta(T)$ and $\Delta(I)$ equal zero, i.e., such a phase transition which is not accompanied by a step change in the enthalpy or the other extensive quantity and which is called a *second-order phase transition*. These phase transitions are classified on the basis of discontinuity of the second derivatives of the general thermodynamic potential, or

$$\Delta(T,T) = (\partial^2\Phi^1/\partial T^2) - (\partial^2\Phi^2/\partial T^2) \neq 0 \Rightarrow \Delta C_p \neq 0 \quad 8.2$$

at T_{eq} where $\Delta S = 0$.

The same consideration holds for $\Delta(T,I)$ and $\Delta(I,I)$ (and the value of an uncertain expression of the 0/0 type is then found by using the *l'Hospital* rule indicated in the preceding Table 6.I.). Consequently, the higher-order phase

transitions can be predicted, i.e., a third-order phase transition, where $\Delta(I,I)$'s are zero and only the third derivatives differ from zero – however, experimental evidence of such processes is yet absent.

For thermal analysis experiments it is important to compare the main distinctiveness of these first- and second-order phase transitions. With a first-order phase transition, each of thermodynamic potentials can exist on both sides of the boundary, i.e., the functions Φ^1 can be extrapolated into the region of Φ^2 and vice versa, denoting thus a *metastable state* of the phase (1) above T_{eq} and vice versa for (2) below T_{eq} . From this it follows that the phase Φ^1 can be *overheated* at $T > T_{eq}$ (less common) and phase 2 *undercooled* at $T < T_{eq}$ (quite frequent).

On contrary, the feature similar to overheating and/or to undercooling is *impossible* with the second-order phase transitions because each phase, 1 and 2, is *restricted* to exist only on its own side of the phase boundary. This is caused by the fact that there is a break in the first derivatives of the entropy but the entropy itself remains continuous ($S^1 \Rightarrow S^2$). Therefore the function Φ has a certain singularity causing different behavior on the two sides of the phase transition.

Landau [84] has shown that a general theory can be developed using certain assumptions without a more detailed knowledge of the singularity of Φ . For a generalized phase transition, the function Φ can be written as the sum of contributions supplied by the 1st- and 2nd-order phase transitions, multiplied by appropriate distribution coefficient whose sum equals unity. In view of the non-ideality, the degree of the closeness to a first-order phase transition is denoted as p , see Fig. 8.1., showing the limits, $p=1$ and $p=0$, and the intermediate cases.

$$\begin{array}{llll} p = 1 & \Delta(T) \neq 0, \Delta(T,T) = 0 & \text{ideal 1}^{\text{st}} \text{ order} & 8.3 \\ p \leq 1 & \Delta(T) \gg \Delta(T,T) & \text{real 1}^{\text{st}} \text{ order} & \\ p \cong 0.5 & \Delta(T) \cong \Delta(T,T) & \text{broadened or lambda PT} & \\ p \geq 0 & \Delta(T) \ll \Delta(T,T) & \text{real 2}^{\text{nd}} \text{ order} & \\ p = 0 & \Delta(T) = 0, \Delta(T,T) \neq 0 & \text{ideal 2}^{\text{nd}} \text{ order} & \end{array}$$

For a mathematical description of generalized course of phase transitions a complementary parameter is introduced [25,84] and called the *ordering transition parameter*, ξ , which can reflect a regular distribution of atoms, spontaneous magnetization or polarization, etc. For the initial parent phase, 1, this parameter is assumed to be zero ($\xi = 0$ for the ordered phase) and for the resultant phase, 2, nonzero ($\xi \neq 0$ for the disordered phase). It is obvious that ξ changes stepwise for the first-order transition and is continuous for the second-order or broadened phase transitions. The main significance of the *Landau* theory lies in the fact that the principal physical quantities can be expressed as functions of the instantaneous value of ξ . This approach can also be taken to express the general thermodynamic potential, Φ , which can be expanded in a series using the integral powers of ξ . From the condition of equilibrium it holds that $\xi^2 \cong a_0 (T_0 - T) / 2b_0$ where the constant a_0 and b_0 are the coefficients of the expansion. It gives further possibility to approximate the entropy, $S = a_0^2 (T_0 - T) / 2b_0$, as well as the heat capacity, $C_p = a_0^2 T_0 / 2b_0$. Therefore, the transition from the ordered

phase to the disordered phase ($\xi=0 \rightarrow \xi \neq 0$) is always accompanied by a finite increase in the heat capacity.

Let us now consider the behavior of an ideal first-order transition exposed to an thermoanalytical experiment, in which the temperature of the system continuously increases and when the kinetics of the process does not permit the phase transition to occur infinitely rapidly, i.e., at a single point of the discrete equilibrium temperature. Therefore it is often important to find the temperature shift of the ΔH value including the possible effect of a complementary intensive parameter, I , which could act in parallel with T , i.e. the dependence of $\Delta H = \Delta H \{I, \Delta S(I, T)\}$ type. Then

$$d\Delta H/dT = \Delta C_x + \Delta H/T - d \ln \Delta X/dT \cdot \Delta H \quad 8.4$$

where ΔX can be replaced by corresponding differences in ΔV or ΔM or others depending on the transformation type. It is worth mentioning that if only one of the externally controlled parameters become uncontrolled, the transition process become undefined. This is especially important for the so-called 'self-generating' conditions, during the work at a non-constant pressure (i.e., under static atmosphere during decomposition reactions carried out at a sealed chamber) or which can happen under the other hesitating force fields.

b) Broadened phase transitions

In an experimental study of phase transitions, the equilibrium dependence of measured quantity, $Z(T)$, on temperature, which is representing the given system can be organized as follows [25,83]:

- a) The phase transition point is simply situated in the inflection point of an experimental curve

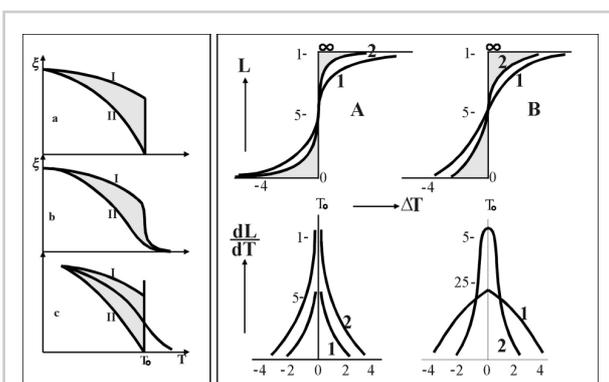


Fig. 8.1. Left: The dependence of the degree of disorder, ζ , on temperature, T , for (a) ideal limiting phase transitions of the Ist and IInd order, (b) diffuse phase transition of the Ist and IInd order and (c) an approximate function – the degree of assignment of $Z(I)$ and $Z(II)$

Right: the approximation of phase transitions using two stepwise Dirac δ -function designated as L and their thermal change dL/dT . (A) Anomalous phase transitions with a stepwise change at the transformation point, T_o (where the exponent factor n equals unity and the multiplication constant has values -1 , -2 and ∞). (B) Diffuse phase transition with a continuous change at the point, T_o with the same multiplication constant but having the exponent factor $1/3$.

- b) The magnitude of phase transition broadening occurs as the difference of the temperatures corresponding to the beginning (onset) and the end (outset).
c) The degree of closeness of the experimental curve to the Ist- and IInd-order theoretical curve can be expressed by a suitable analytical formula.

The viewpoint of curves closeness between limiting cases of $p_I(T)$ and $p_{II}(T)$ can be approximated by $p_I(T) + p_{II}(T) = \{Z(T) - Z_{II}(T)\}/\{Z_I(T) - Z_{II}(T)\} - \{Z_I(T) - Z(T)\}/\{Z_I(T) - Z_{II}(T)\} \cong 1$, while the individual experimental curve can be approximated by $Z(T) = p_I(T) Z_I(T) - [1 - p_I(T)] Z_{II}(T)$ or by means of an *arctan* function. Practical merit has the approximation of the C_p values as a power function of the temperature difference from the beginning, T_o , e.g., $C_p(T) = a_0 + a_1 (T - T_o)^{a_3}$. There is a frequent use of the so-called *Dirac* δ -function $L(T) = \int_0^T \delta(T - T_o) dT$, see Fig. 8.1b., so that a general thermodynamic potential of a broadened phase transition of the Ist order can be expressed as $\Phi(T) = \Phi_I(T) + \Delta\Phi(T) L(T)$, where $\Phi_I(T)$ is the normal part of the potential corresponding to the initial phase, I, and $\Delta\Phi(T)$ is the anomalous part connected with character of phase transition. If the analytical function of $L(T)$ is known, the corresponding thermodynamic quantities can also be determined, e.g., regarding entropy it holds that $S = -\partial\Phi/\partial T = S_I + \Delta S L(T) + \Delta\Phi(T_o) \{\partial L(T)/\partial T\} = S_I + S_{anom}$ with analogy for $C_p = C_{pI} + C_{p_{anom}}$. Using *Clapeyron* equation (cf. Table 6.I) we can find anomalous parts of entropy and heat capacity on the bases of volume as $(\Delta S/\Delta V) V_{anom}$ or compressibility as $(\Delta C_p/\Delta \alpha_v) \alpha_{v, anom}$. For the functional determination of $L(T)$ the *Pippard* relation is often used [85] in the general form, $L(T) = \{1 + \exp [a_0(T - T_o)^{a_1}]\}^{-1}$, often modified for a broadened phase transformation as, $L(T) = \{1 + \exp [3.52 [(T - T_o)/(T_{init} - T_{fin})]^{a_1}]\}^{1/2}$, with the exponent $a_1 < 1$. For non-symmetrical anomalous phase transitions the asymmetry is included by adding the temperature differences in assorted powers, a_1 and a_1+1 , i.e., $L(T) = \{1 + \exp [a_0(T - T_o)^{a_1} + b_0(T - T_o)^{a_1+1}]\}^{-1}$.

For the anomalous case of non-equilibrium glass transition (see the preceding Chapter 7) we can predict the behavior of the heat capacity changes according to the above sketched models, i.e., stepwise, diffuse and linearly decaying and lambda shaped. Bringing into play the concept of normalized parameters in the form conveniently reduced by the temperature of melting, e.g., $T_{gr} = T_g/T_{melt}$, $T_{or} = T_o/T_{melt}$, $T_r = T/T_{melt}$ or even $\Delta C_{pr} = \Delta C_p/\Delta C_{melt}$, we can assume a certain limiting temperature where the difference between the thermal capacities of solid and liquid/melt vanishes. Using $T_{gr} = 2/3$ and applying some simplified manipulations [86,87], such as $C_p^{liq} - C_p^{sol} = \Delta C_p^{liq-sol} \cong \text{constant}$, we can assume that $\Delta C_p^{liq-sol}/\Delta S_{melt} \cong \Delta C_{po} \cong 1.645$ at $T_r > T_{or}$ and zero at $T_r = T_{or} (= (2/3)^{2/3} = 0.54)$. Using molar quantities it comes to pass that $\Delta S_r = \Delta S^{liq-sol}/\Delta S_{melt} \cong 1 + C_{po} \ln T_r$ possibly to be approximated at $T_r > T_{or}$ by a constant value of $1/3$ as the entropy difference frozen-in due to the liquid vitrification. It provides the related values of $\Delta H \cong 1 - C_{po} (1 - T_{gr}) \cong 0.452$ and of $H_o \cong 1 - C_{po} (1 - T_{or}) \cong 0.243$. It can be extended to the limiting case of T_g of $1/2$ and to a wider range of ΔC_{pr} 's (down to 0.72) to calculate not only approximate values of H 's but also μ 's [66,79].

c) Equilibrium background and the kinetic degree of a phase transition

Practically, a transition under experimental study is defined as the development of states of a system in time, t , and at temperature, T , i.e., a time sequence of the states from the initial state (at starting time, $t = t_0$) to the closing state (at final time, $t = t_F$, corresponding to the temperature T_F). It associates with the traditional notion of *degree of conversion*, α , normalized from 0 to 1, i.e., from the initial stage at the mole fraction $N = N_0$ to its final stage at $N = N_F$. Then it holds that

$$\alpha = (N - N_0)/(N_F - N_0), \quad 8.5$$

or, alternatively, as $(Z - Z_0)/(Z_F - Z_0)$, if we substitute the thermodynamic parameter, N , by the experimentally determined, Z , which is a particularly measured value of the property under observation. This expression, however, is appropriate for strict *isothermal measurements* because for non-isothermal measurements we should introduce a more widespread expression, called the *non-isothermal degree of conversion*, λ , related to the ultimate value of temperature, where $T_F \rightarrow T_{F\infty}$. It is defined as [88,89]

$$\lambda = (N - N_0)/(N_{F\infty} - N_0), \text{ or } = (Z - Z_0)/(Z_{F\infty} - Z_0), \quad 8.6$$

where the value indexed by infinity (F_∞) expresses the maximum value of Z that can be reached at the concluding temperature, $T_{F\infty}$. Introducing the previously defined *equilibrium advancement of transformation*, λ_{eq} , discussed in the preceding Chapter 7, we can see that there is a direct interrelation between α and λ , i.e., through the direct proportionality

$$\lambda = \alpha \lambda_{eq}.$$

It follows that the isothermal degree of conversion equals to non-isothermal degree of conversion only for invariant processes, where $\lambda_{eq} = 0$. The difference of these two degrees of conversion was already revealed in the preceding Chapter 7, Fig. 7.9., where we can see that in the isothermal measurement the system reaches a final, but incomplete value of $Z = Z_{FT}$, which corresponds to the given temperature, T_F , whereas on continuous increase of temperature the system always attains the ultimate value of measured property, $Z_{F\infty}$, corresponding to the ultimate completion of reaction, see Fig. 8.2. Practical application of λ_{eq} is shown in the functional case of non-stoichiometry interactions of Mn_3O_4 (see Fig. 8.3).

This description is closely related to the preceding definition of the *equilibrium advancement of transformation*, λ_{eq} , which, however, is not exhaustive as more complex processes can be accounted for by multi-parameter transitions, such as segregation in solid-state solutions or solid-spinodal decompositions. Here we ought to include new parameters such as the *degree of separation*, $\beta \{ = (N_M - N_N)/N_T \}$, together with the complex *degree of completeness of the process*, $\zeta \{ = (N_T - N_M)/(N_N - N_M) \}$, based on the parallel formation of two new phases, whose graphical representation leads to four-dimensional space [88,89], see Fig. 5. The degree of conversion of such a process is then characterized by three measurable parameters, i.e., by the composition of the initial phase,

N_T , and the two newly formed phases, N_M and N_N . The composition of newly formed phase can be then expressed as $N_M = N_T(1 - \zeta\beta)$ or $N_N = N_T(1 - \beta - \zeta\beta)$ and the overall equilibrium degree of conversion of the process, λ_{eq} , is then represented by a spatial curve in the coordinates of ζ , β and T , pretentious that the degree of separation is normalized to vary from zero through a maximum (at one) back to zero. Such a course can be termed as the *multi-parametric* process and can become useful in the description of special cases of diffusionless mechanism of martensitic transformation. If such two simultaneous processes have the identical initial states, the resultant curve can be given by a superposition of two partial complex curves which may require another complication, newly defined degree of separation, $\delta = (N_T - N_M)/(N_N - N_M)/(N_N - N_M)^2$ making experimental evidence almost impracticable.

d) Constitutive equations applied in chemical kinetics

Chemical kinetics is based on the experimentally verified assumption that *the rate of change, dz/dt , in the state of a system (characterized by) z is a function, f , of the*

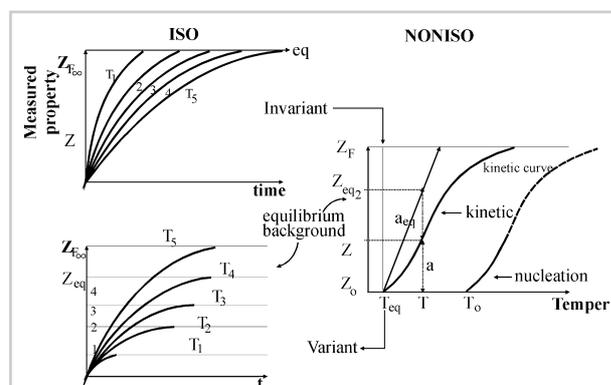


Fig. 8.2. Detailed specification of possible variants of the degree of reaction progress based on the experimentally measured property, Z , which can reach the instantaneous value $Z_{F\infty}$ or the intermediate value, Z_{eq} . We can distinguish two limiting courses of invariant (sudden change) and variant (continuous change) processes, their equilibrium background and actually measured (kinetic) response.

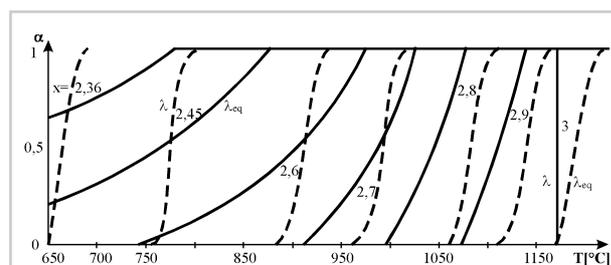


Fig. 8.3. Practical cases of the course of equilibrium background, λ_{eq} , and actual kinetic degree of transformation, λ (dashed), for the variant processes taking place during the tetragonal-cubic transformation of manganese spinels of the composition $Mn_xFe_{3-x}O_4$ for the various levels of manganese content, see the inserted values, x , in the region from 2.3 to 3.0.

state alone, i.e., $dz/dt = z' \approx f(z)$. Using this traditional postulation, the appropriate constitutional equation can be written in the principal form of the dependence of the reaction rate, expressed as the time development of the degree(s) of change (transformation) on the quantities that characterize the instantaneous state of the reacting system (chosen for its definition). In a simplified case, when $\lambda_{eq}=1$ (i.e., $\lambda=\alpha$), and under the unvarying experimental conditions (maintaining all intensive parameters around the sample constant, e.g., $T' = 0$, $P' = 0$, etc.), we can write the set of *constitutive equations* with respect to all partial degrees of conversion, $\alpha_1, \alpha_2 \dots \alpha_i$, thus including all variables in our spotlight, see Fig. 8.4. In relation to our earlier description we can summarize it as [90]:

$$\alpha' = f_\alpha(\alpha, \beta, T) \text{ and } \alpha_1' = \beta' = f_\beta(\alpha, \beta, T), \quad 8.7$$

$$T' = f_T(\alpha, \beta, T).$$

(where the apostrophe represents the time derivative). Such a set would be apparently difficult to solve and, moreover, experimental evidence usually does not account for all phase-separation particularities, so that we can often simplify our account just for two basic variables, i.e., α and T , only. Their change is traditionally depicted in the form of a set of two equations:

$$\alpha' = f_\alpha(\alpha, T) = k(T) f(\alpha), \quad 8.8$$

$$T' = f_T(\alpha, T) \equiv T_o + f(T)_{outer} + f(T)_{inner}.$$

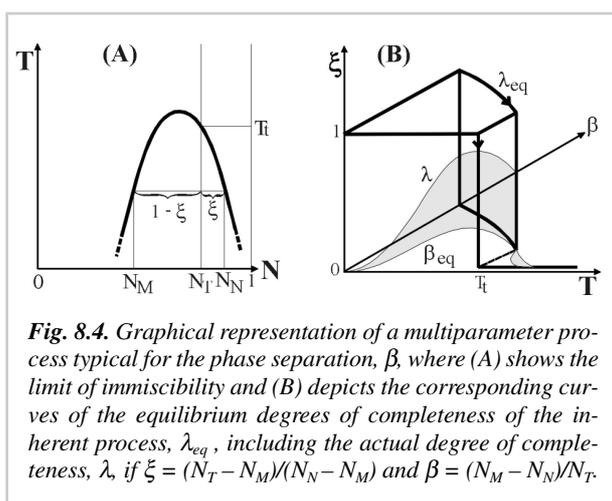


Fig. 8.4. Graphical representation of a multiparameter process typical for the phase separation, β , where (A) shows the limit of immiscibility and (B) depicts the corresponding curves of the equilibrium degrees of completeness of the inherent process, λ_{eq} , including the actual degree of completeness, λ , if $\xi = (N_T - N_M)/(N_N - N_M)$ and $\beta = (N_M - N_N)/N_T$.

The analytical determination of the temperature function, f_T , becomes the subject of both thermal effects:

- 1) the *external temperature*, whose handling is given by programmed experimental conditions, i.e., thermostat (PID) control when $f_T(T) = T_o + f(T)_{outer}$, and
- 2) the *internal temperature*, whose production and sink is the interior make up of process investigated, $f_T(\alpha) = T'_o + f(T_\alpha)_{inner}$.

In total effect these quantities govern the heat flows outwards and inwards the reaction interface. Their interconnection specifies the intimate reaction progress responsible for the investigational quantity, α' , which is derived from the measured properties of the sample under study. Here we can specify the externally enforced pro-

gram of time-temperature change of thermostat, i.e., $dT/dt = f(t) = at^m$, or $T = T_o + at^{(m+1)}/(m+1)$, which can have the following principal forms:

Program:	f(t) function:	a:	m:
Constant	0	0	0
Linear heating	ϕ	ϕ	0
Exponential	at	a	1
Hyperbolic	bt^2	b	2
Parabolic	$1/ct$	$1/c$	-1

Even more important is to see the properties of the first function, f_α , because the long-lasting practice accredited the routine in which the function $f_\alpha(\alpha, T)$ is divided into the two independent functions $k(T)$ and $f(\alpha)$. This implies that the *rate of change*, α' , is assumed to be proportional to the product of two separate functions only, i.e., the rate constant $k(T)$, dependent solely on the temperature $\{\approx \exp(-E/RT)\}$ and the mathematical portrayal of the reaction mechanism, $f(\alpha)$, reliant on the variation of the degree of conversion, only.

The entire temperature progress, $f_T(\alpha, T)$, is the matter of external and internal heat flow contributions usually reduced to that which is simply provided by externally applied temperature program, $T_o + f(t)_{outer}$, specifying the external restraint of the reaction progress in relation to the reaction rate, r^{\rightarrow} , derived from the factually measured properties of the sample.

When accounting for $\lambda_{eq} \neq 1$, the constitutional equation holds as, $\lambda = f(\lambda, \lambda_{eq}, T)$, and the true non-isothermal rate of chemical reaction, $d\lambda/dt$, becomes dependent on the sum $\{d\alpha/dt \lambda_{eq} + \alpha d\lambda_{eq}/dt\}$. Then the modified rate of a non-isothermal process, r^{\rightarrow} , becomes more complicated [78]:

$$r^{\rightarrow} = [d\lambda/dt - \lambda dT/dt (d \ln \lambda_{eq} dT)/\lambda_{eq}] \equiv k(T) f(\alpha) \quad 8.9$$

This expression, however, is of little practical use as the term, $d\lambda_{eq}/dt$, tends to be zero for equilibrium-near conditions.

In the region of significant contribution of *reversible reaction* [90] (i.e., if the measurement is performed at the temperatures below or close to the thermodynamic equilibrium temperature, $T < T_{eq}$), another solution can be found beneficial to account for the instantaneous value of equilibrium constant, ΔG , of both reversal reactions, or

$$\alpha' = k(T) f(\alpha) [1 - \exp(-\Delta G/RT)] \equiv k(T) f(\alpha) [1 - (\lambda/\lambda_{eq})^v]. \quad 8.10$$

We can assume that the change of *Gibbs energy*, $\Delta G = -v RT \ln(\lambda/\lambda_{eq})$ where the ratio λ/λ_{eq} can factually be the same as the thermodynamic yield of reaction, become significant at the end of reaction reaching, at most, the value of the conversional degree equal to, λ_{eq} , at the given temperature, T . We can even continue applying the modified *van't Hoff* equation, introducing thus the proportionality $\ln \lambda_{eq} = (\Delta H/vR)(1/T - 1/T_{eq})$, when $T = T_{eq}$ and $\lambda_{eq} = 1$.

Another extension would be insertion of the effect of pressure, P , into the set of constitutive equations, i.e., $\alpha' = f(\alpha, T, P) = k(T, P) f(\alpha) = k(T) K(P) f(\alpha)$. The

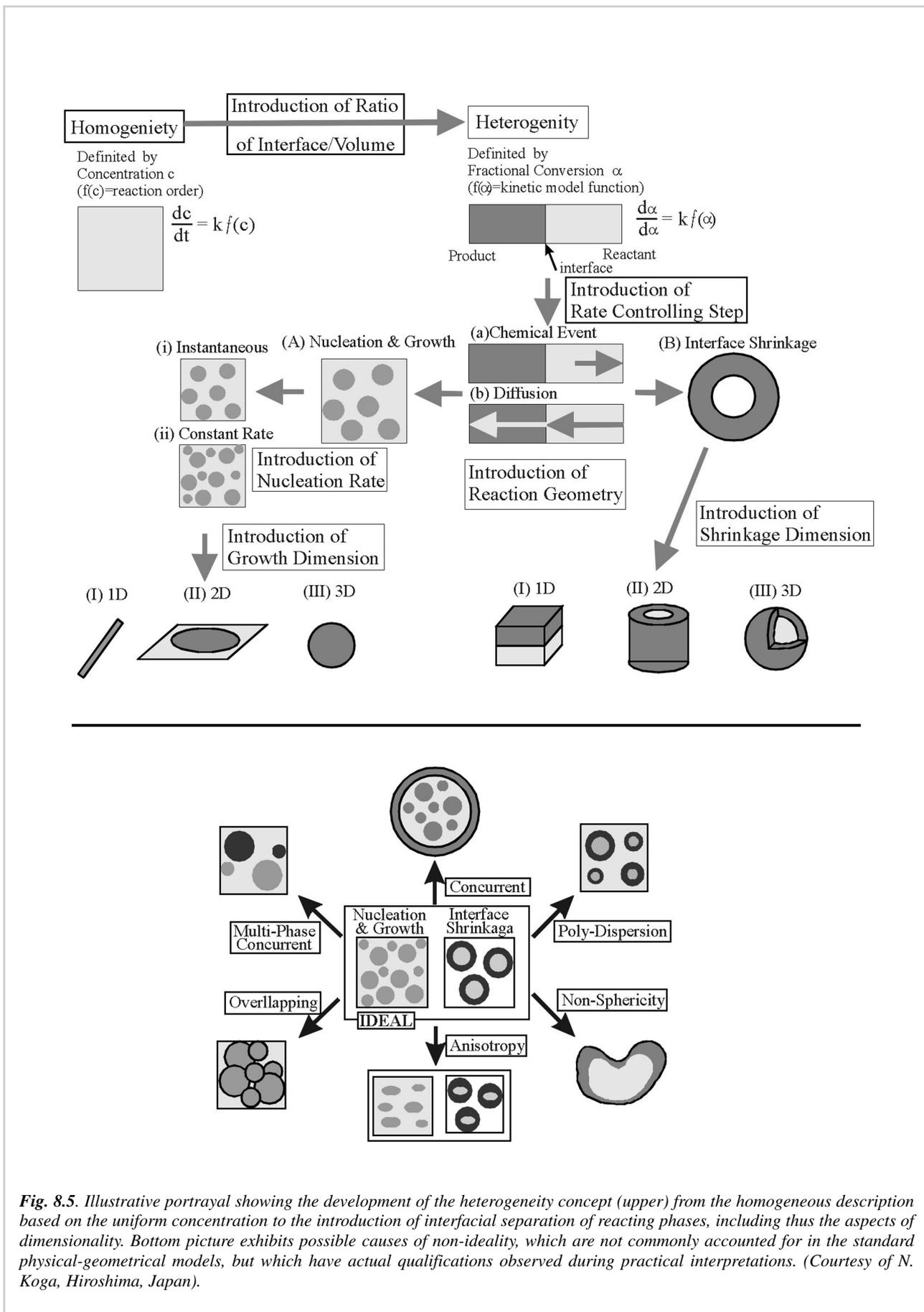


Fig. 8.5. Illustrative portrayal showing the development of the heterogeneity concept (upper) from the homogeneous description based on the uniform concentration to the introduction of interfacial separation of reacting phases, including thus the aspects of dimensionality. Bottom picture exhibits possible causes of non-ideality, which are not commonly accounted for in the standard physical-geometrical models, but which have actual qualifications observed during practical interpretations. (Courtesy of N. Koga, Hiroshima, Japan).

dependence of the reaction rate on the pressure can than be expressed by an asymptotic function of the *Langmuir* type, e.g., $\alpha' = k(T)[a_0P/(1+a_1P)] f(\alpha)$, or by a more feasible, general *power type* function, $\alpha' = k(T) P^m f(\alpha)$, where a and m are constant.

Often misguided concept of an erroneous application of constitutional equations in chemical kinetics is worth of a special note. This is the famous 'puzzle' of the apparently blindfold misinterpretation of the degree of conversion, α , insensibly understood as the state function of both parameters involved, i.e., the temperature and time, $\alpha = f(T, t)$. It was introduced as early as in the turn of 1970's [91] and challenged to the extensive discussion whether the consequential total differential, $d\alpha$, exists or not [92]. Curiously it has been surviving until the present time and is aimed at the inquiry whether the following equation is valid or whether it is only mathematical fudge:

$$d\alpha = (\partial\alpha/\partial T)_t dt + (\partial\alpha/\partial t)_T dT \text{ and thus} \\ d\alpha/dT = (\partial\alpha/\partial T)_t/\phi + (\partial\alpha/\partial t)_T \quad 8.11$$

The downright analytical solution for $d\alpha/dT$, assumes (for the simplest case of controlled linear heating, i.e., $dT/dt = \text{constant} = \phi$) the direct substitution of the standard reaction rate, α' for the 'isothermal' term $(\partial\alpha/\partial t)_T$, which thus yields a newly modified rate equation in the extended form

$$(\partial\alpha/\partial t)_T = k(T) [1 + E(T - T_0)/RT^2] f(\alpha), \quad 8.12$$

A question arises whether this unusual alteration is ever (and thus more broadly) applicable if it puts on display an extra term, $[1 + E(T - T_0)/RT^2]$.

This somehow curious version has both the supporting [93,94] as well as early abandoning [25,78,92] mathematical clarifications. Avoiding any deeper mathematical proofs let me show its absurdity using a simple example of the change in the water content in an externally heated reaction chamber. The process, taking place inside the chamber, is under our inspection and can be described on the rate of water content change (denoted as $d\alpha$), which just cannot be a mere function of the instantaneous temperature, T , and time, t , elapsed from filling the chamber with water, regardless of whether any water is remaining in the chamber. Instead, the exactly and readily available constitutional equation says that the instantaneous rate of water removal, represented by the change of water content, $d\alpha/dt$, must be a func-

tion of the water content itself, α , and its temperature, T , at which the vapor removal occurs. This reasoning cannot be obviated by any re-derivation of the already integrated form of basic kinetic equation [94] although the reverse treatment of effortless relation, $g(\alpha) = \int^\alpha d\alpha/f(\alpha)$, (see also consequent equation 12.6) can have some almost reasonable impact because such a mathematical procedure is next to leap-frog of the physical sense of a chemical reaction [92].

e) Modeling used in the description of reaction mechanism

In chemical kinetics, the operation of $k(T)$ function is customarily replaced with the known and well-defined analytical form of the *Arrhenius* exponential function, $k(T) = A \exp(-E/RT)$, thoughtfully derived from the statistics of evaporation. The inherent constants are the so-called *activation energy*, E ; identified as the energy barrier (or threshold) that must be surmounted to enable the occurrence of the bond redistribution steps required to convert reactants to products. The pre-exponential term, or *frequency factor* A (or Z , Chapter 12), provides a measure of the frequency of occurrence of the reaction situation, usually envisaged as incorporating the vibrational frequency in the reaction coordinate. There are also alternative depictions related to the activated complex theory and the partition functions of the activated complexes to give limited freedom along the reaction coordinate [25].

The validity of the Arrhenius equation is so comprehensively accepted that its application in homogeneous kinetics normally requires no justification. Although the Arrhenius equation has been widely and successfully

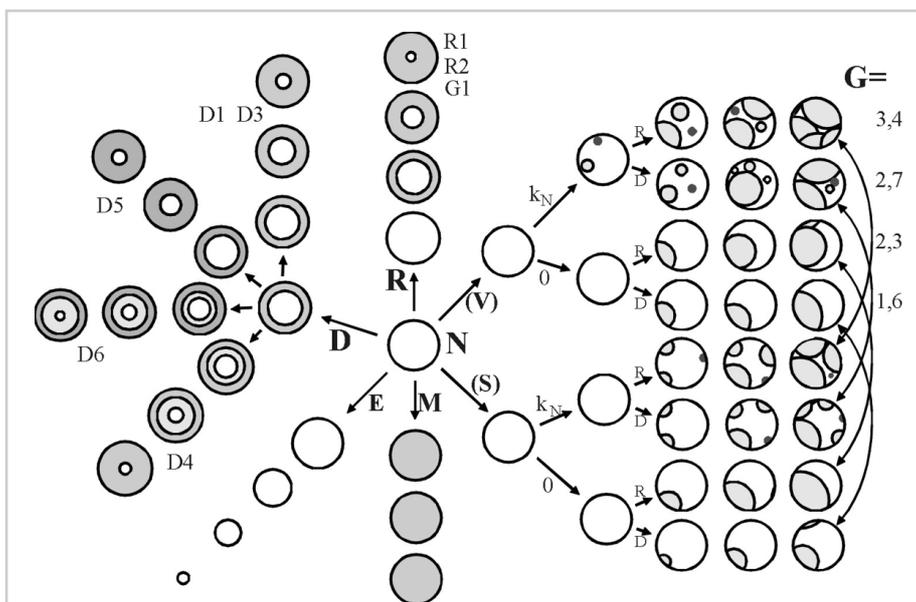


Fig. 8.6. Schematic representation of the basic types of heterogeneous processes using the model of a spherical particle, where (N) stays for the nucleation, (D) for the diffusion, (R) for the boundary chemical reaction, (E) for the evaporation, sublimation or dissolution, (M) for a diffusionless phase separation or nucleation-absent martensitic-type change, and (G) for the growth controlled process occurring for the given nucleation type, specified either by diffusion (D) or surface chemical reaction (R). The numbers identifying the individual reaction mechanisms agree with the description used in the text.

applied to innumerable solid-state reactions, this use factually lacks a theoretical justification because the energy distribution, particularly amongst the immobilized constituents of crystalline reactants, may not be adequately represented by the *Maxwell-Boltzmann* equation. Due allowance should be made for the number of precursor species within the reaction zone as well as for the changing area of the reaction interface. It can affect the enhancement of reactivity at the active sites (reactional contact), exaggerated by strain (between the differently juxtaposed networks), defects, catalytic activity of newborn sites, irreversible re-crystallization, or perhaps even by local volatilization (if not accounting for the thickness of reacting zone contoured by local heat and mass fluxes across and along the interfaces). It brings multiple questions about its applicability and we can humorously cite from ref [95] “Everybody believes in the exponential law of energy distribution, the experimenters because they think it can be proved mathematically, and the mathematicians because they believe it has been established by observations”.

Nevertheless, it was shown [96,97] that energy distribution functions of a similar form arise amongst the most energetic quanta. For values significantly above the *Fermi* level, both electronic energy (*Fermi-Dirac* statistics) and phonon energy (*Bose-Einstein* statistics) distribution approximate to the same form as that in the *Maxwell-Boltzmann* distribution. Also the interface levels, capable

of accommodating electrons, are present within the zone of imperfections where chemical changes occur. These are analogous to impurity levels in semiconductors, imperfections levels in crystals (F-centers) and, similarly, can be located within the forbidden range between the energy bands of the crystal. Such levels represent the precursor energy states to the bond redistribution step and account for the increased activity relative to similar components in more perfect crystalline regions. Occupancy of these levels arises from activation through an energy distribution function similar in form to that characteristic of the *Maxwell-Boltzmann* equation and thereby explains the observed fit of $k(T)$ data to an *Arrhenius*-type equation.

However, for the resolution of function, $f(\alpha)$, we must act in a different way than above because the exact form of this function [25] is *not a priori known* and we have to determine its analytical form (taking frequently into account its diagnostic potential, too). The specification of $f(\alpha)$ is thus required by means of the substitution by a definite analytical function derived on basis of modeling the reaction pathway usually by means of physico-geometric suppositions. Such models usually incorporate (rather hypothetical) description of consequent and/or concurrent processes of the interface chemical reaction, nucleation, crystal growth and diffusion structured within the perception of simplified geometrical bodies being responsible for the incorporated particles. Such derived function $f(\alpha)$ depends on both these physical-chemical and geometrical relations at the interface between the product and the initial reactant. When not accounting on these interfaces or other inhomogeneity phenomena we deal with homogeneous reactions and $f(\alpha)$ is paying attention to a most simplified description, only, which is associated with the so-called *reaction order*. However, for solid-state reactions heterogeneity effects ought to be included, which is actually accounting the interfaces as ‘defects’. The mathematical description becomes thus more complicated due to the fact that *not ‘bulk concentration’ but the ‘phase interfaces’ carry out the most significant role* in controlling the reaction progress, as illustrated in Fig. 8.5.

The most common models are derived isothermally and are associated with the shrinking core of particles, which maintains a sharp reaction boundary [25,98]. Using a simple geometrical representation, the reacting system can be classified as a set of spheres where the reaction interface must be reached by reacting components through diffusion. Any interfacial (separating) layer bears the role of kinetic impedance and the slower of the two principal processes, diffusion and chemical interface reaction, then become the *rate-controlling process*.

Reaction rate is often proportional to the interface area, A , i.e., $\alpha \propto k(T) A/V_0$, where V_0 is the initial particle volume. Its mathematical rearrangement yields the most famous model of three-dimensional diffusion called the *Jander* parabolic Law. Substituting the chemical rate constant, $k(T)$, by the diffusion constant, $D(T)$, responsible for transport in order to pass through the separating layer, the *Ginstling* and *Brounshtein* equation is obtained. It can be further modified by the inverse proportionality between $D(T)$ and t , as the counter-current diffusion, etc.; possible models are collectively illustrated in Fig. 8.6. As

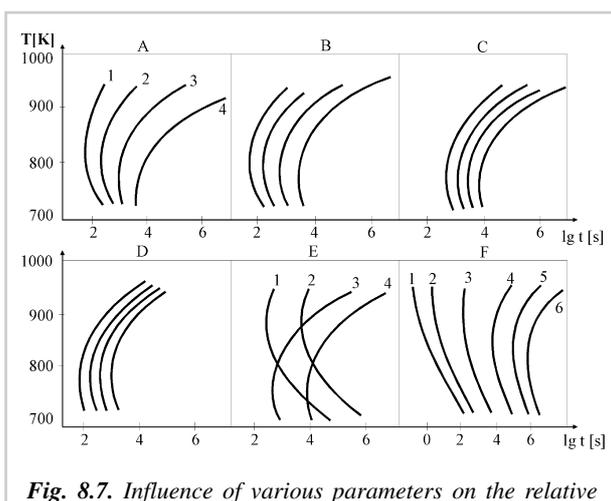


Fig. 8.7. Influence of various parameters on the relative positioning of T-T-T curves for a model case (corresponding to the real issue of $\text{Li}_2\text{O-SiO}_2$ melt/glass) assuming a range of the input experimental values (clockwise): (A) Gradual decrement of the equilibrium temperature, T_{eq} , from 1400, 1350, 1300 down to 1250 [K] (respective curves 1, 2, 3 and 4). (B) Change of the latent heat of crystallization, ΔH_{eq} , from 10, 9.5, 9 to 8.5×10^{19} [J/molecule]. (C) Change of the surface tension, σ , from 0.148, 0.152, 0.156 to 0.160 [J m⁻²] and crystallized fraction, α , from 10^{-6} , 10^{-5} , 10^{-4} to 10^{-3} . (D) Various approximations of supersaturation, curves 1 and 2 are drawn under assumption of $\Delta\mu = \{\Delta H_{eq}(T_{eq} - T)/T_{eq}\}/(T/T_{eq})$, $\sigma = 0117$ [J m⁻²] and $\alpha = 10^{-6}$ while curves 3 and 4 follows from simpler representation of $\Delta\mu = \Delta H_{eq}(T_{eq} - T)$ with $\sigma = 0.160$ [J m⁻²] and $\alpha = 10^{-1}$. Finally the wetting angle, Θ , is alternated in (F) within the degrees of 40, 60, 80, 120 and 140° marked by curves 1 through 6. (Courtesy of Z. Kožíšek, Praha, Czechia).

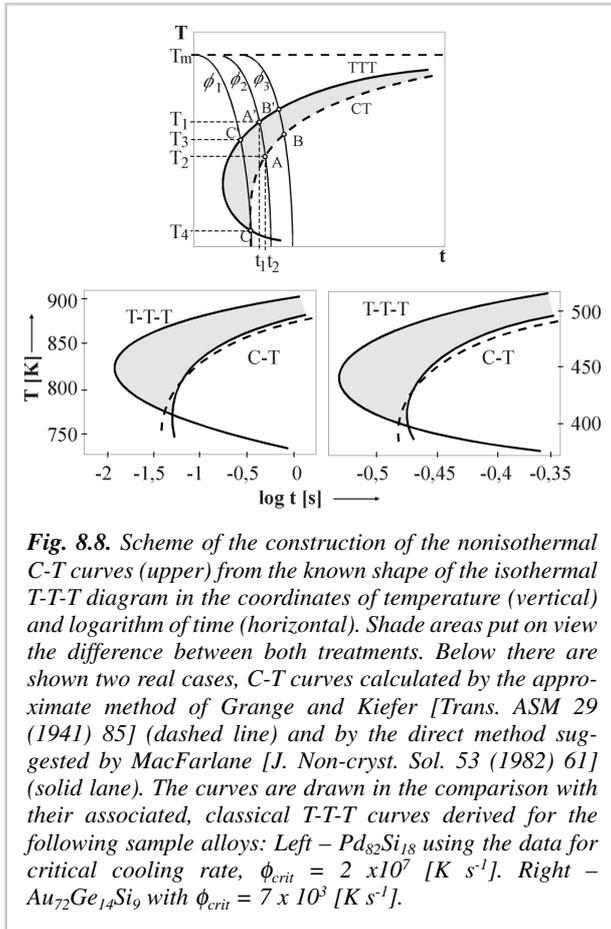


Fig. 8.8. Scheme of the construction of the nonisothermal C-T curves (upper) from the known shape of the isothermal T-T-T diagram in the coordinates of temperature (vertical) and logarithm of time (horizontal). Shade areas put on view the difference between both treatments. Below there are shown two real cases, C-T curves calculated by the approximate method of Grange and Kiefer [Trans. ASM 29 (1941) 85] (dashed line) and by the direct method suggested by MacFarlane [J. Non-cryst. Sol. 53 (1982) 61] (solid line). The curves are drawn in the comparison with their associated, classical T-T-T curves derived for the following sample alloys: Left – Pd₈₂Si₁₈ using the data for critical cooling rate, $\phi_{crit} = 2 \times 10^7$ [K s⁻¹]. Right – Au₇₂Ge₁₄Si₉ with $\phi_{crit} = 7 \times 10^3$ [K s⁻¹].

a rule, the processes controlled by the chemical event and diffusion are respectively dependent on $1/r_0$ and $1/r_0^2$, where, r, is the radius of incorporated particles³. Most of individual equations derived for particular cases [99-101] are summarized in the Table 8.I. together with their integral forms useful for their experimental assessment (see consequent Chapter 12).

f) T-T-T and C-T diagrams

During the last decades a considerable utilization has been made for the so-called *T-T-T diagrams* (Time-Temperature-Transformation) as well as their further derived form of C-T diagrams (Cooling-Transformation) particularly in assessing the critical cooling rates required for tailoring quenched materials (initially metals) and their disequilibrium states (glasses). Important factor is the critical cooling rate, ϕ_{crit} , defined as the minimum (linear) cooling at which the melt must be quenched to prevent crystallization. Certainly, the ϕ_{crit} determination can be performed only in limited, experimentally accessible regions, ranging at present from about 10⁻⁴ to as much as 10⁷ K/s. Critical cooling rates are an integral part of the glass-forming theories, which view all liquids as potential glass-formers if, given a sufficiently rapid quench, all crystal-forming processes are essentially bypassed.

In this prospect a simplified kinetic model was developed based on the previously discussed JMAYK equation assuming the limiting (already indistinguishable) volume fraction of crystalline phase, traditionally assumed to be about 10⁻⁶ % [102]. Neglecting transient time effects for the steady-state rate of homogeneous nucleation, the ϕ_{crit} is given by a simple proportionality $\phi_{crit} = \Delta T_{nose}/t_{nose}$, where $\Delta T_{nose} = T_{melt} - T_{nose}$, and T_{nose} and t_{nose} are temperatures and time of the nose (extreme) of the time-temperature curve for given degree of transformation. The actual application of this kinetic analysis to wide variety of materials led to the development and construction of T-T-T diagrams [103]. It was found [102] that the ratio T_{nose}/T_{melt} falls in the range from 0.74 to 0.82 and that the ϕ_{crit} decreases with decreasing T_{gr} – for its value of 0.7, metallic glasses could be formed even under such a mild cooling rate as 10 K/s. If for the given fraction, T_{nose}/T_{melt} is moved to higher values, the T-T-T boundary is shifted to lower time and results can be seen from Fig. 8.7. [66,104,]. Practically ϕ_{crit} implies the maximum sample thickness, δ , that can be wholly vitrified in one

Table 8.I. Typical physico-geometric (kinetic) model functions derived for some particular solid-state reactions.

Model:	Symbol:	function f(α):	integral form g(α) = ∫ ^α dα/f(α):
<u>Nucleation-growth</u> (JMAYK eq.) (Johnson-Meal-Avrami-Yerofeev-Kolmogorov)	A _m m = 0.5, 1, 1.5, 2, 2.5, 3 and 4	m(1-α)[-ln(1-α)] ^{-1/m}	[-ln(1-α)] ^{1/m}
<u>Phase boundary</u> n-dim.:	R _n n = 1, 2 and 3	n(1-α) ^{1-1/n}	[1 - (1-α) ^{1/n}]
<u>Diffusion controlled</u>	D _i		
1-dim. diffusion	D ₁	1/2α	α ²
2-dim. diffusion	D ₂	- [1/ln(1-α)]	α + (1-α) ln(1-α)
3-dim. diffusion (Jander)	D ₃	(3/2)(1-α) ^{2/3} / [(1-α) ^{-1/3} - 1]	[1 - (1-α) ^{1/3}] ²
3-dim. diffusion (Ginstling-Brounshtein)	D ₄	(3/2)/[(1-α) ^{-1/3} - 1]	1 - 2α/3 - (1-α) ^{2/3}
3-dim.counter dif. (Komatsu-Uemura, often called ‘anti-Jander’ equation)	D ₅	(3/2)(1+α) ^{2/3} / [(1+α) ^{-1/3} + 1]	[(1+α) ^{1/3} - 1] ²
<u>Unspecified – fractal approach (extended autocatalytic)</u> fractal-dim (Šesták-Berggren)	SB	(1 - α) ⁿ α ^m	no particular analytical form

quenching stage is $\delta_{\text{crit}} \cong \sqrt{(\lambda t_{\text{nose}})}$ and will increase with decreasing ϕ_{crit} and increasing T_{gr} , certainly dependent on the sample thermal property (λ). In addition, a simple relation between ϕ_{crit} and undercooling, ΔT_{crit} , was devised in the logarithmic form $\log \phi_{\text{crit}} = a - b/\Delta T_{\text{crit}}^2$ [105], where a and b are constants. It can further provide an estimate for the change of fraction crystallized, α , with undercooling, so that $(d\alpha/d\Delta T)_{\Delta T_{\text{crit}}} \cong 3b/(\Delta T_{\text{crit}}^3)$ being useful for various numerical computations. For silicate materials the important factor, viscosity η , may also be fitted within about an order of magnitude by the traditional *Vogel-Fulcher-Tamman* type of logarithmic equation in the form, $\log \eta = -1.6 + 3.12/(T/T_g - 0.83)$.

A more realistic estimate of ϕ_{crit} can be obtained when constructing the continuous-cooling-curves, often called C-T diagrams [103,106,107]. It is based on the additivity following from the assumption that the momentary value of rate, α' , which depends merely on α and T and not on the temperature history of the transformation process. In comparison with the classical T-T-T diagrams the same α is reached at relatively lower temperatures and in longer times. During the construction of C-T curves we can assume that α crystallized from temperature T_1 to T_2 (corres-

ponding to t_1 and t_2) depends on the related values from the T-T-T diagram read out for the mean temperature $(T_1 + T_2)/2$. Similarly α formed during cooling up to the point given by the intercept of ϕ and T-T-T curve is found to be negligible in comparison to α corresponding to isothermal condition of this point, see Fig. 8.8. It should be noted that the value of ϕ_{crit} found by the nose method are typically larger than those computed by other techniques [108–113] because appreciable crystallization does not occur at temperatures below the nose, and thus the basis for the nose method theory needs additional inquiry [110].

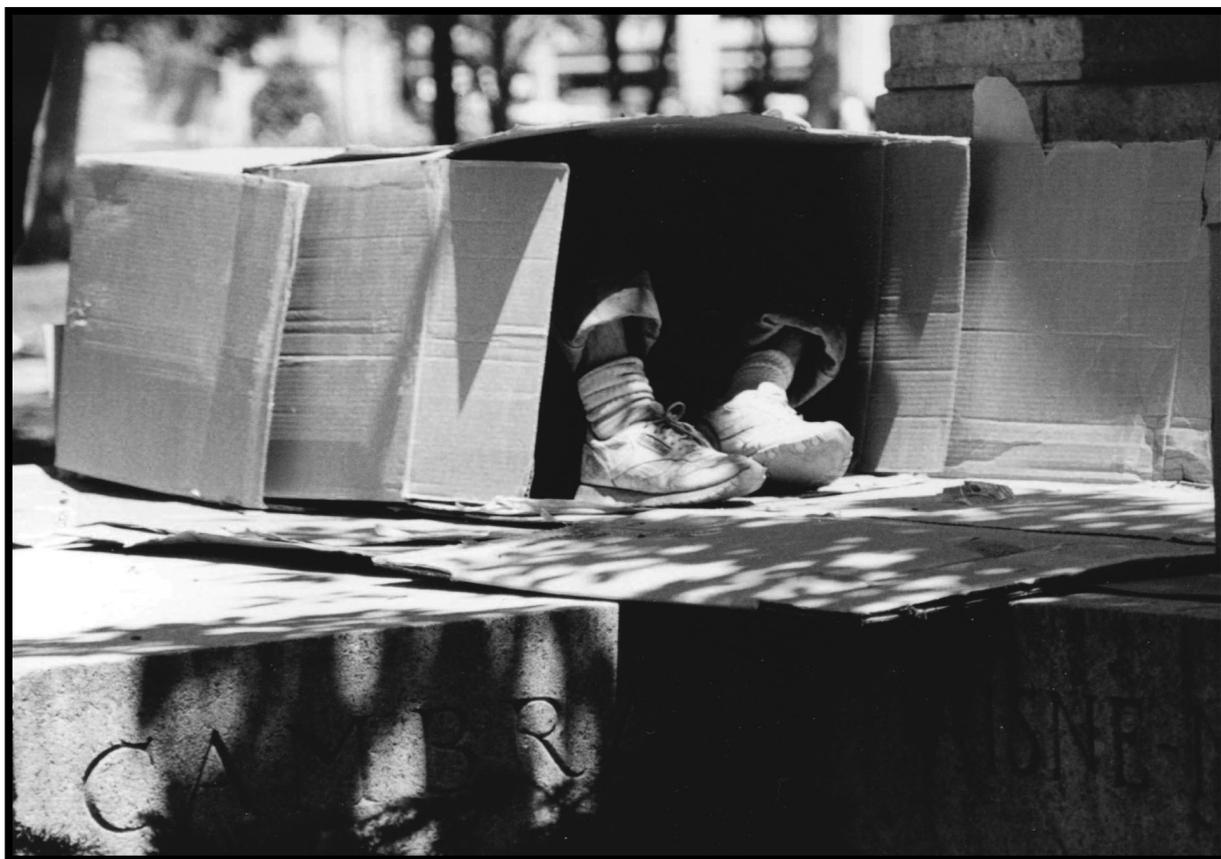
There is a close link between the particular crystallization mode and the general resolution of the T-T-T or C-T diagrams. The time needed to crystallize a certain fraction, α , at a given temperature, T , can be conveniently obtained by the DTA/DSC measurements, see Chapter 10. On the basis of nucleation-growth theories the highest temperature to which the kinetic equation can reasonable well reproduce the T-T-T or C-T curve was estimated [110] to be about $0.6 T_{\text{melt}}$. There are certainly many different methods used for numerical modeling [110], which detailed analysis [66,104] falls, however, beyond the scope of this yet introductory chapter.

¹ Certainly, this is a simplified analysis practiced within the “thermostatic” approach to kinetics. There are many complementary accesses such as the rate equation can be used to check the validity of two commonly postulated extensions of the Onsager relations into the nonlinear domain. It shows that a generalized dissipation potential can be determined, which condition involves the dissipation aspects [J. Bataille, D.G. Edelen, J. Kestin “Nonequilibrium Thermodynamics of the Nonlinear Equations of Chemical Kinetics” J. Non-equilib. Thermod. 3 (1978) 153. The notion of a chemical network can also be exemplified using electrical representation, which demonstrates that the mathematical formulation of chemical reactions can be viewed as a subset of abstract circuit theory [G.F. Oster, A.S. Perelson “Chemical Reaction Dynamics: Part I. “Reaction Network” and Part II “Geometrical Structure”, Arch. Rat. Mech. Anal. 55 (1974) 230 and 57 (1974) 31]. The description of stationary states and the solution of homologous differential equations can endure the portrayal of oscillatory chemical reactions [A. Tockstein “Stationary States in Chemical Kinetics” Chem. Listy (Prague) 81 (1987) 561 (in Czech)], which is dealt with in detail in the Chapter 16.

² Let us clarify the problem by specifying the classes of following processes (where ϕ is the constant T'):

isothermal:	nonisothermal:
$\alpha = \alpha_T(t, T)$	$\alpha = \alpha_\phi(t, \phi)$
$\alpha' = (\partial\alpha_T/\partial t)_T + (\partial\alpha_T/\partial T)_T T'$	$\alpha' = (\partial\alpha_\phi/\partial t)_\phi + (\partial\alpha_\phi/\partial T)_T \phi'$
because $T' = 0 = \phi$	because $\phi' = T' = 0$
→ then ←	
$(\partial\alpha_T/\partial t)_T = \alpha' = (\partial\alpha_\phi/\partial t)_\phi$	

³ It is clear that any reaction rate, particularly at the beginning of its acting-ion-exchange, must depend upon the size of the solid grains, which undergo formation, growth or dissolution. Reaction rate, r^\rightarrow , should thus be proportional to the particle size, r , in the form of a power law, $r^\rightarrow = r^{D_r-3}$ (cf. Chapter 13), where D_r is the characteristic (reaction) fractal dimension [O. Pfeifer, Chimia 39 (1985) 120]. It follows that a mere use of integral dimensions is oversimplification (cf. Chapter 12). Moreover, the initial rate is directly proportional to the extent (availability) of ready-to-react surface as well as its roughness (fractality). It seems that this concept can be very useful to describe the behavior of a reacting object towards the reaction while the reaction fractal dimension relates the sum of all events occurring during the overall heterogeneous process. The mobile size of propagating particles inserts another significant contribution, which are the relative slip velocities of the particle surroundings, particularly influential in the fluid media. The growing particles can be observed as compact Brownian particles (for $r < 10 \mu\text{m}$, with the slip velocity naturally increasing with the decreasing size, $D_r \geq 1$) or as non-Brownian particles (where the slip velocity increases with the increasing size but only for mechanically agitated systems, $D_r \geq 2$) not accounting on the clustered Smoluchowskian particles ($r < 100 \text{ nm}$, as ‘perikinetical’ agglomerates induced by Brownian motion and/or $r > 100 \text{ nm}$, as ‘orthokinetic’ agglomerations induced by shear fluid forces, both exhibiting $D_r \geq 0$). However, the so-called multi-fractal behavior is often involved, which yields more than one fractal dimension at different levels of resolution or sizes of objects. It can be summarized in the three major categories: boundary (B) fractal dimension, which characterizes the boundaries of objects (with the values $1 \leq D_B \leq 2$); surface (S) fractal dimension, which describes the quality of surfaces of objects (with values $2 \leq D_S \leq 3$); and the mass (M) fractal dimension, which gives a measure of the way in which the individual sub-units of a whole are packed into the structure (falling in the range of $1 \leq D_M \leq 3$). [D. Avnir “Fractal Approach to Heterogeneous Chemistry” Wiley, New York 1989 or Nature 308 (1984) 261]. To ease the fractal interpretation a certain scaling rule must be applied, which defines the specific overall linear growth rate, g^\rightarrow , as the ratio of the true linear growth rate, G , to the particle size, L . Particles with variable size, $L_1 \leq L \leq L_2$, are considered self-similar within the lower (1) and upper (2) cut-offs so that a range of D_r 's is obtained ranging from 0 to 5 [J. Stávek, J. Ulrich, Cryst. Res. Technol. 29 (1994) 763 and J. Cryst. Growth 166 (1996) 1053].

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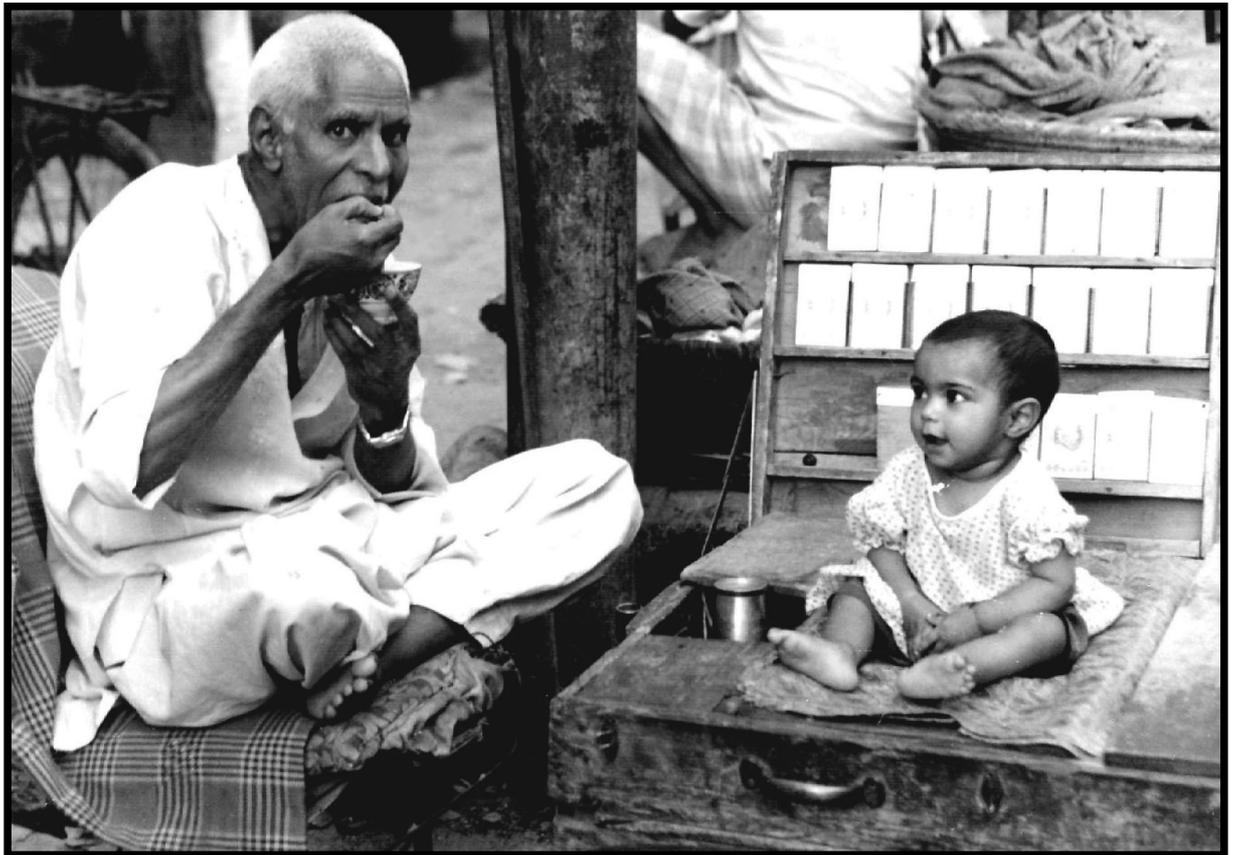
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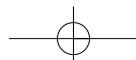
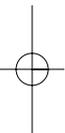
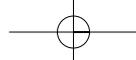
Volume three
**THERMAL TREATMENT AND THE METHODS
OF THERMAL ANALYSIS**

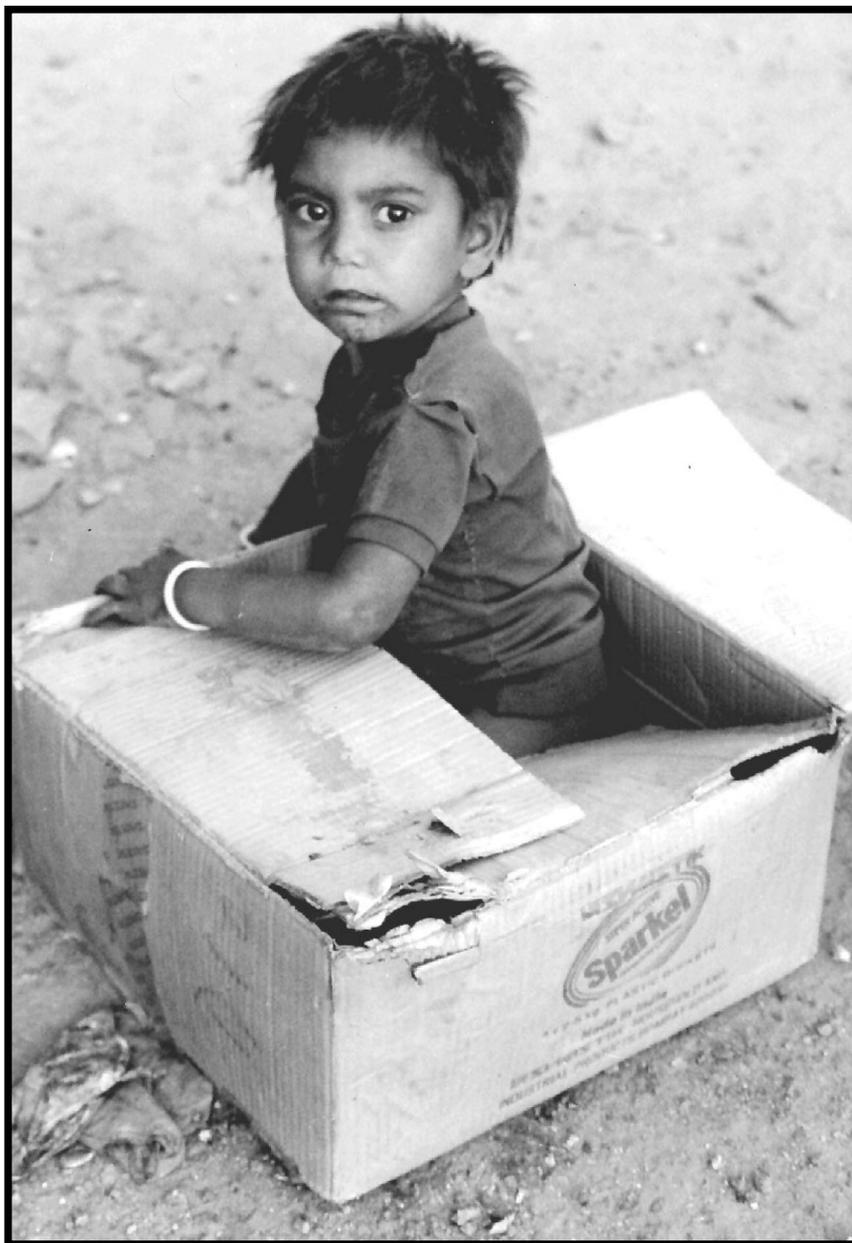
Thermophysical examination and temperature control

Thermal study of materials and substances

Thermal analysis and calorimetry

Nonisothermal kinetic by thermal analysis





CHAPTER NINE

9. Thermophysical examination and temperature control

a) Measurements and modes of assessment

Measurement is generally understood to be the conversion of a *selected physical quantity*, worthy of note due to its intended interpretation, into a *basic quantity*, i.e., the quantity that can be identified and detected with the available instrumentation [1,2]. Such basic quantities are usually electric voltage and current, or sometimes frequency. If the originally recorded physical quantities are not electrical, various *transducers* are employed to convert them duly (e.g., pressure, temperature, etc.). The measurements thus yields data on the *sample state* on the basis of the response of physical quantities investigated under certain measuring conditions applied, i.e., *experimental conditions* to which the measured object (that is called sample) is subjected. The initial conditions are understood as a certain set of these physical parameters adjusted and then applied to the sample.

In order to carry out a measurement on the sample, A, (see Fig. 9.1 – block) it is necessary that a suitable set of generators be in the block, B, acting on the sample whose response is followed in the measuring system with inputs connected to the sample. Service block, C, controls the proper setting of the generators and evaluation of the response of the measuring instrument, according to the requirements for the measurement set by block, D. The service block coordinates the overall procedure and development of the measurement, sometimes on the basis of an interpretation of the results obtained. Thus, from the point of view of the system, the experiments represent a certain flux of information through three communication levels designed in Fig. 9.1 as contacts a, b and c. Contact a represents the actual measuring apparatus which is an extremely variable and constructional heterogeneous element in each experimental arrangement. Block B generally contains the necessary converters on the input side (heating coils, electromagnets, etc.), as well as on the output side (thermoelectric cells, tensometers, etc.). If the individual parts of block B have a certain local autonomy in their functional control the block is termed an *automated measuring system*.

Block, D, contains a set of unambiguously chosen requirements defined so that the measurement results are obtained in an acceptable time interval and reliable format. It is actually a prescription for the activity of previous service block, C, and contains the formulated algo-

rithm of the measuring problem. The usual requirements for measurements actually bear typical algorithmic properties, such as unambiguous attainment of certain data at a final time, accuracy qualifying factors, etc. The service block must react to both the recording of the algorithm of the investigated problem and the correct control of setting the generators and measuring instruments. i.e., interpret the information at contacts b and c in both directions. Auxiliary service functions, such as the sample and algorithm exchange, calibration, etc., also belong here. The service block, C, must have the greatest flexibility in predicting possible effects requiring certain inbuilt smartness of algorithm applied. The manual servicing often brings certain subjective effects into the process of measurement, which can be suppressed by various inbuilt checks. On the other hand, the good quality service can compensate for poor quality in the other parts of the scheme depicted in Fig. 9.1., which can be abused so that the imperfect measurements are improved by intelligence, diligence and perseverance in the service and use. Programmable interpreters – commuters have effectively improved the performance of measurements replacing communication between service and algorithm by formal language in the strictly defined machine code.

A problem is the tendency of instruments to become over-sophisticated, in the form of impersonal “black boxes” (or less provoking “gray boxes”) that are easy to operate providing pre-analyzed results and nicely smoothed and methodical data. Attached computers, equipped with powerful programs, allow analysis and solution of most mathematical and interpretative tasks. Nonetheless, it is easy and persuasive to pass the entire responsibility for results evaluation and interpretation merely in the hands of computers. If a user agrees with such a policy, that means he accepts the ready-calculated data without taking notice of the error analysis, is inattentive to the instru-

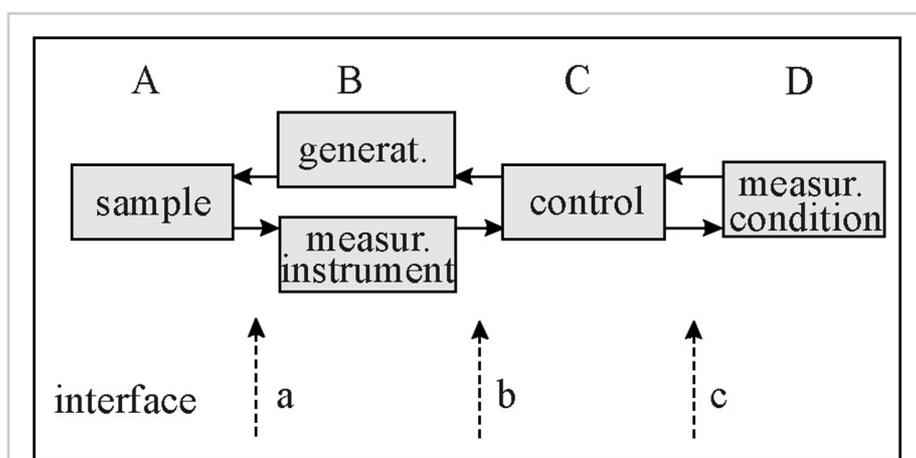


Fig. 9.1. Block schema illustrating the basic arrangement of a physical experiment, where the individual blocks A, B and C represent the essential parts of setup (e.g., sample, measuring and controlling assembly, services and established experimental conditioning). Very important role is played by interfaces (depicted as a, b and c showing the mutual contacts taking place during the measurements), namely: the sample versus detector, detector versus service and service versus surroundings.

ment calibration and performance, or does not even aspire to learn what physical-chemical processes have been really measured, it is not the manufacture's, instrument's or computer's fault, but it is sluggishness of the scientific operator.

In this respect, progress in thermoanalytical instrumentation is apparently proceeding in two opposite directions:

- (i) towards „push-and-button“ instruments with more and more functions being delegated to the computer and, in somewhat opposite direction,
- (j) towards more „transparent“ (flexible and easy to observe) instruments with well allocated all functions, that still require the researcher's involvement, experience and thus his explicit 'know-how' and perceptive scientific 'sense'.

While the first type have their place in routine analysis, mostly required in the industry, the transparent-type piece of equipment (substituting once popular, laboratory self-made instruments, where each piece was intimately known in its operative functioning) should become more appreciated in the scientific and industrial research.

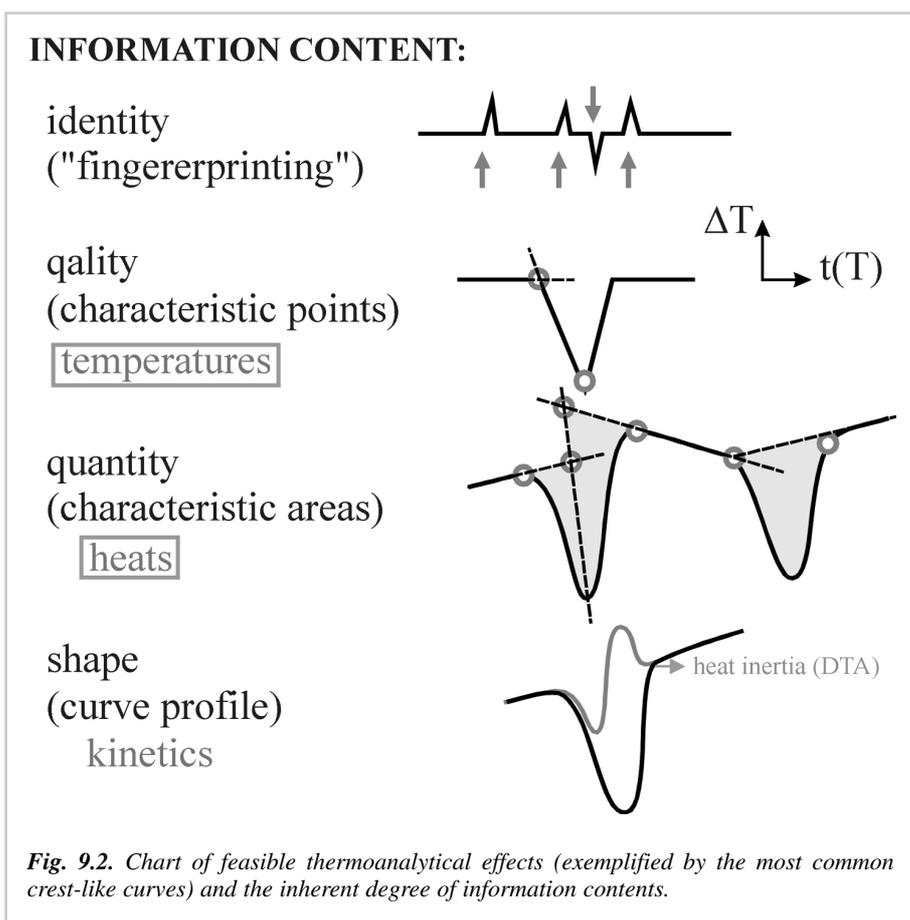
One of the most frequently controlled experimental parameter, defining the sample and its surroundings, is *temperature* leading thus to the general class of *thermo-physical measurements* [1-3]. Derived methods of *thermal analysis* include all such measurements that follow the change in the state of the sample, occurring at step-

wise or constantly changing temperature implemented around the sample (see next section). Most systematically, however, thermal analysis is understood to include mostly the dynamic procedures of temperature changes (heating, oscillations). In this sense, thermal analysis is really an *analysis* (cf. previous Fig. 1.4.) as it enables identification of the chemical phases and their mixtures on the basis of the order and character of the observed changes for a given type of temperature change. Just as in classical chemical analysis, where chemical substances act on the sample and data on the reagents consumption and the laws of conservation of mass yield information on the composition of the sample, the 'reagent' effect of heat (better saying the heat exchange between the sample and its surroundings) is found responsive to the shape of thermoanalytical curve obtained and is interpreted using the laws of thermodynamics, see schema in Fig. 9.2.

The *basic thermoanalytical methods* reveal changes in the state of the sample by direct determination of the sample single property, Fig. 9.3. In addition to such most widespread measurements of the pre-selected physical property of the sample, *indirect measurements* can also be carried out to follow the properties of the sample adjacent environment as an implied response to changes in the sample properties. If the sample property serves, at the same time, as a measured quantity to indicate the requested property of the test material, we deal with *single arrangement*, such as temperature in the case of heating and

cooling curves. *Differential methods* are those in which the measured quantity is the difference between that for the test sample and that for a reference site. The behavior of the reference specimen (a specific site) can be simulated by computer, which factually analyses the course of the temperature increase if the sample were to behave as reference material. Consequent superposition of the actual (including changes caused by the reactions involved) and the idealized (reference) curve makes it possible to calculate differences in any desired form (such as the common DTA-like trace). This method, moreover, does not require a specific temperature program as it works with any type of a smooth temperature change, e.g., self-exponential achieved by the regular sample insertion into a preheated furnace.

Simultaneous methods are those that permit determination of two or more physical para-



meters using a single sample at the same time. However, the determination of a parameter and its difference with a reference site is not considered as a simultaneous method. *Complementary methods* are those where the same sample is not used during simultaneous or consecutive measurements. *Coupled simultaneous techniques* cover the application of two or more techniques to the same sample when several instruments involved are connected through a joining interface. *Discontinuous methods* generally include the application of two or more simultaneous techniques on the same sample, where the sampling for the second technique is discontinuous. *Oscillatory and jumps methods* cover dynamic procedures where the controlling parameter is time-temperature modulated.

(5) *structural characteristics* of the sample, where the instantaneous state of the sample is given by the shape of the functional dependence (i.e., spectrum recorded for X-ray analysis or spectroscopy provided by oscillatory scanning). They are sometimes called as special methods for structural measurements. They can cover optical properties (photometry, refractometry, microscopy, luminescence, and spectroscopy) or diffraction (X-rays) and acoustic (sonometry, acoustometry) characteristics.

Detailed table, providing a more complete survey of thermoanalytical methods comprehended more universally as thermophysical measurements, was published in the appendix of my previous book [1]. Though conceptually

at little variance from the classification published by the Nomenclature Committee of ICTAC it upholds its 'thermoanalytical' philosophy. Linguistic and methodological aspects of the ICTAC accepted nomenclature, and the associated classifications, were the long-lasting subject of ICTAC activity, which is accessible elsewhere, being also the subject of internal analysis for the qualified formulation of the Czech-Slovak nomenclature [4].

The concept of experimental arrangement (often referred to and specified as the 'measuring head') is comprehended to include the positioning of the sample(s) and measuring sensor(s) as well as the type of contact between the sample and

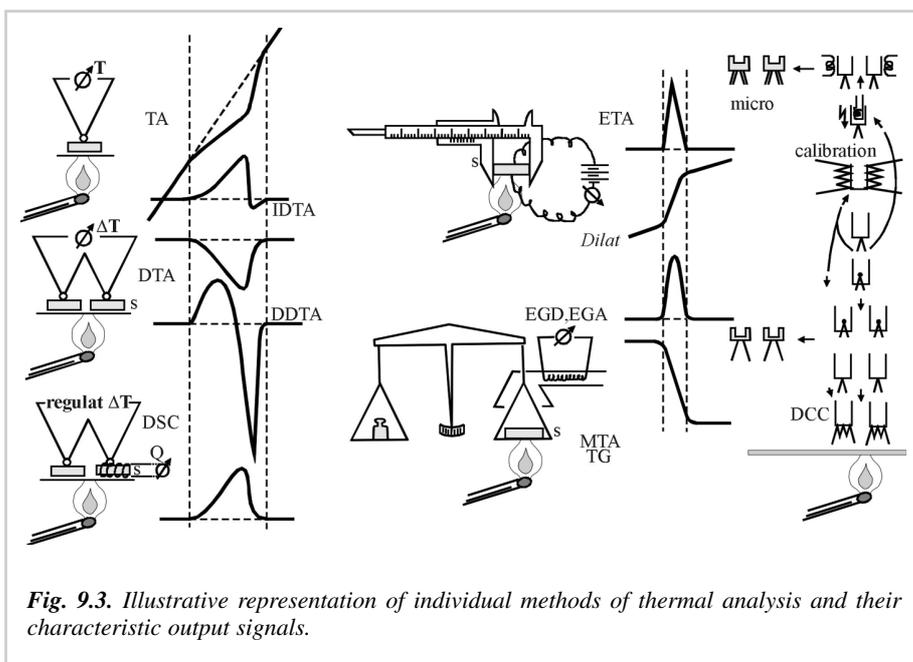


Fig. 9.3. Illustrative representation of individual methods of thermal analysis and their characteristic output signals.

Modes of thermal analysis, cf. Fig. 9.3, can be conveniently classified in the following five general groups [1] so that each measuring method is connected with a certain change in:

- (1) the *content of volatile component* in the sample (change in mass – Thermogravimetry, evolution of gas and its composition – Evolved gas analysis);
- (2) *thermal properties* of the sample (such as temperature – Heating and cooling curves, DTA, Heat flux – DSC, Power compensation – DSC; heat and pressure – Hydrothermal analysis);
- (3) other *thermodynamic properties* of the sample (electric polarization – Dielectric TA, magnetization – Magnetometry, dimension – Dilatometry, deformation – Mechanical measurements, dynamic modulus – Dynamic thermomechanometry);
- (4) *flux properties* of the sample (electric current – Electrometry; gass flow – Permeability; temperature gradient – Thermal conductivity; concentration gradients – Diffusion measurements; release of radioactive gas – Emanation analysis);

its environment, etc. These data are necessary for describing the experiment as such, especially in relation to its possible reproducibility.

Most important is the *measuring system isolation*, which can assure no exchange of heat and mass (*isolated*), enabling only heat exchange (*closed*) and making possible that all components are exchangeable (*open*). Most usually, only one particular volatile component is exchanged with the surroundings, to give a system that is termed *partially open*. Last two types of isolation are most difficult to handle, although most common, so that we shall deal with them in more details (thermogravimetry) latter on. In the actual arrangement, two types of experimental arrangement can be differentiated, the *simple arrangement* common for basic instrumentation and the *double arrangement* used in differential measurements having respectively *single* or *twin holders* to contain or to support the test specimen (sample containing cells). The *sample* is understood to be a part of the actually studied material (including the material used for dilution, if necessary) which is located in the sample holder. The

reference specimen is that part of the reference (inert) material whose behavior is known (usually not responding to changes in the state of surrounding, particularly thermally inactive over the temperature range of interest).

We can distinguish the *single point measurements* of the so-called *centered temperature* where the thermal gradient existing within the sample bulk are averaged by high enough thermal conductivity of the sample and/or its holder. *Multipoint measurements* (thermopile) make it possible either to scan temperature gradients or to localize the reaction interface or to read the mean surface temperature of the bulk. When seeking a gradientless setup, the sample size has to be miniaturized, which consequently brings problems with the appropriate sample starting weight/volume and a threshold dilemma where is the limit when we start observing surface properties of very small samples (prevailing characteristics for bulk). It can be assisted by a specially shaped sample holder, (e.g., multistory crucible where the sample is thin-layered on each ribbon), which was found suitable in thermogravimetry but which can conflict with common requirements of the sufficiently sensitive, simultaneous measurements of heat. Hence the development of apparatuses designed to indicate either intensive (e.g., *temperature*) or extensive (e.g., *heat*) properties may not follow the same path in further development.

The classification and utilization of thermal methods are matters of tradition and of specialization for individual scientific workers in the given field of science. Among traditional methods, thermoanalysts would customarily include those methods, which are associated with the detection of thermal properties (DTA, DSC) complemented by the detection of sample mass (TG) and size (dilatometry). Determination of other non-thermal properties is thought to belong more to the field of thermal physics so that magnetic, conductivity, structural measurements, etc. can thus be merely judged as complementary. It is evident that non-traditional methods used in one branch of learning can become superior in other fields of studies, e.g., solid-state chemistry would not exist without XRD or SEM, nor would physics without electric and magnetic measurements. In the latter cases,

DTA and DSC would then serve as a supplementary source of information, often considered of exploratory value, only. Simultaneously, there arise another problem how to compare correctly the results from different kinds of static (XRD, SEM, magnetic) and dynamic (DTA, TG) measurements. Individual methods can also reveal a different picture of the process/material investigated depending on the nature of physical property under measurement and its relation to the degree of observability or detectability related to the elementary subject matter.

b) Treatment of the output signal

The manner in which the value of the studied physical property is obtained, as a particular signal at the output of the measuring instrument, is determined by a number of experimental factors which can be localized in three basic parts of the measuring apparatus [1–3] (see Fig. 9.4.).

(1) The test sample

The sample response to changes in its surroundings, particularly assuming temperature, depends on its size and shape, thermal conductivity and capacity and other kinetic factors affecting the rate of production and/or sink of heat during the process. The instantaneous value of the measured quantity then depends on the character of this quantity and on the responding (consonant) physical properties of the sample investigated. Experimental arrangement is also associated with two contentious viewpoints of data interpretation, such as:

- (i) scientific search for reaction kinetics and
- (j) practical need for engineering applications.

The latter often requires:

- (a) determination of the optimum temperature region (from the economic viewpoint) for carrying out the industrial process,
- (b) prediction of the yield after a specific time of a thermal process, and
- (c) estimation of the time necessary to achieve a specific yield.

On the other hand, the kinetics seeks the determination of the characteristic parameters (whatever one wishes to

call them) and of the dependence of their values on the process progression as well as the definition of the character of the process mechanism (macro/micro-nature of the rate controlling process). Engineers aspire to use large sample to approach practical conditions of pilot processing while scientists try to diminish disturbing factors of gradients by the sample miniaturization.

(2) The measuring head

It provides the thermal and other (flow) controlled resistance at the contacting surfaces be-

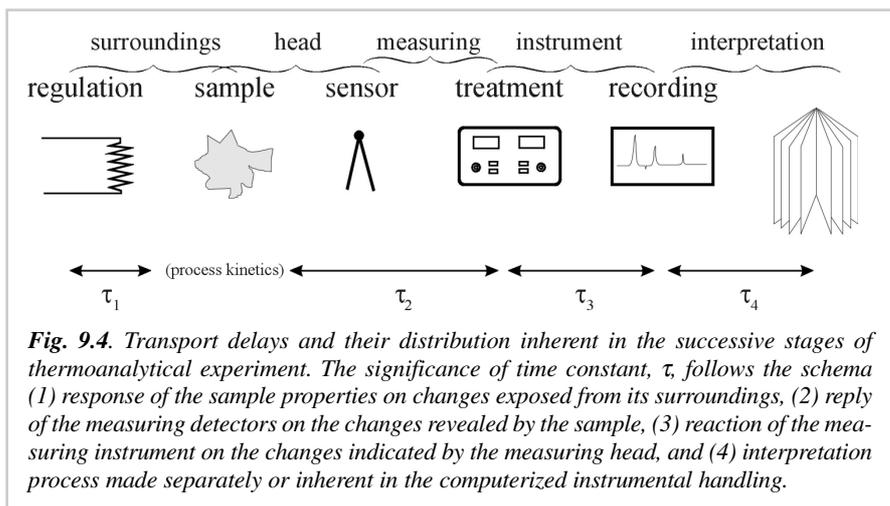


Fig. 9.4. Transport delays and their distribution inherent in the successive stages of thermoanalytical experiment. The significance of time constant, τ , follows the schema (1) response of the sample properties on changes exposed from its surroundings, (2) reply of the measuring detectors on the changes revealed by the sample, (3) reaction of the measuring instrument on the changes indicated by the measuring head, and (4) interpretation process made separately or inherent in the computerized instrumental handling.

tween the sample, sample holder and the sensor, or the chamber.

Worth separate mentioning is the process of *weighing*, which is one of the oldest and the most useful analytical methods. When it became associated with temperature changes, it matured into the recognized method called *thermogravimetry* (TG) [5–9]. Traditionally, thermobalances have been used mainly to study thermal decompositions of substances and materials; broadly speaking, in „materials characterization“. However, more and more research is being done in the field of controlled chemical reactions (including synthesis) at elevated temperatures, explored gravimetrically. The sphere of increasing importance of vapor thermogravimetry includes not only the traditional sorption research, but now also the study of equilibrium by conducting TG measurements at controlled partial vapor pressures and the desired partial pressure can be achieved either by controlled vacuum, or by dilution of the vapor with an inert gas. Modern TG instruments are capable of producing astonishingly precise data (e.g. some of them can record microgram weight changes of large samples, weighing up to 100 g). At the same time, if less-than optimum conditions are applied, the balance readings can be heavily distorted, because balances do not distinguish between the *forces of interest* and *disturbing forces*. The full extent of the balance performance is achievable and spurious phenomena can be controlled, provided that they are understood.

The most common sources of TG disturbances and errors in the sequence of the frequency of their occurrence [9] are: unstable buoyancy forces, convection forces, electrostatic forces, condensation of volatile products on sample suspension, thermal expansion of the balance beam (as a severe problem in horizontal TG's) or turbulent drag forces from gas flow. Note that the first item is the *static* buoyancy (related to the gas density), and the last one is the influence of dynamic forces of flow and of thermal convection. It is a common mistake to use the term „buoyancy“ when meaning drag. Both drag and buoyancy depend on the size and the shape of the pan plus sample, on their distance from the baffle tube, as well as on the velocity and the density of the gas. Any instability of those factors will cause erroneous weight readings. TG experiments often require a controlled environment around the sample. Operating the instrument filled with static gas would be expected to be better for the stability of the balance readings than maintaining a gas flow, but the reality is the opposite. A TG run with no forced gas flow produces an uneven and irreproducible temperature build-up in the system, resulting in irreproducible weight baseline deviations. In most instruments, it is almost impossible to have a static gas during a TG experiment. Systems containing any gas other than air must be tightly sealed or air will diffuse into the system. If the system is sealed, the pressure will build up and an unstable pressure will result. In both cases the weight readings will drift due to the buoyancy changes which result from heating.

Factors other than buoyancy also make flow beneficial for TG. Gas flowing downwards helps keep the furnace heat away from the balance mechanism. Although some TG balance mechanisms are protected against corrosion, exposure to corrosive gases should be restricted to the reaction zone (hang-down tube). Thermal decomposition often produces volatile and condensable matter, which settles on everything in its path. Whether the balance mechanism is corrosion resistant or not, there can be no protection against contamination – if the contaminants reach the balance mechanism. Some TG instruments can be used to study very large samples of plastics, rubber, coal etc., without any contamination of the moving parts of the system. These instruments require a constant flow of carrier gas. So, a flow of gas, both through the balance chamber and through the reactor tube, prevents the temperature and pressure building up and the baseline is stable. Flow also protects against corrosion and contamination. So, if „to flow – or not to flow?“ is the question, then the answer is supporting the procedure of dynamic atmospheres. Another general recommendation is to ensure that there is no gradual change in the composition of the gases inside the TG system (both locally and generally) due to incomplete replacement of the previous gas with the new one when the gases are switched. The balance chamber takes longest to switch gases completely. It may be possible with some TG models to evacuate the previous gas from the system and fill it with the new gas. Obstruction of the outlet, changing of the flow rates or the gas pressure, and shutting the purge gas off, even for a short while, can result in an unnoticed surge of the reactor gas into the balance chamber. The start of a run may have to be postponed until the intruding gas has had time to escape.

There are some golden rules of gas handling worth mentioning for any TG measurement:

- (i) It is necessary to establish (often experimentally) the optimum flows of the gases before the run and
- (j) It is not recommendable to change any settings during the entire series of tests; if gases are switched or mixed, the total flow-rate should be kept constant.

In this view, the capability of changing the flow rate (not switching the gases) by computer, would be a feature of little practical value. TG instruments are also able to operate with samples exposed to corrosive gases such as ammonia, water vapor, solvent vapors, HCl, SO₂, fumes and smoke of burning rubber or plastics, coal, etc. In most of these extreme environments, the balance chamber is isolated from the reaction chamber by purging and/or by the procedure known as „Gas-Flow Separation“. An additional and severe problem is encountered in TG studies in vapors of liquids. Unless proper techniques are used, the data may become erroneous. Attack by aggressive environments, condensation and contamination, as well as unstable buoyancy forces, are best addressed by two kinds of flow pattern:

- (i) Downward, concurrent flow of the gas which purges the balance chamber (“purge gas”) and the reaction gas or

- (j) Counter-directional flow (“gas-flow separation”) of the purge gas and the reaction gas. The first flow pattern can be generally recommended, due to its simplicity and effectiveness, whereas the latter is invaluable in those difficult cases, where no purge gas can be allowed in the environment of the sample. Gas-flow separation is possible only if:
- the purge gas used is much lighter than the reaction gas (helium is the gas of choice),
 - both gases are flowing continuously or
 - a suitable type of baffling is used.

(3) The measuring instrument

As a whole it accounts for the delays between the instantaneous values of the measured quantity provided by the sensor, i.e., the effect of electronic treatment of the basic quantities using converters. The value of beginning of the recorded signal, Z_{record} , is then related to the actual value of beginning of the studied process, Z_{proc} , by the relation ship:

$$Z_{record} = Z_{proc} + \phi (\tau_1 + \tau_2 + \tau_3) \quad 9.1$$

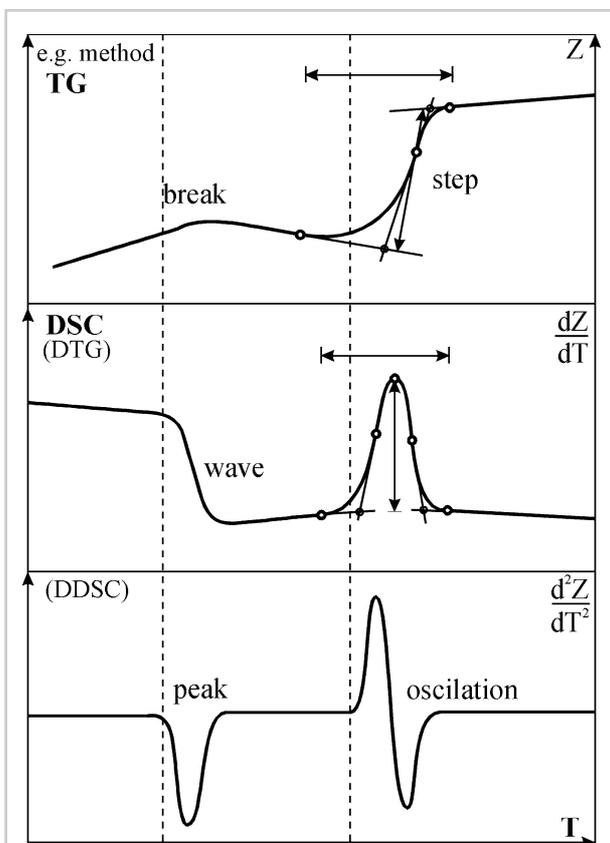


Fig. 9.5. Typical shapes of the thermoanalytical curves recorded by individual instruments in dependence to the monitored physical property, Z , as a function of temperature, T . Simpler shapes can be gradually converted into more complicated ones by dual differentiation (break to wave through mathematical manipulation, dZ/dT) or by simple geometrical combination (wave is composed of two subsequent breaks, etc.). Characteristic points marked by circles are described in the text.

where ϕ is the rate of change of the controlled parameter in the vicinity of the sample and τ are the *time constants* corresponding to the processes given under point (1), (2) and (3). Some experimentations have *detectors located outside* the chamber with the sample such as is typical for analysis of gaseous products in a stream of carrier gas or emanation TA. The description of the process, which takes place due to the interface – connecting tube is then coded into gas flow as changes in the concentration of selected products. To this detector responds and the values read at the detector output are apparently shifted in time with respect to the resultant process. It is caused by slowness of transport delay and because of distortion of the concentration profile as a result of variability of the flow of the carrier gas in the connecting tube. The detector responds to the process occurring in the measuring head only after time, $\tau = l/2 v$, where l and r is the tube length and radius and v is the mean flow-rate of the gas at a given cross-section πr^2 . An originally sharp concentration edge is washed out and transformed to a wedge-like profile on passage through the connecting tube and the overall volume of gas, v_{transp} entering the detector, or $V_{transp} = \pi r^2 v [(\tau - t) + (l/2 v)^2 (1/\tau - 1/t)]$.

(4) Kinetic aspects

We should note again that simple outcome by means of thermoanalytical kinetics (cf. Chapter 12) is generally not employed in practical engineering studies. A few engineering researchers employ the literature models of their preference, simply, using the algorithms they have purchased with their instruments, with sometimes misleading and ungrounded claims, where yet another data reporting (publication) can be the only benefit. The discrepancies and inconsistencies reported in the literature are sometimes large. Some calculated values are obviously nonsensical, e.g., negative activation energies, and there is often virtually no correlation of the values obtained from thermal analysis experiments with those typical for larger-scale industrial processes. Therefore the chances of practical utilization of the kinetic data to predict real-life processes are greatly diminished.

To minimize diffusion effects, established kinetic practice requires that samples should be as small as possible (thin layers spread on multistory crucible [10,11]). However, the smaller the sample, the greater is the ratio of its surface to its bulk and this may overemphasize surface reactions and make correlation with large-scale processes poorer. Experience shows, however, that even very small samples (less than 1 mg) are far from being small enough to be free of diffusion inhibition. To justify the obvious errors, the adjectives: „apparent“, „formal“ and „procedural“ are used in conjunction with the otherwise strictly-defined terms of “activation energy” and “reaction order” as established in homogeneous chemical kinetics. The value of the activation energy calculated for a reversible decomposition of a solid may thus be just a procedural value of no real physical meaning other than a number characterizing the individual thermoanalytical

experiment. Many sophisticated kinetic methods neglect the distinction between micro-kinetics (molecular level, true chemical kinetics) and macro-kinetics (overall processes in the whole sample bulk). The conventional process of the type, $A_{\text{solid}} = B_{\text{solid}} + C_{\text{gas}}$, as applied to the entire solid sample, consists of many elementary processes, some of them of purely physical in nature (e.g. heat transfer, diffusion). The experimentally obtained kinetic data may then refer to only one of these processes, which is the slowest one, often difficult to link up with a particular reaction mechanism.

(c) Characterization of experimental curves

The graphical or digital recording of sequences of experimental data, called the thermoanalytical curve, is the basic form of thermal analysis output and thus represents the primary source of information on the behavior of the sample [1]. Although most such curves are digitized the interpretation ability and experience of the scientist and even his subjective evaluation sense „at first glance“ will remain important. A further advantage of graphical recording is its lucidity, which is advantageous for illustrative comparison of the actual course with theoretical, or otherwise obtained one. The recording of the dependence of the measured quantity on time or temperature can be divided into two regions, cf. Fig. 9.2:

- (a) *Baselines*, i.e., regions with monotonous, longitudinal and even linear curves, corresponding to the steady changes in the state of the sample.
- (b) *Effects* (singularities) on the measured curves, i.e., regions in which at least the slope of the tangent to the curve changes (so-called stepwise changes).

The part of the baseline preceding the changes is termed the *initial baseline* and the part after the completion of the changes is called the *terminal baseline*. While a horizontal baseline is typical (and desirable) for most TA methods (TG, DTA, DSC) it may be a generally curved line (dilatometry), an exponential line (emanation TA) or even a hyperbolic line (thermomagnetometry). In most computer controlled instruments the baseline is self-corrected by inbuilt program which provides a nice result (straight line) but sometimes misleading to interpretation. Therefore both types of baselines should be available, instrument native and corrected.

The simplest pattern on the experimental curve is a *break* (or bend). It is characterized by the *beginning* and *end of the break* (and/or by the extrapolated onset point), see Fig. 9.5-shapes. Higher class of singularity is a *step* (or half-wave) which is the most typical shape to appear on experimental curves. It joins baselines of different levels and is characterized by the *inflection point* in addition to previous beginning and end points. It is composed of two consequent breaks. The difference between the value of the measured quantity at the beginning and end is termed the *height* of the step and the difference in its time or temperature coordinates is the *length* of the step (also called *reaction interval*). A *peak* is that part of the curve, which departs from, and subsequently returns back

to the baseline and factually is composed of two consecutive steps or four breaks. The peak is characterized by its *maximum point* besides the (*frontal and terminal*) inflection points and beginning and end points. The extrapolated *onset* is found as the intersection of the extrapolated initial baseline and the tangent to the frontal inflection point. The extrapolated end point (*outset*) is obtained analogously. The linearly interpolated baseline is then found by suitable joining these points. The actual peak background may, however, be different as is found for DTA peak in the form of its S-shaped base-boundary, see Chapter 11. The *tip* of the peak is the point through which the tangent constructed at the maximum deflection parallel to the peak background passes. The peak *height* is thus vertical distance to the time or temperature axis between the value of the measured quantity at the peak tip and the extrapolated baseline. The peak *area* is that enclosed between the peak and its interpolated baseline.

Generally, simpler shapes can be converted into more complicated ones by dual differentiation and/or combination. A step is the derivative of a break and similarly a peak is the derivative of a step. Differentiation of a peak yields an oscillation with three inflection points and two extremes. This shape is most sensitive to the determination of characteristic points (the initial and end points of the peak appear roughly as the inflection points, while the inflection points of the peak appear as extremes which are most noticeable). The oscillation, however, no longer contains the original quantitative information, such as the peak height or area. The gradual succession of derivatives bears the same sequence as the progressive extraction of thermodynamic quantities, e.g. from heat/entropy to heat capacity.

- The information coded in a thermoanalytical curves can be found gradually richer, increasing in the dependence on the type of experiment carried out, cf. Fig. 9.2:
- (a) qualitative information about the *identity* (fingerprinting) of the test sample
⇒ spectrum effects
 - (b) location in the temperature axis, i.e., the *temperature region* in which a state change of the sample occurs
⇒ position of the effect
 - (c) quantitative data on the *magnitude* of the change
⇒ size of the effect
 - (d) *course* and rate of the change (kinetics)
⇒ shape of the effect.

From the point of view of *information gain* (understood as the determination of effectiveness of our efforts) the TA experiment must be considered as means for decreasing the inexactness of our knowledge. If the position of a TA effect is found directly from the tables without measurements, then irrelevant (zero) information is obtained. If, however, one of the four possible phases of a material is found on the basis of identification of a TA effect between the other singularities on the TA curve, then the information gain equals two

Objective evaluation for furnishing a suitable equipment for TA laboratory, automated data treatment and the

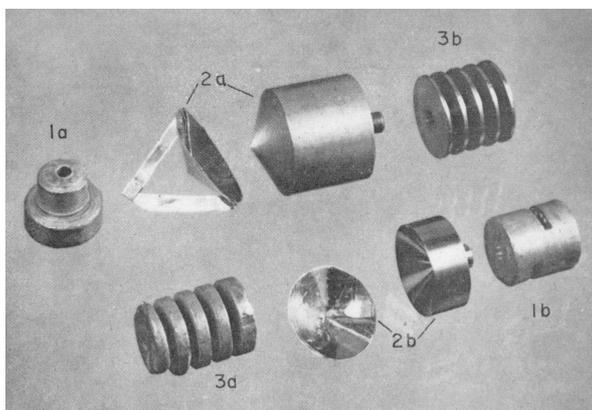


Fig. 9.6. Practically employed crucible-holders suitable to enhance the study of the decomposition of solid substances (designed by the author and self-constructed in the laboratory of the Institute of Physics at the turn of nineteenth sixties): 1a) Perforated silver block with the multiple of shallow

hollows (containing the investigated sample in the outer-wall) while the viewed hollow in the inner wall serves for the setting in of the corundum double-capillary with a thermocouple. The version with the narrow hollows (about 1mm diameter capillaries) and with different depth, see 1b, was used to investigate diffusion progress through the given sample deepness. 2a) A conical silver block with a very light fitting lid (left) on which the investigated sample is spread out in a thin layer and which is set to fit on the tapering top of the metal block (located in a furnace with the stabilized temperature). This arrangement was found convenient for isothermal decompositions because it helped to attained suitably rapid temperature equilibration between the inserted lid with the sample and the preheated block held at selected temperature. 2b) this is the similar arrangement as before but made of platinum with the sample-cone adjustment in reverse position. 3) The ribbed crucibles intended to carry out non-isothermal decompositions for a thin layer of sample spread on the ribs of such a multistory holder in order to diminish the temperature gradient within the sample using two construction materials: platinum (b) and silver (a).

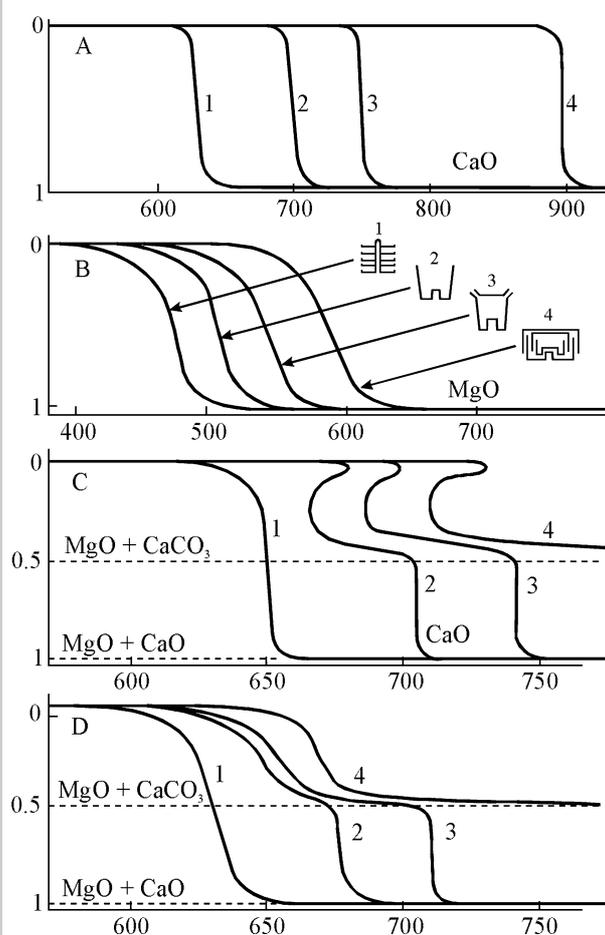


Fig. 9.7. Examples of the so called 'quasi-isothermal' curves determined by once very popular thermoanalytical instrument 'Derivatograph' (produced commercially by the brothers Pauliks in Hungary from the beginning of sixties). A special

case of monitoring the sample temperature during the thermogravimetric measurements (for preferably decomposition-type processes) employed different types of gas-tightened crucibles being capable to enrich the disconnection of individual reaction steps and hence provide a more selective differentiation of the consecutive responses. It literally falls into a more general fashion of the so called 'constant decomposition rate thermal analysis' (later more precisely diagnosed by Rouquerol). The individual curves correspond to the crucibles employed, i.e., (1) multistory (ribbed) sample holder enabling free gaseous products exchange out from the sample thin layer, (2) a deep crucible without any cover self-hindering easy path of gaseous products through the sample mass, (3) yet more constricted passage by well adjust lid and (4) stepwise escape of gaseous products through a multiple-lid arrangement called a composite crucible with labyrinth. The crucibles were applied to investigate following samples: (A) Decomposition of calcite (CaCO_3), which is strongly dependent on the partial pressure of CO_2 any increase of which above the sample surface is necessarily accompanied by a shift in the decomposition temperature above its normal equilibrium value. (B) For the case of magnesite, MgCO_3 , the decomposition already proceeds above its equilibrium temperature so that even the decomposition temperature stays roughly unchanged with increasing CO_2 partial pressure but the curve shapes are affected. (C) Decomposition of dolomite, $\text{MgCa}(\text{CO}_3)_2$, is the symbiosis of the two previous cases. After a delay caused by equilibrium set-up of decomposition due to the accumulation of CO_2 , the measured curves have a tendency to return to their original decomposition course. (D) An addition of a suitable component (nucleator such as 2% of NaCl) can lead to disappear the incubation period enabling the early decomposition to proceed at lower temperatures while the second-bottom parts remain approximately unaffected. More detailed analysis of such environmental effects due to the gaseous products buildup become very important in distinguishing the macroscopic and microscopic effects responsible for the determination of overall kinetics. [Courtesy of F. Paulik, Budapest, Hungary]

choice of most relevant information out from possibly parallel figures and successful solution of a given problem, lead to a more responsible direction of the progressive enhancement of research work. The main problem of such quasi-stationary measurements is the intricacy to decipher all the complex information hidden in a single curve.

d) Purpose of the measurement – exemplifying thermogravimetry

Most experiments are carried out in order to evaluate the course of a certain process and can be carried out in the following manner [9]:

- (1) By studying one or a few partial, isolated processes, using suitable arrangement of the experimental set up. The results can be interpreted within a suitable physical framework.
- (2) By studying the process as a whole, possibly simulating industrial conditions, and interpreting the result either empirically or within engineering convenience [12].

For thermogravimetry the decomposition rate of the same sample, in the same vessel, but at various values of the isothermal temperature should preferably be recorded. If the process is *diffusion-controlled*, measuring the magnitude of the influence of diffusion-related factors, e.g., the size and shape of the sample, or can confirm this by varying the partial pressure of the volatile decomposition product, up and down from the basic conditions of the experiment. The magnitude of the resulting variation in the reaction rate is then compared to the magnitude of the change calculated for a diffusion-controlled process. If, for example, the decomposition of a hydrate is studied in an environment of 10 mbar of water vapor, the run should be repeated twice: say under 9 mbar and under 11 mbar (such instruments are now commercially available). If the magnitude of the change in the reaction rate by diffusion-related factors is negligible, but the temperature dependence is strong, the process may follow the *Arrhenius* equation and kinetic equations based on it. If the magnitude of the measured temperature-related changes in the reaction rate is in the range typical of diffusion-controlled processes, the process probably is diffusion-controlled. A simplified way of determining whether a given reaction is mass-transport controlled would be to compare (in a non-quantitative way) the TG curves obtained when the degree of the transport hindrance of removing the volatile products of the decomposition is changed. This could be diminished by spreading the sample into a thinner layer placed onto the large enough surface such as on the shaped sample holder having the plateau (multi-store or ribbed crucible), first introduced

to TG practice by Šesták at the turn of sixties. [10,11] Fig. 9.6. On the contrary, the diffusion can be slowed down when the powder samples is well packed into capillaries [11]. Alternatively the same sample can be sited in a more voluminous crucible, which is covered by less or more tightened lid to restrain volatile products from being easily taken away. As a result, the labyrinth-type crucibles were invented by the brother *Pauliks* and put in a very popular practice elsewhere [8], often known under the name of *derivatography*, see Fig. 9.7.

Relatively minor changes in the reactant diffusion paths should not significantly affect the rate of bond-breaking steps. Heat exchange, however, may be affected more, but that is likely to be a negligible factor, again. If heat transfer controls the process (hence this applies only to programmed temperature experiments, or the initial stage of heating to the isothermal temperature), this can be confirmed by slightly increasing the ramping rate. If heat transfer is the controlling process [13], the rate of the weight loss will not increase, or the approximately straight segment of the TG curve (plateau on the DTG curve) will become straighter and longer. The temperature range of the decomposition process will not shift towards higher temperatures. The magnitudes of the influences of temperature-related factors, e.g., changing the thickness of the walls of a highly-conductive sample holder; adding or removing thermal insulation; comparing the decomposition in shiny and in black sample holders, or by making the temperature oscillate (square wave) very slightly around the set isothermal level, can all be investigated. Where heat flow is rate controlling, the response should be directly proportional to the magnitude of the temperature jumps.

To illustrate the problems discussed, we refer to some published TG results for the hydrates of copper sulfate

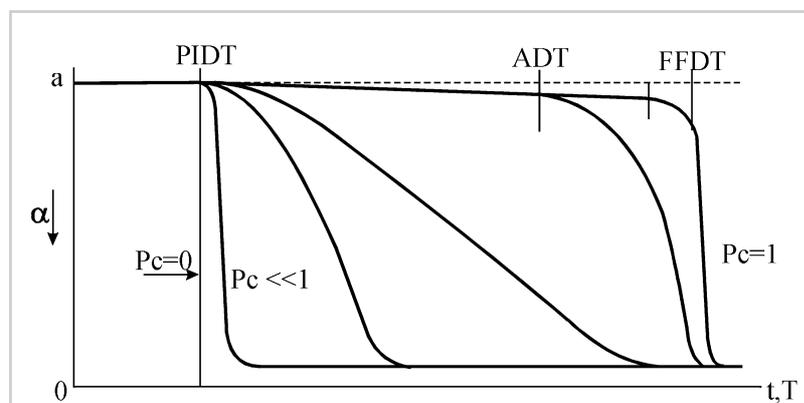


Fig. 9.8. Graphical representation of thermal decomposition at various constant values of concentration of the gaseous products – from the left vertical line, at $p_c \approx 0$, to the far right curve, at $p_c \approx 1$. Explanation of proposed definitions for TG curves obtained at various degree of hindrance of escape of the gaseous products of the decomposition: PIDT – procedure independent decomposition temperature ('pivoting point'), ADT – augmented decomposition temperature (often called procedural decomposition temperature) and EFDT – forced flow decomposition temperature. The dashed line is extension of the initial, perfectly horizontal section of the TG curve.

and magnesium sulfate [14], which were obtained over a broad range of conditions of hindrance of water vapor escape. What causes these hydrates, commonly believed to be stable at room temperature, to decompose rapidly and release their water much below the boiling point of water? Let us visualize the processes involved, and discuss in detail the concept of decomposition temperature. The observed behavior of the hydrates can be explained if the kinetics of these decompositions is limited by the rate of escape of the gaseous product, C (water). Even at room temperature, the decomposition is fast whenever the volatile product is being rapidly removed. When C is not removed, the decomposition almost stops and the reactant seems (erroneously) to be stable. It would be unreasonable to interpret this behavior in any micro-kinetic terms. This means that the decompositions of these, and many other hydrates, which behave similarly, are diffusion-limited (but the controlling factor is effectively the concentration of C). At a given temperature, either solid, A or B, is the energetically stable form, but not both. When the temperature of the substance rises, at the point marked [9,14] as „PIDT“, i.e., *Procedure-Independent (equilibrium-like) Decomposition Temperature*, the decomposition and the recombination have equal likelihoods, see Fig. 9.8. Above the PIDT point, the decomposition into B + C is energetically favored, but the decomposition would be suppressed if molecules of C are present in the immediate vicinity of the surface of A. In that case the equilibrating temperature is increased to a new value; let us call it the “ADT” for the „*Augmented (pseudo-equilibrium) Decomposition Temperature*“.

If the pressure of C is constant with time and uniform in the whole sample, and there is no air or other gas in the vessel, the ADT is still a sharp point. If it is not a sharp point, this indicates a coexistence region of solid mixtures of A and B. Such coexistence means the existence of a reaction front, or possibly enforced metastability, of A beyond its true stability range. Such metastability can occur when the partial pressure, p_c , is not a constant value, that is if p_c varies with time, location, or both. The section of the TG curve associated with the ADT is the temperature range where both A and B forms co-exist in a negative feedback of a dynamic pseudo-equilibrium (see Fig. 8. again). Labyrinth crucibles [8] are found as useful qualitative tools for making available saturation conditions of the volatile decomposition products, and improving the reproducibility of the data.

Let us return to the concept of the PIDT point that separates two sections of a TG curve: the *perfectly* horizontal section (if it exists), and the inclined one. It is usually possible to see the PIDT if the TG curve was obtained without diffusion hindrance (samples usually not larger than 1 mg, under vacuum). Even if these two slopes differ almost insignificantly, that elusive point remains the borderline between the stability ranges of the substances A and B. By hindering the escape of gas we can decrease the slope of the inclined section even to zero, and then the point PIDT would *seemingly* disappear. The reason why

the distinction between the perfectly horizontal and the inclined section of TG curves is important is as follows. Below the PIDT, curves are horizontal because decomposition cannot occur due to thermodynamic factors. Above the PIDT, curves can still be horizontal because decomposition cannot *proceed* due to accumulation of the product. Another important difference between the two sections is that only in the inclined section is the slope diffusion-dependent, because in the true-horizontal region molecules of the gaseous product C do not form. It may not be possible to see the PIDT point on a TG curve and only the ADT instead, but this does not make the ADT the same as the PIDT. Even if the PIDT is hidden, its value is fixed. Extrapolation of such a TG curve produces the ADT, not the PIDT.

If the escape of gas C is *completely* free, the ADT will disappear and the true pseudo-equilibrium PIDT emerges. Such elimination should be ensured and verified, not just assumed. A suggested procedure, which satisfies such requirements, would be as follows:

- (i) place not more than 1 mg of the powdered sample in a TG sample holder, at ambient pressure and temperature, and record the mass for at least several hours;
- (ii) continue the recording for several more hours while evacuating the TG system;
- (j) keep evacuating and apply very slow linear heating;
- (jj) the lowest temperature that will start a measurable slope, is the PIDT.

There may be cases when the PIDT cannot be obtained because the substance can decompose under vacuum even at room temperature (so no true horizontal baseline is obtained under vacuum). The PIDT then lies in a lower temperature range than that being considered.

Does a “decomposition temperature” actually exist? By definition, as long as the reaction is reversible, there is a never-ending competition between decomposition and recombination. At equilibrium, molecules of C are constantly being produced and consumed, but if the liberated C molecules are removed, then we have a non-equilibrium situation and substance A decomposes irreversibly until it disappears completely. These processes take place at any temperature within the reversibility range. Most such decompositions are endothermic and the entropy of decomposition is also positive, so the Gibbs energy change for decomposition will only be negative at high T and positive at low T (ΔG at temperature T will be given by $RT \ln(Q_p/K_p)$ or $RT \ln(p/p_{eq})$, where Q_p is the reaction quotient, p is the actual pressure of C, and p_{eq} is the equilibrium pressure of C at T). When p is kept small, ΔG will be negative at all temperatures T, but the rate of decomposition will be determined by the Arrhenius equation. Therefore there is no unique decomposition temperature. The term „decomposition temperature“ has a thermodynamic meaning of the switching point at which the decomposition reaction replaces the recombination reaction as the thermodynamically favored process (with other conditions such as pressures of any gases held constant).

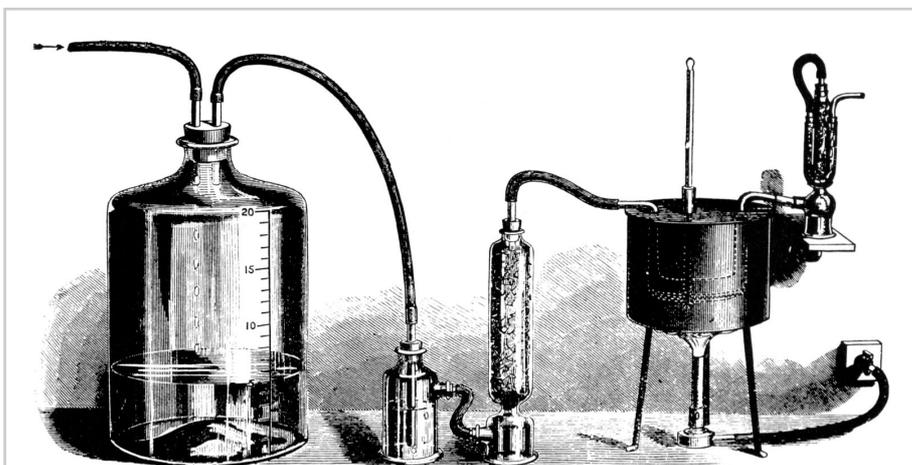


Fig. 9.9. Apparatus used by Hannay in the 1877 to obtain isothermal mass-change curves.

Not only the physical meaning, but also the earlier metrological definitions of „Decomposition Temperature“ do not seem to be consistent. The terms „Decomposition Temperature“, „Procedural Decomposition Temperature“ („PDT“) or „Initial Temperature“ (T_i) are often defined as the lowest temperature at which the rate or the cumulative weight change of the decomposition is measurable. The symbol T_i is also used for that, sometimes marked as $T_{0.01}$ (for the transformation ratio, $d\alpha/dt$, as low as about 0.01). A „Temperature of Thermodynamic Stability“ (T_{th}) is defined as the „temperature at which the partial pressure of the gaseous product equals the ambient pressure.“ It is believed that for the decomposition to take place, the temperature must be „the lowest temperature at which the decomposition is measurable“ (T_1 , $T_{0.01}$, T_i , PDT). The physical meaning of lowest temperature, at which the rate or the cumulative decomposition is *measurable*, is inevitably narrowed to the particular conditions and sensitivity of the thermoanalytical experiment. In the first approximation it has no absolute value, in the same way, as the beginning of a TG-recorded evaporation of a liquid below its boiling point would be a merely procedural value, lacking any absolute physical meaning. It has also very limited practical significance. The literature abounds in examples of the fact that appreciable decomposition is often recorded at temperatures much below the values generally accepted or expected. For example copper sulfate pentahydrate is capable of producing TG curves, for which the T_1 , $T_{0.01}$ or T_i can be sometimes as high as 100 °C, and as low as 40 °C. One can justifiably interpret these facts in the following way: copper sulfate pentahydrate decomposes below room temperature, but it appears stable because the decomposition in a closed container at room temperature is hindered. Therefore neither 40 °C nor 100 °C are values of any absolute meaning. If the TG examination of a small sample of that hydrate had started, not at 20 °C but below room temperature, the apparent decomposition temperature would be even lower than 40 °C. For very

carefully planned TG experiments, „practically horizontal“ curves can be obtained and the PIDT, measured as the „first detectable deviation“, then becomes an absolute value. Relying on the ADT as an indication of the limits of thermal stability of a substance can be a dangerous mistake. The only reliable value representing thermal stability is the PIDT.

The future role of TG instruments is anticipated to become gradually reduced to verification of the validity of highly computerized modeling that would gradually include all the possible processes discussed

above. Such an extensive theoretical treatment, that would comprehensively cover all the various aspects of a detailed scientific and engineering description, would become the principal method for the forthcoming prediction of the behavior of materials. It would essentially lower the number of instrumental measurements and save both time and labor. Experimentation would, however, need to be perfected to such an extent that each measurement is reliable and meaningful. Not all measurements are yet adequately reliable. Artifacts are easily produced if we allow a computer to plan an experiment for us. This is frequently the case when „rate-controlled TG“ is used. Many thermal processes are characterized by TG curves consisting of more than one weight-loss step. This may result from a sample being a mixture, or from the reactant undergoing a multi-step thermal transformation. These TG steps may overlap partly or completely. When the stoichiometry of a multi-step TG process is determined, the weight value at the horizontal section of the TG curve is used as the indicator of the stoichiometry. This is the basis for „compositional analysis“. If no horizontal section between the steps exists, the inflection point is used for that purpose. The inflection point on a TG curve can be precisely determined from the DTG curve, but the inflection point is *not* a direct indication of the stoichiometry in the common situation of incompletely separated TG steps. The mathematical addition of partly overlapping individual TG steps (or of any other curves of similar shape) produces TG curves whose inflection points consistently fall below the stoichiometric values. This fact (belonging to analytical geometry) is seldom realized in thermal analysis. It is frequently observed that the location of the inflection point varies for TG curves obtained under different conditions. These shifts are attributed to experimental parameters, such as sample geometry. In the case of partly-overlapping TG steps, the common practice of using the inflection points to obtain stoichiometric values, may lead to systematic errors of up to 20%. Moreover, the common practice of attributing

those „shifts in the stoichiometric values“ to changes in the reaction mechanism seems to be disputable, unless supported by other facts. A practical way of finding the inflection point is to use an appropriate deconvolution program on the DTG curve. The largest errors can result when the single steps that make a combined two-step TG curve are symmetrical. Asymmetrical steps produce smaller errors, because the weight changes are much slower at the beginning of the second step, than at the end of the first one. Therefore, the error caused by including the initial weight changes of the second step into those of the first step is less significant.

e) Origins of modern thermal analysis

Thermal analysis [1,5,15–17] did not, as frequently inferred, suddenly appear in the year 1887, their roots extended back to the eighteenth century where temperature became an observable, experimentally decisive and monitorable parameter. Indeed, its development was gradual and somewhat international so that it is difficult to ascribe an exact date. First accepted definition of thermal analysis permits, however, identification of the earliest documented experiment to meet current criteria. In Uppsala 1829, *Rudberg* recorded inverse cooling-rate data for lead, tin, zinc and various alloys. Although this contribution was recognized in Russia (*Menshutkin*) it was overlooked in the interim and it is, therefore, worthwhile to give a brief account here.

The equipment used consisted of an iron crucible suspended by thin platinum wire at the center of a large double-walled iron vessel provided with a tight-fitting, dished with iron lid, through which passed a thermometer with its bulb in the sample. The inner surface of the outer container and the outer surface of the crucible were blackened to permit maximum heat transfer and the spaces between two walls of the outer large vessel, as well as the top lid, were filled with snow to ensure the inner walls were always at zero temperature. In this way a controlled temperature program was ensured once the crucible with molten metal or alloy had been positioned inside and the lid closed. Once the experiment was set up *Rudberg* noted and tabulated the times taken by the mercury in thermometer to fall through each 10 degrees interval. The longest interval then included the freezing point.

The experimental conditions were, if anything else, superior to those used by careful experimentalist, *Robert-Austin*, some 60 years later. The next experiment that falls into the category of thermal analysis was done in 1837 when *Frankeheim* described a method of determining cooling curves on temperature vs. time. This method was

often called by his name as well as by another, e.g., the so-called “*Hannay's time method*”, when temperature is increased every time so that the plot resembled what we would now call ‘isothermal mass-change curves’ (see Fig. 9.8.). *Le Chatelier* adopted a somehow more fruitful approach in 1883 that immersed the bulb of thermometer in the sample in an oil bath maintaining a constant temperature difference of 20° between this thermometer and another one placed in the bath. He plotted time temperature curve easily convertible to the sample vs. environmental temperatures, factually introducing the ‘constant-rate’ or ‘quasi-isothermal’ program. Thermocouples were at that time liable to give varying outputs but *Le Chatelier* first attributed the arrest at about red heat in the output of the platinum-iridium alloy to a possible phase transition and deduced that varying output could result from contamination of one wire by diffusion from the other as well as arising from the non-uniformity of wires themselves. The better homogeneity of platinum-rhodium alloy led him to the standard platinum – platinum/rhodium couple so that almost seventy years after the observation of thermoelectricity, its use in pyrometry was finally vindicated.

The development of thermocouple, as an accurate temperature measuring device, was rapidly followed by

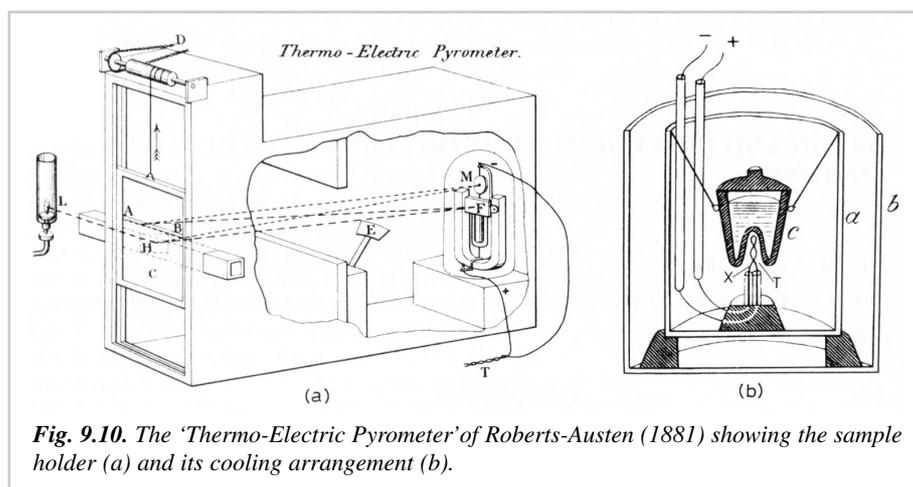


Fig. 9.10. The ‘Thermo-Electric Pyrometer’ of Roberts-Austen (1881) showing the sample holder (a) and its cooling arrangement (b).

Osmond (1886) who investigated the heating and cooling behavior of iron and steel with a view to elucidating the effects of carbon so that he introduced thermal analysis to then most important field of metallurgy. *Roberts-Austen* (1891), however, is known to construct a device to give a continuous record of the output from thermocouple and he termed it as ‘Thermoelectric Pyrometer’, see Fig. 9.10. Though the sample holder was a design reminiscent of modern equipment, its capacity was extremely large decreasing thus the sensitivity but giving a rather good measure for reproducibility. It was quickly realized that a galvanometer was too insensitive to pick up small thermal effects so that it was first improved by using two galvanometers simultaneously and later the reflected light beam was directed to the light-tight box together with the slit system enabling exposition of the repositioned photographic plate.

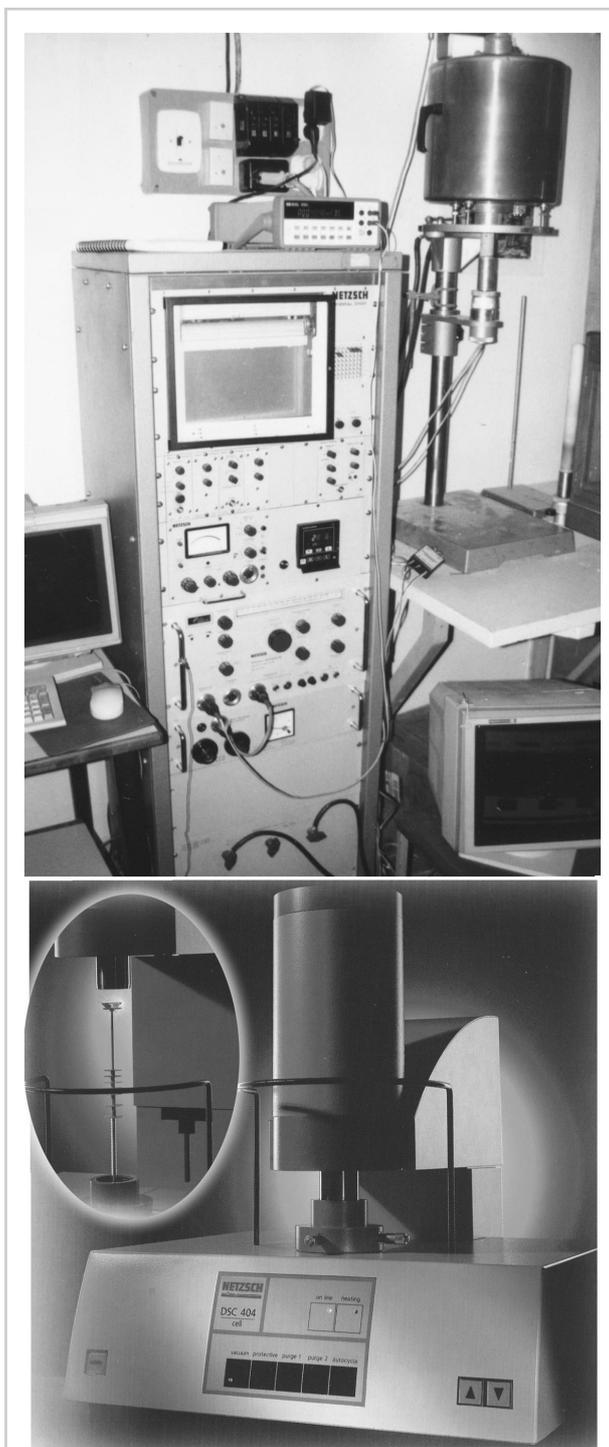


Fig. 9.11. Photo of once very popular and widespread high-temperature DTA instrument (produced by the Netzsch Gerätebau GmbH in sixties), that survived in operation in our laboratory until now while subjected to computerization and modern data processing). Below is shown the new, third-generation version of the high-temperature DTA (DSC 404 C Pegasus) produced recently by Netzsch-Gerätebau GmbH, which is capable to adjust wide range of heating from low (-50) up to very high temperatures (1650 °C). The experimental examples displayed within the text of this book were made on either of these instruments.

Stanfield (1899) published heating curves for gold and almost stumbled upon the idea of DTA (*Differential Thermal Analysis*) when maintaining the ‘cold’ junction at a constant elevated temperature measuring thus the differences between two high temperatures. *Roberts-Austen* consequently devised the system of measuring the temperature difference between the sample and a suitable reference material placed side-by-side in the same thermal environment, thus initiating development of DTA instruments. Among other well-known inventors, Russian *Kurnakov* should be noticed as he improved registration building his pyrometer on the photographic, continuously recording drum, which, however, restricted his recording time to mere 10 minutes. The term thermal analysis was introduced by *Tamman* (1903) [18] who demonstrated theoretically the value of cooling curves in phase-equilibrium studies of binary systems. By 1908, the heating or cooling curves, along with their rate derivatives and inverse curves, assumed enough sufficient importance to warrant a first review and more detailed theoretical inspection, *Burgess* [19].

Not less important was the development of heat sources where coal and gas were almost completely replaced by electricity as the only source of controllable heat. In 1895, *Charpy* described in detail the construction of wire-wound, electrical resistance, tube furnaces that virtually revolutionized heating and temperature regulation [20]. Control of heating rate had to be active to avoid possibility of irregularities; however, little attention was paid to it as long as the heat source delivered a smooth temperature-time curve. All early users mention temperature control by altering the current and many descriptions indicate that this was done by manual or clockwork based operation of a rheostat in series with the furnace winding, the system still in practical use up to late fifties. The first published automatic control was published by *Friedrich* in 1912, which used a resistance box with a specially shaped, clock-driven stepped cam on top. As the cam rotated it displaced a pawl outwards at each step and this in turn caused the brush to move on to the next contact, thus reducing the resistance of furnace winding. Suitable choice of resistance and profiling of the cam achieved the desired heating profile. There came also the reduction of sample size from 25 g down to 2.5 g, which reduced the uncertainty in melting point determination from about 2 °C to 0.5 °C. Rates of about 20 K/min were fairly common during the early period latter decreased to about quarter. It was *Burgess* who considered significance of various curves in detail and concluded that the area of the inverse-rate curve is proportional to the quantity of heat generated divided by the rate of cooling.

The few papers published in the period up to 1920 gave little experimental details so that *White* was first to show theoretically in 1909 the desirability of smaller samples. He described an exhaustive study of the effect of experimental variables on the shape of heating curves as well as the influence of temperature gradients and heat fluxes taking place within both the furnace and the sample

[21]. It is obvious that DTA was initially more an empirical technique, although the experimentalists were generally aware of its quantitative potentialities. The early quantitative studies were treated semi-empirically and based more on instinctive reasoning and *Andrews* (1925) was first to use *Newton's Law* while *Berg* (1942) gave the early bases of DTA theory (independently simplified by *Speil*). In 1939 *Norton* published his classical paper on techniques where he made rather excessive claims for its value both in the identification and quantitative analysis exemplifying clay mixtures [22]. *Vold* (1948) [23] and *Smyth* (1951) [24] proposed a more advanced DTA theory, but the first detailed theories, absent from restrictions, became accessible by *Keer, Kulp, Evans, Blumberg, Erikson, Soule, Boersma, Deeg, Nagasawa, Tsuzuki, Barshad, etc.*, in the course of fifties. For example, *Erikson* (1953) reported that the temperature at the center of a cylindrical sample is approximately the same as that for an infinitely long cylinder if its length is at least twice its diameter. Similarly, the diameter of a disk-shaped sample must be at least four times its thickness.

Most commercial DTA instruments can be classified as a double non-stationary calorimeter in which the thermal behaviors of sample are compared with a correspondingly mounted, inert reference. It implies control of heat flux from surroundings and heat itself is understood to be a kind of physico-chemical reagent, which, however, could not be directly measured but calculated on the basis of the measurable temperature gradients. We should remark that heat flow is intermediated by massless phonons so that the inherent flux does not exhibit inertia as is the case for the flow of electrons. The thermal inertia observed in DTA experiments is thus caused by heating a real body and is affected by the properties of materials, which structure the sample under study.

Theoretical analysis of DTA is based on the calculation of heat flux balances introduced by *Factor* and *Hanks* [25], detailed in 1975 by *Grey* [26], which premises were completed in 1982 by the consistent theory of *Šesták* [1]. It was embedded within a 'caloric-like' framework (cf. Chapter 4) as based on macroscopic heat flows between large bodies (cells, thermostats). The need of a more quantitative calibration brought about the committed work of ICTAC [1,4,30] and the consequently published recommendations providing a set of the suitable calibration compounds. It was extended by use of pulse heating by

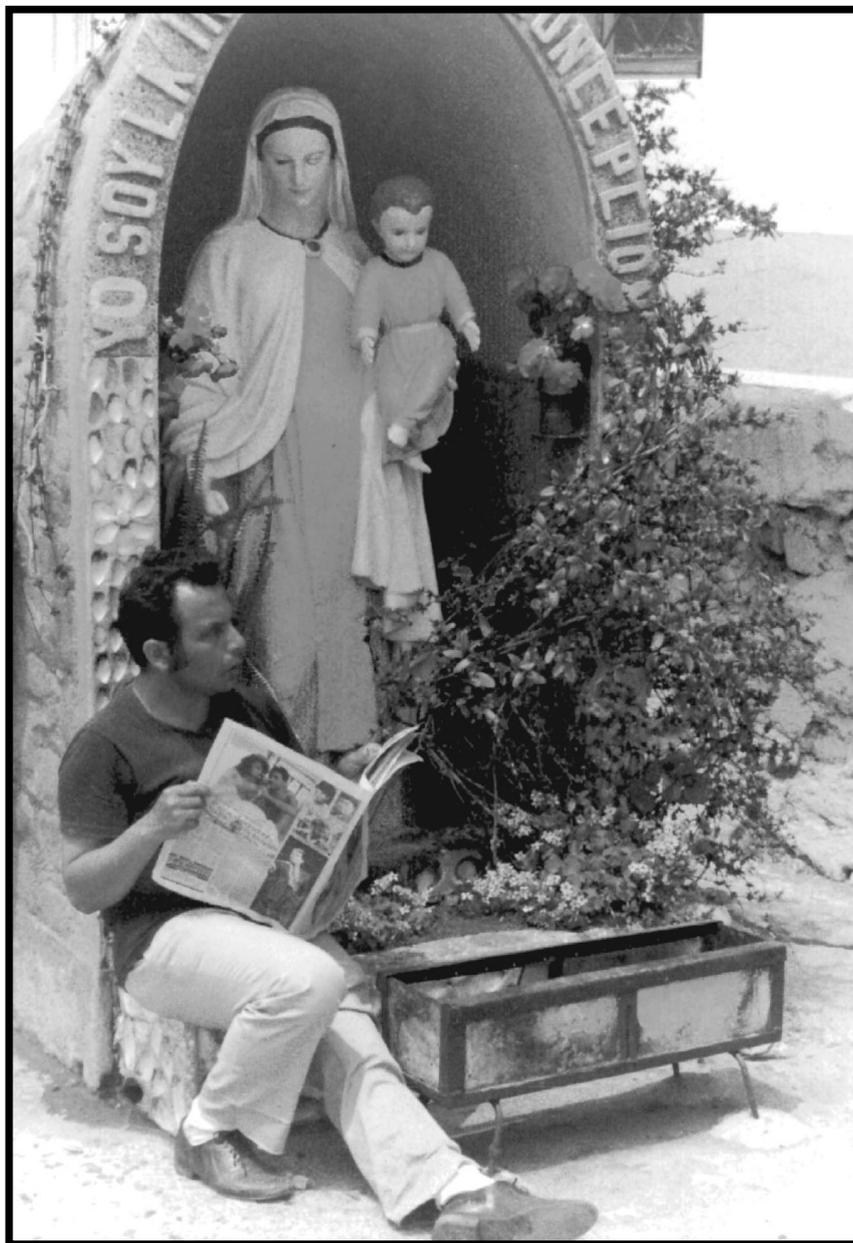
defined rectangular or triangular electric strokes (see the following Chapter 11).

Calorimetrically 'pure' (i.e. heat inertia absent) became the method of DSC (*Differential Scanning Calorimetry*), which is monitoring the difference between the compensating heat fluxes (by two extra micro-heaters respectively attached to both the sample and reference in order to keep their temperature difference minimal) while the samples are maintained in the pre-selected temperature program (*Eyraud* 1954) [27]. Such an experimental regime is attained by the altered set up where temperature difference is not used for the measurement itself but is exclusively employed for regulation. It is the way for attaining the most precise measurements of heat capacity (close to adiabatic calorimetry) technically restricted, however, to the temperature range up to about 700 °C, where heat radiation become decisive and makes regulation complicated.

Another modification was found necessary for high-resolution temperature derivatives to match to the 'noise' in the heat flow signal. Instead of the standard way of eliminating such 'noise/fluctuations' by more appropriate tuning of an instrument, or by intermediary measurements of the signal in distinct windows, the fluctuations were incorporated in a controlled and regulated way. The temperature oscillation (often sinusoidal) were superimposed on the heating curve and thus incorporated in the entire experimentation – the method known as *temperature-modulated DTA/DSC* (*Reading* 1993) [28]. This was preceded by the method of so-called *periodic thermal analysis* (*Proks* 1969), which was aimed at removing the kinetic problem of undercooling by cycling temperature [29]. Practically the temperature was alternated over its narrow range and the sample investigated was placed directly onto a thermocouple junction) until the equilibrium temperature for the coexistence of two phases was attained.

In the sixties, various thermoanalytical instruments became available on the market [5], see Fig. 11., and since that the experienced and technically sophisticated development has matured the instruments to a very advanced level, which certainly includes a comprehensive computer control and data processing. Their description is the subject of numerous manufacturers' booklets and manuals so that it falls beyond the scope of this more theoretically aimed book.

¹ One of the most discussed cases is the decomposition of limestone in vacuum and/or under different atmospheres using its real piece or thick layered sample [12]. Reaction interface can thus move from the outer surface (crucible walls) towards the center of the sample as a macroscopic boundary whose movement is controlled by physical processes related to heat and mass flows. Similar flows can also be located along and across the reaction interface to determine consequently the fractal interface geometry. Chemical reaction becomes then a rate-controlling process only in a very limiting case. The temperature dependencies of heat and mass transfers can thus differ from those derived for purely chemically controlled reactions. It can be mentioned that the approximately linear *Newton's Law* can contrast with the exponentially reliant *Loeb* and/or *Lonius* equations [9]. If, in the first approximation, the actual temperature dependence is known, the value of the logarithm of this dependence can presumably indicate what the limiting step may be. If the logarithm is around unity, the limiting step could be related to heat transfer, while if the logarithm falls within 1.5 to 2, diffusion controlled process is more likely to occur, and if the logarithm attains any significantly higher values, chemical control (following the traditional *Arrhenius* equation) may be indicated. The currently accepted thermoanalytical kinetic treatment (see Chapter 12) will be adequate only in this last case.



CHAPTER TEN

10. Thermal study of materials and substances

a) Temperature control

Knowledge of the *sample temperature* [1,3] is a unifying and necessary requirement for all-successful temperature treatments and/or analysis. Moreover the temperature is the basic quantity which is naturally involved in all types of physico-chemical measurements regardless what physical quantity is chosen to represent the sample state and no matter if the temperature is accounted for observation or not. As mentioned above, in thermal analysis it is traditional to investigate the state changes exhibited by sample exposed to steady conditions of a constant temperature environment subjected to certain temperature program traditionally operational as a result of external heating or cooling. Consequently, the changes observed during the measurement possess characteristic temperature-dependent shapes responsible for individual processes under the investigation, which are mutually connected either geometrically or mathematically. This transformation, however, is formal and does not give rise to other thermoanalytical methods (cf. preceding Figs. 9.2 and 9.5).

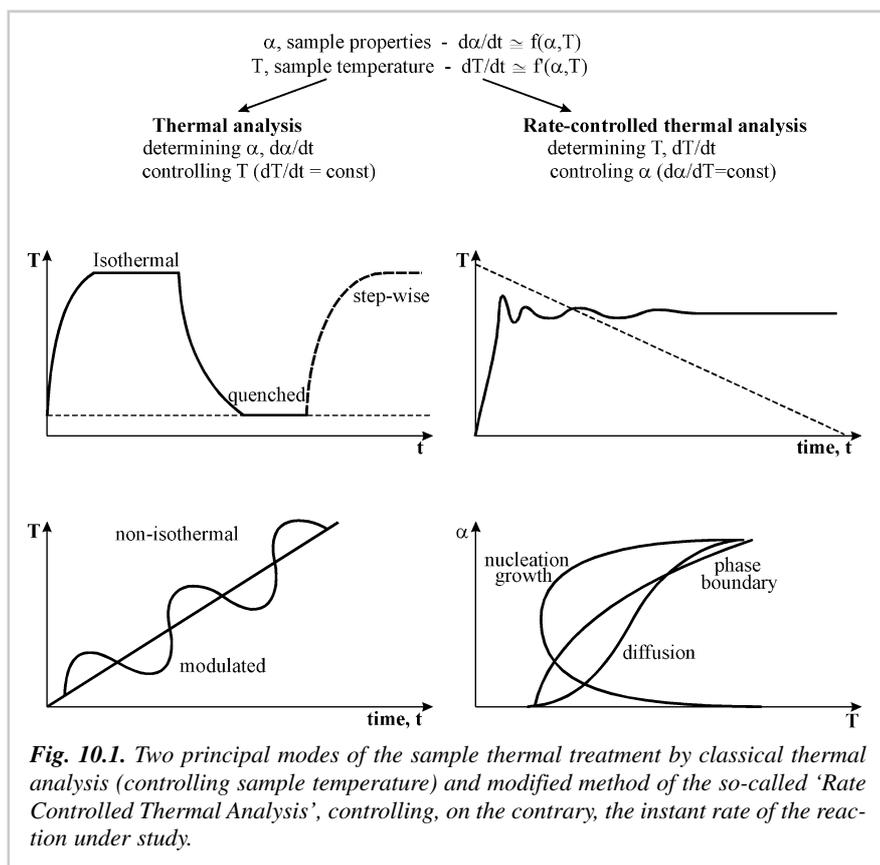
Most methods of experimental physics, however, try to study equilibrated states of the sample under (preferably) stationary temperature conditions (usually chosen as isothermal). Apart from the direct low- and high-temperature investigations, most thermo-physical measurements are carried out at room temperatures, which, however, require a suitable method of quenching so as to preserve the equilibrated (mostly high-temperature) state of the sample down to the laboratory temperature. Such a thermal pretreatment is usually necessary to carry out outside the standard measuring head.

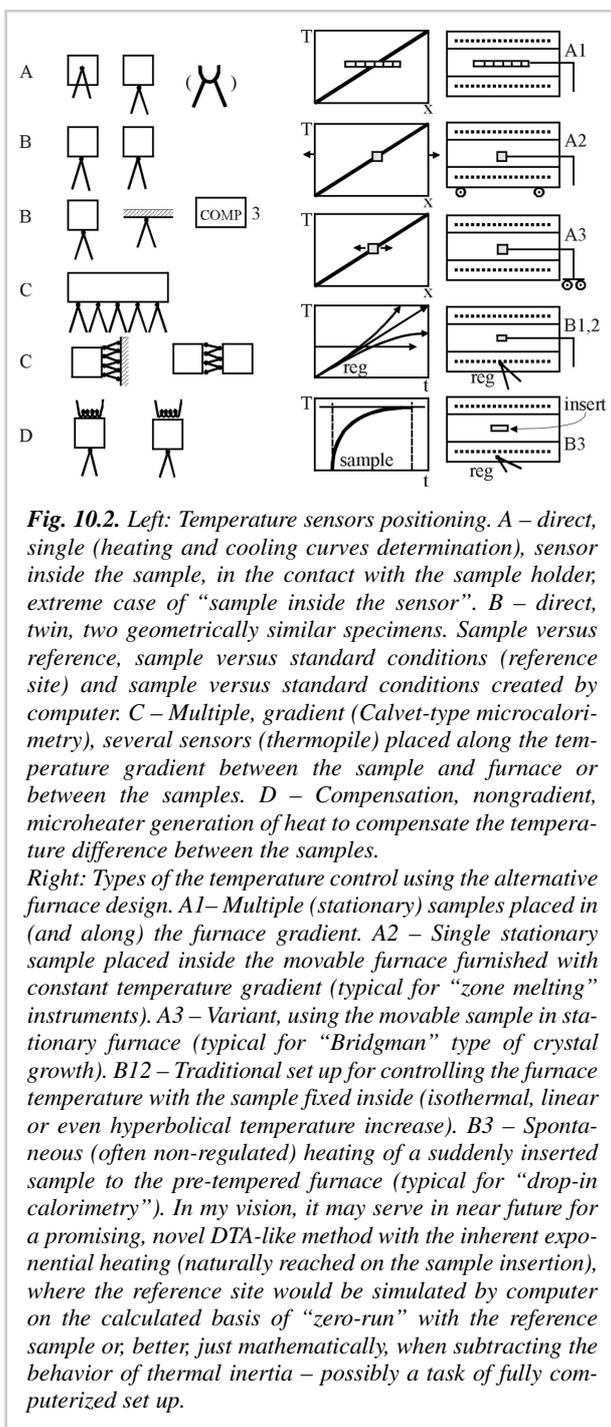
An important aspect of the recent development in thermal analysis is the diversification of temperature control modes [1,29], which besides classical isothermal runs (including stepwise heating and cooling) and constant-rate heating and cooling account at the present time for the *in-situ* temperature control of sample history. These are, in particular, the temperature jump and rate jump methods, the repeated temperature scanning and finally innovative and the most progressively escalating method of temperature modulation. The last two methods are rather different in data processing. In the temperature modulated methods, the oscillating change of a physical property is observed and analyzed by *Fourier analysis*. The amplitude of oscillating rate of transformation is compared with that of temperature modulation imposed by controlling program. On the other hand, the

repeated heating and cooling of the sample often employs triangular saw-teeth pulses and, on assumption that the rate of conversion is the same at a given temperature/conversion, equivalent isothermal curves of the transformation against its rate are extracted. The method controlling the sample history tries to elucidate the nature of an observed physical transition by using a thermal instrument as a tool for both the sample heat treatment (to provide the desired thermal record) and the entire observation consequently made during a single measurement.

There is yet another mode of temperature control called the sample controlled-rate thermal analysis, which is different in the nature of regulation because we control the temperature as a response to the required course of reaction rate (obligatorily taken as constant), see Fig. 10.1. It is evident that the wide range of controlling modes put an increased demand on the improvement of regulators and computer command.

The most thermal regulators in commercial production traditionally control heating and/or cooling of a furnace upon a solitary response signal from an often single-point temperature sensor placed in a certain thermal contact with the heater (which customarily surrounds the measuring head, see Fig. 10.2.). However, such a conservative system often lacks a feedback connection to provide interrelation between the required temperature of the sample and the actual temperature program controlling the temperature of a heater. It is now approved due to the multi-point detection, heater segmentation, heat shielding, etc., which are the most appropriate setups providing an advanced capability for computerized control. The feed-





back response to the entire sample temperature was ordinarily available only in fine calorimetric apparatuses where, moreover, heat generators and/or sinks are incorporated to the measuring head to help precisely maintain the pre-selected temperature conditions. However, new spheres of oscillatory programming put the stage of controllers a step forward.

For a successful temperature control, the sample location is very important as it can be placed within a homogenous or heterogeneous gradient of temperature distribution, which is a result of the perfectionism in the design of the surrounding heater. The sample is normally

exposed to a conservative treatment, which means the application of continuous, constant (or even oscillatory) temperature program conveniently employing a static arrangement of the measuring head (sample) and the furnace (heater). So far, such a furnace temperature control is a common arrangement for all commercially produced thermoanalytical instruments and other apparatuses used in physical technology (e.g., single crystal growth). Slow temperature changes are thus relatively easily attainable by any commercially available thermoanalytical equipment, while rapid changes require a special set up. For fast cooling the application of high velocity flowing gas is usually applied (practically carried out by using helium because of its high thermal conductivity) and the stream is directed against a sample holder, which should preferably exhibit larger surface (ribbons, filaments). Fast heating can be achieved with the aid of concentrated external heat source (e.g., focused microheater, laser or other high-energy beam).

Under standard instrumentation, however, the temperature jumps are difficult to enforce accurately due to the thermal inertia of surrounding furnaces, which are the controlled heat source. Therefore, sharp stepwise changes are imposed more conveniently using a modified assembly where the sample is inserted into and shifted along the preheated furnace with the known temperature profile, cf. Fig. 10.2. This design complies with a less conventional experimental arrangement of the mutually movable sample and the furnace, which requires, however, a definite, continuous and preferably linear distribution of temperatures (steady gradient) along the furnace. Continual temperature control can be then carried out mechanically with sufficiently high precision by sensitively moving either the sample against stationary furnace or, *vice versa*, the furnace against stationary sample. In contrast with traditional (temperature controlling) systems this makes possible to realize any type of programmed changes, even relatively fast jumps from one temperature to another and back, the exactitude of which depends on the inertia of sample holder only. In addition, it also allows inflicting relatively very low rates of cooling often needed for specific time-consuming procedures (such as crystal growth experiments).

We can provide certain predictions for possible future trends in the instrumentation entirely based on computer handling out the thermal data without any need of temperature regulation (cf. also Fig. 10.2.). The low-inertia measuring head is inserted into a suitable preheated furnace and the heating curve is recorded for both the sample and the reference. The computer program makes then possible to evaluate any desired type of outcome (DTA) just by appropriate subtraction and combination of active (sample) and passive (reference) curves computationally suited to fictitious conditions of the requested temperature program. In the age of computers, such a relatively simple arrangement would substantially reduce the need of yet expensive instrumentation based on temperature control.

The temperature controller (applicable for any ordinary type of a heater), together with the controlled system consisting of a sample, its holder and temperature sensor,

form a closed dynamic system in which the temperature is both measured and compared with the preset value given by the temperature program (see Fig. 10.3.). Depending on the sign and magnitude of the detected difference, a regulation action is taken aiming to decrease this difference down to the required and thus permitted level. Upon introducing heating bursts, which can be normally represented by periodical heat pulses (or harmonic oscillation) at the acting heater, the consequent response of the

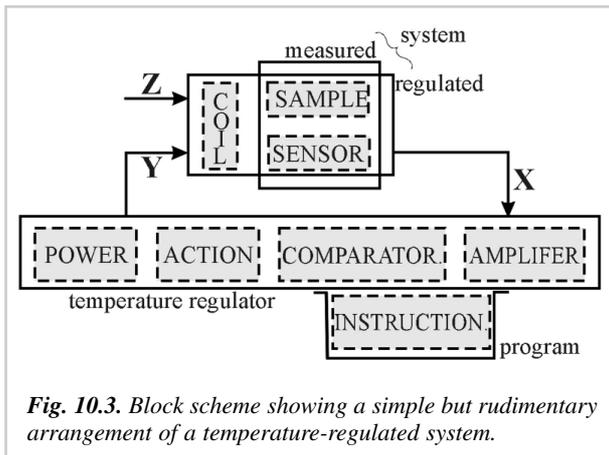


Fig. 10.3. Block scheme showing a simple but rudimentary arrangement of a temperature-regulated system.

detecting system at the sensor output is also periodic of the same frequency but with lower (generally different) amplitude. Sometimes, this response has a distorted shape and often a phase-shift caused by the transport delay due to the heat inertia of the furnace structure. The regulation function is to prevent (uncontrolled) fluctuation in the system by damping the output signal of the sensor, so that the output signal of the regulator (and thus new input signal for heating) is appropriately reduced. The precision of regulation is thus given by the error permitted in maintaining the regulated quantity within the given limits (often specified in percentage of the original value of the regulated quantity in a stationary state). The related dynamic precision of regulation then expresses the error with which the regulated quantity follows a change in the controlled quantity. The area due to regulation under the curve of the transition process, which should be minimal, characterizes the quality of regulation. The time of regulation is the duration of the transition process and must be minimal particularly for oscillatory regimes.

Because of high quality and fast progression of digital regulators widely available on the market the more detailed description of individual parts of a controlling system falls beyond the capacity of this text and the reader is referred to special literature or my previous book [1]. We just want to mention some basic terms used in theoretical concepts that encounter the regulated quantity (X) that is the output value of the system and also the characteristic quantity of the regulated system, which has to be maintained by the regulator at a required level corresponding to the present value of the controlling quantity (W). Their difference ($X - W = \Delta X$) is the error fed to the input of the regulator, whose output is the action quantity (Y). The latter quantity acts on the regulated system and en-

sures that the regulated quantity is kept at the required level. The perturbation quantity (Z) acts on the regulated system and affects the regulated quantity, being thus actually an input quantity of the system. Regulating circuits have two input quantities and thus two transfers have to be considered, i.e., the control transfer, X/W , and the perturbation transfer, X/Z . Basically, regulated systems are divided into static and dynamic, according to the kind of response: the first tend to stabilize spontaneously (having a characteristic constant of auto-regulation) while the second never stabilize just on its own accord. Differential equations are used to specify the relationship between the output and the input signals with respect to time. The type of differential equation distinguishes linear regulation (with constant coefficients) from a more complex but broad-spectrum regulation with non-linear characteristics. The transfer function and the transition and frequency characteristics add the dynamic properties. In both simple and complex regulation circuits the temperature regulators perform certain mathematical operations, such as multiplication, division, integration and differentiation and the regulators are often named after the operations they perform. In order to find the dynamic properties of a selected regulator, a unit pulse is usually fed to the input, the response being regarded as the transition characteristic. The selection of an appropriate regulator is then determined by the functional properties of the regulated system in question.

Worth mentioning is also the use of power elements to control heating. They extend from an obsolete continuous mechanical powering of voltage by means of an auto-transformer, along a discontinuous automaton with a relay system of variation of the powering voltage, either for a constant magnitude or constant time of heating pulses, to a thyristor opening or frequency control of the power half-waves. The interference from the line voltage higher harmonics is minimal with the whole-wave regulation disregarding thus the phase regulation. Altogether, it is clear that the entire process of temperature regulation is a delicate procedure because it involves both the knowledge of intact temperature and the nature of temperature transfer, cf. the previous Chapter 9. Any heat input, introduced by the heater or due to the sample enthalpy changes, pushes the system out of the previous steady state, which is exaggerated by the peculiarities of transfer characteristics associated with the particular construction (the measuring head and heater and the rapidity of their mutual response).

For temperature modulation methods the subject of the system's sufficiently fast reaction reply became a very insightful point to see whether the measured temperature of imposed oscillation is known accurately or is merely predicted. Correspondingly a question might be enhanced whether the consequent mathematical analysis of modulation is trustworthy or is only a desired but fictitious mathematical outcome. Despite the advanced regulation and measuring technique and smoothly looking results, we cannot be completely without doubts whether some thermal artifacts do not distort the traced data. Moreover, it has not been fully open to discussion as yet, whether the thermally uneven interfaces for miniature samples can provide the unwanted fluctuations and thus periodic solu-

tion (cf. Chapter 5), which can even turn out to be in competition with the temperature oscillations purposely furnished by external regulation.

b) Temperature detection

Temperature sensors are constructional elements for measuring temperature and employ the functional dependence of a certain physical property of the sensor material on temperature, which is customarily recognized. Practically, resistance or thermoelectric thermometers are most often used, whereas thermistors, ion thermometers, optical pyrometers and low-temperature gas, magnetic or acoustic thermometers are employed less frequently.

Resistance thermometers are the passive elements in electric circuits, i.e., a current powers them and the dependence of their resistance on temperature is measured. It must not be forgotten that the measuring current heats the thermometer, so that it must be as low as possible. Metals whose electric resistance increases roughly quadratically with increasing temperature are usually used. The actual sensor is a platinum, nickel, copper, pal-

adium or indium wire or, at low temperatures, germanium wire. The most common Pt-thermometers employ wires 0.05 to 0.1 mm thick, wound on mica holder or inside a ceramic capillary or otherwise specially packed or self-supported. The range of standard applicability extends up to about 700 K (special designs exceeding even 1200 K), with time constant depending on the sensor type being in the order of seconds.

For the international practical temperature scale the platinum thermometers serve as standard (interpolation) instruments with characteristics values such the reduced resistance, the temperature coefficient of the resistance and the platinum temperature. Interpolation polynomials of the third to fifth degrees, using as the principal reference points 0, 100 and 419.58 °C (fusion of Zn) are used most frequently (as a standard accessory of commercial products). Another form of resistance thermometers are films or otherwise deposited layers (0.01 to 0.1 μm thick). They can be suitably covered to protect against corrosive media and platinum deposited on ceramics can withstand temperatures up to 1850 K. Non-metals and semiconductor elements can be found useful at low temperatures.

Thermoelectric thermometers (often called thermocouples) are contact thermometers, whose sensor is a thermoelectric couple. In spite of the number of apparent drawbacks, they have retained their importance for most thermoanalytical instruments. These are active measuring elements, whose thermoelectric voltage depends on many factors, such as chemical and structural homogeneity, quality of junction, material aging (grain coarsening, component evaporation, external diffusion) and adjustable calibration (connection to etalon, reference junction). The indisputable advantages of thermoelectric couples include the very small dimensions of the sensing element (junction), a small time constant, rather high thermoelectric voltage, and wide temperature range (exceptionally up to 3000 K, depending on the type), cf. Table I.

Thermoelectric couples are tested by using secondary standards of the first or second order and are often accompanied by a certificate expressing the relationship between the signal and the actual value. The measuring uncertainty is then considered as the width of a range within which the accurate value lies with 99% probability – which is, for the most common PtRh10-Pt thermocouple from 0.5 to 2 K from temperatures up to 1200 °C. The constant of interpolation quadratic equation are approximately $a_0 = 2.982 \times 10^2$, $a_1 = 8.238$ and $a_2 = 1.645 \times 10^{-3}$ (based on melting data of Sb, Ag and Au).

The thermoelectric voltage developed in a thermoelectric couple is a function of the temperature difference between the measured and reference sites. The reference ends must be connected with further conductors in an electrically and thermally insulated space to avoid parasitic voltages (compensation leads, shielded conductors, shortest path to encircle smallest possible, holder induced leaks). Temperature measurements by thermoanalytical instruments are conventionally calibrated by a set of above-mentioned ICTAC-approved standards, convenient for both the DTA/DSC [1] (cf. Chapter 10) and TG [30] techniques.

Table I: Survey of Some Thermoelectric Cells.

Thermocouple (composition)	The temperature range [in K]			EMF at a permanent maximal value related to 0°C
	minimal	maximal perma- nent	maximal tempo- rary	
Cu – AuCo	4	300		
Cu – AuAg	17	270		
Cu – Ag	3	270		
AuCo – AuAg	18	103		
AuFe – ch	3	870		4.05
Cu – co	3	670	870	20.19 ^{x)}
Fe – co	70	870	1170	33.66
ch – co		870	1170	45.10
ch – cp	220	870	2070	49.01
NiCr – co		970	1170	52.06
Fe – CuNi	60	1470	1570	64.9
Cu – CuNi	73	670	770	5.47
NiCr – CuNi	3	1270	1470	78.03
NiCr – Ni	73	1170	1470	86.50 ^{x)}
NiCr – NiAl	3	1640	1470	29.42
Ag – co		1170		54.49
ch – al	220	1270	1570	41.27
AuPd40 – PtRh10	170	1370	1570	50.54
Au65Pd35 – pl		1370	1470	
PtRh10 – pl		1470		57.30
Pt – PtRh10	270	1570	1870	13.12
Pt – PtRh13	220	1570	1970	14.62
PtRh5 – PtRh20	270	1670	2070	8.65
Pt – PtRe		1670		ca 34
PtRh30 – PtRh6	270	1870	2020	11.24
Ir – IrRh40	1270	2070	2270	9.65
Ir – W	1270	2370	2570	41.59
W – Mo		2470		
W – WRe26		2670	3070	ca 39

Symbols: co (constantan: 58 Cu, 42 Ni), ch (chromel: 89 Ni, 10 Cu, 1 Fe), al (alumel: 94 Ni, 2 Al, 1.5 Si, 2.5 Mn), cp (copel: 55 Cu, 45 Ni), pl (palaplat: 60 Au, 30 Pd, 10 Pt), ^{x)} the reference junction temperature 20 °C.

c) Extreme temperature changes and the sample preparation methods

Nature is the best instance to learn how the different ways of temperature changes [1,32] can alter from very slow, taking place within geological changes, to extremely fast, occurring as a result of fast energetically changes (e.g., impact of meteorites), see Fig. 10.4. *Slow cooling* is a commonly applied procedure for growing single crystals [31,33,34] (Fig. 10.5.) where we usually focus our concern to follow very intimate temperature changes and profiles consequently responsible for the desired high perfection of crystals. On the other hand, *fast cooling* is a domain of the artificially enforced preservation of high-temperature states [35,36] all the way down to laboratory temperature. It is accomplished through the quenching procedures applied and needed to preserve the (usually extraordinary) high-temperature property not only for their subsequent investigation at low enough tempera-

tures but also for practical utilization of such so-called 'tailored' materials.

Because of increased reactivity, high temperatures are favored to prepare samples more rapidly than it is possible at lower temperatures. However, we often require to investigate the sample property straight at its high-temperature state, which is difficult and often even impossible because of the inaccessibility of instruments capable to measure directly at high temperatures. Therefore, it becomes necessary to find a suitable method of rapid cooling in order to preserve the required high-temperature state down to lower temperatures [1,31,35–38]. The primary, but often rather neglected step is the mechanical transport of the tempered sample from the heated place to another site of controlled cooling. The transport always requires a definite time delay and this period is most important due to the effect called *self-cooling*, which can be very intensive at high temperatures. The decisively comprehended step is the entire process of rapid cooling itself, which must proceed as long as a certain limiting temperature is reached, under which the required sample and its state is stabilized because of the insufficient mobility of the inherent species to undertake unwanted transformation.

The practical aspects of mastering successfully the technology of rapid cooling are long known in metallurgy. It deals with the so-called *rapid solidification* (or simply the process of *quenching*) where the meaning "rapid" can be taken to imply a short-time interval between initiation and completion of solidification and high velocity of propagation of the advancing solidification front. It occurs either directly, as a result of coupling between external heat extraction and the transport of latent and specific heat required to propagate the solidification front, or indirectly during the recalescence that follows nucleation of solidification at large undercoolings.

First, it should be emphasized that the frequent quenching of a sample by mere immersion into liquids, in particular to liquidified gases (nitrogen, air), is not as sufficient as many experimenters expect regarding the low temperatures of the cooling medium. Intensive heat transfer from the sample is effectively hindered by the immediate occurrence of a gaseous envelope, which factually becomes the heat insulating layer due to its low capability to mediate the heat exchange through gas or liquid vapor. Although the heat of vaporization is the most important type of the heat removal, only solutions with high vapor pressure are effective, especially concentrated solutions or mixtures of liquids, which are capable of dissolving back their own vapors. Very successful and approved by long practice are different sorts of oils. Reasonably, we could measure some actual rates of liquid-based quenching, such as is the case of chalcogenide melts, which are held in a sealed quartz tube (5 mm diameter with the walls less than 0.5 mm) and heated up 900 °C. The tube can be quenched by immersion to various liquids providing, however, rather small changes in the cooling rates, from $5 \cdot 10^2$ (solution of KOH), $4 \cdot 10^2$ (oil), $2 \cdot 10^2$ (mixture of ice and water), 10^2 (liquid nitrogen) down to $8 \cdot 10^1$ K/s (self-cooling in air).

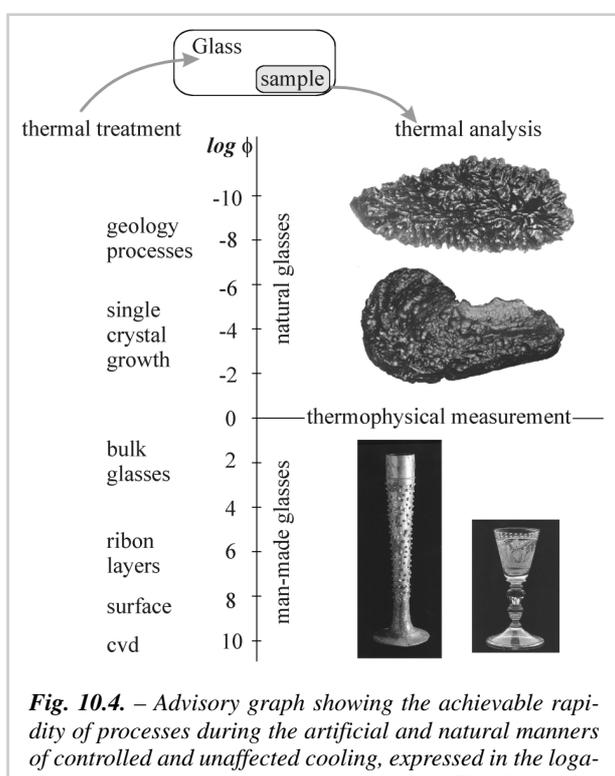


Fig. 10.4. – Advisory graph showing the achievable rapidity of processes during the artificial and natural manners of controlled and unaffected cooling, expressed in the logarithmic scale of the cooling rate (vertical). The illustrative photos give a picture of Moldavites (Vltavins – upper photo) representing the domain of olive-greenish natural glasses, named according to their deposits, tektite-strewn field located near the south part of the major Czech river Moldau (Vltava). They are factually rapid frozen droplets of meteoritic origin have the length up to about 5 cm and are regarded as semiprecious. Below, hard and Clear Mountain (crystal) glass (lower photo) represents the famous man-made Bohemian artifacts (prepared by firing a refined beech and oak ash, rich in lime and potash, with the common additives of chalk and based on the country's quality siliceous). Left: flute-shaped beaker, with minor stuck-on decoration dating from about 14th century. Right: Cut goblet with slight ruby strings in the stern, engraved with the wine-picking motive was made around 1700 (size about 15 cm).

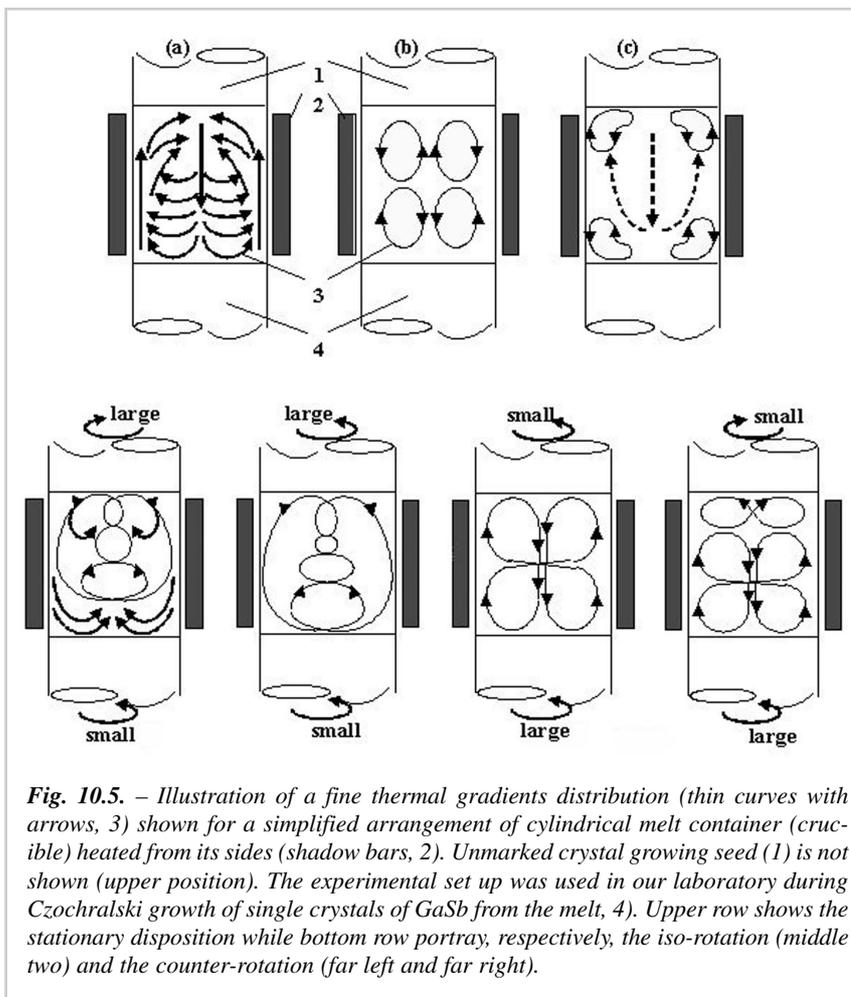


Fig. 10.5. – Illustration of a fine thermal gradients distribution (thin curves with arrows, 3) shown for a simplified arrangement of cylindrical melt container (crucible) heated from its sides (shadow bars, 2). Unmarked crystal growing seed (1) is not shown (upper position). The experimental set up was used in our laboratory during Czochralski growth of single crystals of GaSb from the melt, 4). Upper row shows the stationary disposition while bottom row portray, respectively, the iso-rotation (middle two) and the counter-rotation (far left and far right).

The problem of removing an adhering (often stationary) insulating gas layer stimulated the renaissance of the method of directly blowing a stream of gas with high thermal conductivity (helium) onto the cooled surface, which assured intensive heat convection due to the passing stream at high velocities. This method can attain cooling rates as high as 10^4 K/s for thin layers, or better wires, up to 500 μm in size. Recently, this method was even incorporated into the standard accessory of thermo-analytical instruments, particularly when dealing with dilatometric studies. As experimental evidence, we can compare various cooling rates approximately estimated for quenching of the melt of silicates down from the temperature of about 1200 °C. The maximum cooling rate is in the neighborhood of 10^5 K/s applying either the melt pressing between two moving metallic surfaces (see Fig. 10.6.), which forms a ribbon with the thickness of about 0.2 mm or the melt disintegration to drops of about 0.5 mm in diameter and their centrifugation and splashing against metallic walls. Drawing a fiber into water bath (with a diameter less than 0.5 mm) decreases the cooling rate by more than one order of magnitude and would be similar to the helium fast-flow cooling of thin layers or wires. When dropping droplets of melt (~ 3 mm in diameter) into oil, a further decrease of cooling rate is experienced, to about 10^{2-3} K/s.

We can remind old variants of the long-established technology of making lead shot by teeming molten lead through a preheated steel dish perforated by an array of equal sized holes. Fundamental principle is that a pendant drop or free falling melt-stream tends to break up into droplets because of surface tension. This process can be intensified, for example, by impingement of high velocity jets of a second fluid, by centrifugal force, at the tip of a rotation cup or disc, or by release of pressed gas (explosion, shooting) or by the applied electric or magnetic field. Still, by far the most efficient cooling procedures are individual splats or a thick rapid deposit by impact on to a suitable substrate. These techniques involve the heat extraction through a direct contact between two aligned surfaces (of the sample and substrate), that must exhibit a good thermal conductivity and a suitable heat capacity. It is commonly achieved in the case of metals with negligible surface oxidation (alloyed noble metals) and resistance against wear (Cu-B or Cu-Cr alloys), see the Chapter 19. The best thermal contact is attained when cooling the melts because they are viscous and thus can be suitably pre-shaped to fit well the surface roughness of a cooling

substrate. The method of rapid cooling of melted alloys has been known for a long time, the first patent for the production of wires by drawing was granted as far back as in 1871 and the solidification of the melt on rapidly moving surface was patented in 1908. In comparison with the conventional technology of production of thin sheets by cold drawing and rolling, the direct processing of the melt saves considerable energy and even other complicated operations. The involved procedures of rolling between two calendars, however, have been unemotionally re-adopted.

The increasing quenching rate can diminish the grain size, increase the chemical inhomogeneity and supersaturation and ease the formation of glassy state, which is usually achievable in the systems exhibiting as many components as possible. The components should possess reciprocal low solubility, the highest difference between their melting points (of alloy and the pure components), a suitable ratio between the their atomic radii and also strong mutual interactions. An empirical relation in the form of a power law holds for the dependence of the distance, d , of dendrites on the local solidification time, τ , or on the average cooling rate, ϕ , i.e., $d = a \phi^{-n} = a' \tau^n$, where a , a' and n are characteristic constants. The local conditions of solidification to form glasses (melt vitrification) gives up only its specific heat, whereas coupled

crystallization is accompanied by additional release of the heat of crystallization. The glass-forming ability is related to the ratio of $T_g/T_m = T_{gr}$, the so-called reduced temperature, where T_g and T_m are the temperatures of glass transformation and melting, respectively. The higher value of T_{gr} , the lower the required critical cooling rate.

In order to reach a sufficiently high quenching rate, it is mandatory that the heat transfer coefficient at the boundary of the melt and the cooling substrate be high enough and that the layer of the melt be so thin that the heat may be removed from the whole volume of the sample to the cooling substrate in a sufficiently short time. Therefore, the most suitable substrates are metals possessing the best parameters of heat capacity, internal heat conductivity and surface heat transfer coefficient (often reduced by metal surface oxidation layer). The cooling rate is essentially influenced by the heat transfer coefficient, Λ , and the thickness of cooled sample, d , and relatively less by its temperature. At the condition of ideal cooling, where we assume infinitely high coefficient of heat transfer, the cooling rate is proportional to $1/d^2$, while for Newtonian cooling controlled by the phase boundary ϕ correlates to $1/d$ only. In practice we may adopt the power relation $\phi = 1/d^n$ (where $1 \leq n \leq 2$ is an experimental constant). For illustration we may present the example of cooling, which is close to ideal, with the proportionality coefficient, $\Lambda = 10^4 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1}$, frequently displayed for several real materials. We can guess the minimum cooling rates of 10^2 , 10^6 and 10^{10} K/s for the critical sample thicknesses of 10, $5 \cdot 10^{-2}$ and 10^{-3} mm , respectively. The latter value of thickness is very small, hardly attainable even by intensive laser glazing, which works with very thin layers and assures intimate contact of the *in situ* melt with the surface of solid support. It, however, lies within the possible rates assumed for

vapor/gas deposition onto the solid surface, i.e., within about 10^{11} K/s .

It is, certainly, very difficult to determine exact values of the cooling rate, because the whole process takes place only during an extremely short time interval, the dimensions of ribbons/wires are small and the solidification is sensitive to a number of external parameters. These are, in particular, imperfections and roughness of the matching surfaces, the role of insulating layers (oxides, sticking dirt, and trapped gases-pits) and process changes in the surface of cooling substrate. The influence of the expelling pressure (p), the speed of the cylinder (v_p), the temperature of the melt (T) and the tilting angle of the nozzle are responsible for the ribbon formation. In a simplified calculation of an incompressible liquid with a density π , the *Bernoulli* equation can be applied and, if assuming the densities between melt and glass of ribbon to be roughly equal, the cross-section of the ribbon, A_p , is described by $A_p = A_t (2p/\pi)^{1/2} / v_p$ where A_t is the cross section of the melt stream. The instability of the molten stream can be affected by the interaction of the melt with the surrounding atmosphere, which may result in oscillations of temperature and hence in immediate changes of the surface tension leading to a non-uniform surface of the ribbon, sometimes called *Marrangoni* surface (introverted by use of vacuum or low pressure gas containers). Modeling of the processes, which take place at such high velocities, is difficult and often based on two limiting assumptions:

- (i) The transport of heat is more rapid than the transfer of material and the solidified layer goes continuously over the drop and the thickness of the ribbon and is given by the time of contact of the substrate with the drop, and
- (j) The transfer of material is faster than that of heat and a liquid layer is drawn from the drop by the moving substrate and the solidification proceeds outside the drop.

The first 'difficult-to-prepare' samples of metallic glasses were obtained by shooting the melt against suitably shaped substrates (*gun quenching* technique) receiving thus non-uniform platelets, whose varying thickness (between 0.1 and 0.01 mm) made the estimation of cooling rates locally dependent. An essential improvement of the sample homogeneity was achieved by the automated method called *piston-and-anvil*. Free-falling or shot drop is pressed between two moving plates where the cooling rate can attain 10^6 K/s in limiting cases. Further improvement of the rapid cooling technique was reached by the method of stationary batching on a rapidly moving surface, either an endless metallic belt or, more suitably, on a horizontally rotating plate shaped ac-

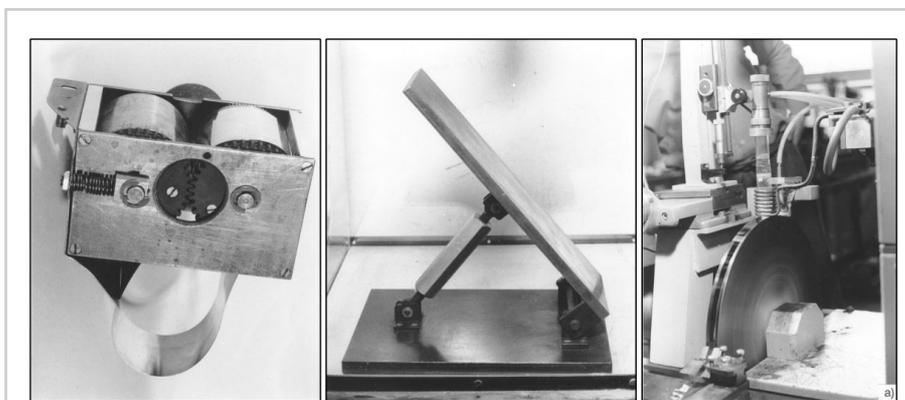


Fig. 10.6. Some examples of the melt quenching instruments (used in our laboratory during eighties): Left – belt running device where the molten drop was let falling in between a modified twin-roller quenching machine, here improved by inserted filament – infinitesimal running metallic ribbon. This adjustment helped to assure prolonged contact of the quenched sample melt onto the cooling substrate (thus avoiding supplementary crystallization of glass after its taking away from the simple wheels' linear contact). Middle – a sloped or slanted plate of metallic (copper) coolant enabling a simple dropping the melt to slip onto the surface. Right – on instrument for continuous casting the melt onto the outside of a rotating drum, which is customarily called 'single roll technique' and which is common for the preparation of metallic ribbons, cf. next figure (and Chapter 19).

ording to the requirements even to a conical form. The continuous production was only made possible by spraying the melt stream onto a rapidly rotating horizontal wheel (*melt-spinning*), latter modified by casting on the inner surface of a cylinder. The familiar method of cooling between two rapidly rotating wheels held together under certain pressure and guaranteeing the given gap of separation, needed to have a strictly synchronized motion. It was called *twin roll technique* and formed the basis for the continuous production of metallic glass ribbons with homogeneous thickness and composition as well as smooth surface on both sides. A relatively short time of effective cooling in the line of the two wheels in contact often causes that the temperature of the departing (cooled) ribbons still remains high enough to enable ribbon re-crystallization or otherwise undesirable relaxation. Together with another disadvantages (such as difficult synchronization of the outlet velocity of the melt with the circumferential velocity of both wheel revolutions at about 15–30 m/s) this method steered preference to practical exploitation of the single wheel quenching. These difficulties, however, can be helped by a specially designed set up of the so-called *continuous belt-running method*, which was developed in our laboratory, as shown in Fig. 10.6.

The most widely used technique has remained that of casting the melt onto a rotating single chill roll surface, which brought, however, the undesired consequences of the instability of the input melt stream due to high surface tension and low viscosity of alloys. The adjustment of the distance of the nozzle from the cooling surface and the quantity of the entrained gas from the environment made the practical preparation of wider ribbons difficult. In order to guarantee laminar flow and so a good stability of the drop, it is necessary that the nozzle have to be as close as possible to the surface of the rotation wheel ($\cong 0.5$ mm). It can diminish the negative influence of both the surface irregularities and the layer of adhered gases (so called air pockets). Rectangular shape of the discharge helps to form a drop retaining the shape of the nozzle opening. The modified method of spraying the melt from the close vicinity of the wheel, called the *planar flow casting*, made it possible to produce the ribbons of width of more than hundred millimeters (cf. Fig. 10.7). The nozzle opening, however, has to keep the shape of an elongated rectangle and must be placed as close as at the distance of few tenths of millimeters from the rotation surface. The need for improvement of the mechanical properties of metallic strips led to developing the multi-layer ribbons formed by simultaneous deposition of the chemically different layers of alloys. There is another variant called *melt extraction*, in which the rotation chill roll forms the product by direct contact with the surface of a crucible melt or the melted extremity of the solid electrolyte, and its derivative known as *melt-overflow*, which does not involve generating a melt-stream.

Continuous, rapidly solidified filament with round section can be produced by the *rotating water bath process* in which a melt-stream emerging from a cylindrical orifice is solidified directly on entry into a rotating annulus of water contained within the lip of a rotating water bath.

This process can also be used to generate powder particulates when the conditions result in the break-up of the melt-stream on the entry of into the water bath. In general, the increasing gas pressure increases the yield of fine particles sizes, while the more effective quench of water atomization leads to shapes that are more irregular. Although particles more and less identical in size and shape from the same powder sample can show quite different microstructure (due to different local conditions), smaller particles tend to cool more rapidly and/or under-cool more prior to solidification, tending to solidify at higher front velocity. There are, of course, many other cooling techniques. They start from the most simple but highly practical derivatives of the *splat quenching method*, where the melt is poured between two solid plates immediately followed by pressing, which can be manual (too slow) or automatic (laser controlled and supplemented by shooting the melt against plates). They range to the conventional *traction of fibers* (if possible according to the melt viscosity) and reach the different types of melt casting against variously shaped, fast rotating bodies.

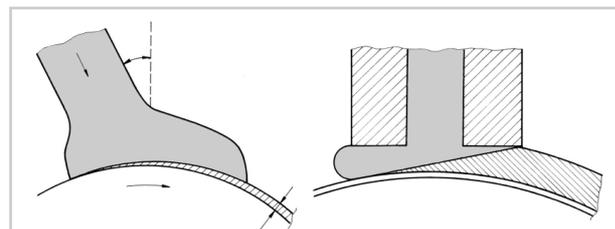


Fig. 10.7. The detailed view of the single roll technique with two alternatives of the molten sample draws (shadow). Left, simple layer deposition by injecting molten stream against the rotation coolant surface the deposited ribbon leaves the roll after its full solidification (dotted). Right, a more advanced deposition through the kneading-like system enabling to form more fixed and thicker ribbons, possible of preparing streamer with multiple compositional layers.

Like the above mentioned, the melt casting may be into a cone, onto a disk, onto the outside of a drum, or into the inside tilted lip of a drum, mostly aimed to produce a continuous sample. There are many other specific methods worth mentioning such as the *spray method* (drop acceleration in electric field), *centrifugal spattering*, or *swinging wing method*, which uses the impact of a plane, fixed perpendicularly onto a rotating disk and, last but not least, *surface melting* (welding) and/or *laser glazing*.

There is also a very important sphere of production quenched powder by employing similar spinning technique but furnishing the wheel surface by nicks and grinders, which enables melt-stream separation, cf. Fig. 10.8. The variability of powder particle size available, their shape and microstructure within bulk-atomized powder samples, splat and spray deposits and the need to consolidate the material for typically engineering applications, has stimulated work on droplet methods. They can employ lower cooling rates and allow measurements or control of the temperature at which the nucleation occurs. Such methods include *emulsification* technique in which a distribution of droplets is produced within a car-

rier liquid, which can be inert, and which can act as a flux for impurities in the droplets that otherwise would activate nucleation at lower undercooling, or which can trigger nucleation at specific conditions. A variant uses rapid solidification to produce a fine secondary network of eutectic in a single-phase matrix. This network is then spheroidized by heat treatment above the solidus to produce a distribution of liquid droplets in the solid matrix. Undercooling of hundreds of degrees can be generated in relatively large volumes of melt by a prior removal of impurities, e.g. by fluxing or levitation (containerless) melting or even when working in the microgravity (in cosmic satellite workstations such as the earlier instrumental experience done by the Institute of Physics with our laboratory designed automatic furnace 'Morava' at the space station 'Mir' aimed to study undercooling, cf. Chapter 19.).

This is certainly not an all-embracing description of every one technique available to produce tailored materials with stipulated metastable and unstable states. We could not include thermal plasma spraying, spray-forming and injection, physical and chemical vapor deposition, combustion synthesis and various methods of powder consolidation or mechanical alloying' [38,39] because it would tremendously inflate the content of this chapter. In the next section we, nevertheless, present some detail on surface treatments as they can be incorporated into the traditional thermoanalytical instrumentation.

Procedures similar to the methods of splat cooling can, on contrary, be used for consequent annealing. In our laboratory, we used a drawn (as-quenched) ribbon, which was continuously passed through a gap in a heated block that provided convenient annealing due to auxiliary heating/cooling. This method can be coupled with the production line (it works with given speed of temperature changes at about 10^2 K/s) or latter can be applied by means of aside mounted blocs. Typical discontinuous aftermath annealing we also be performed by inserting short electric current pulses to flow through the cut pieces

of ribbons, which were hold in massive copper blocks and immersed in a suitable cooling medium (oil) providing characteristic rates of temperature changes as high as 10^3 K/s.

d) Surface treatments by lasers

Surface-melting methods derive from the experience with spot or traverse welding technique and differ from them only in such a way that the depth melted is limited to only ensure that the ensuing solidification will be sufficiently rapid, deep but not disintegrating the supporting shape. In its simplest form, a single pulse or continuous traversing heat source is used to rapidly melt surface of a block material, the unmelted bulk acting as the intensive heat sink itself, which act during the subsequent rapid solidification. The resulting rapidly solidified material has the same composition as the underlying parent material, although through the solidification a different microstructure is formed often improving the resulting properties. A second possibility is to replace or inject alloy or dispersion additions at its surface so they are incorporated into the melt-zone to form a surface region of composition different from the underlying bulk. The third possibility is to melt different materials pre-placed on the surface so that mixing with the underlying material is limited to the minimum required for effective bonding. All three variants offer the practical possibility of generating a more durable surface of the original body with tailored microstructure [40–43].

A special case of controlled heat treatment is the processing of material's surfaces by lasers (light amplification by stimulated emission of radiation), which is a unique source of heat. The radiant power of the laser can be sharply localized, both temporarily and spatially, and programmed with reliable ease, e.g., 30 ps pulses of a Nd:YAG laser, at power density of mere 0.8 J/cm² can easily amorphize about a 100 nm thick surface layer of FeB alloy. These properties allow a substantial increase of the speed and economy of various types of heat treat-

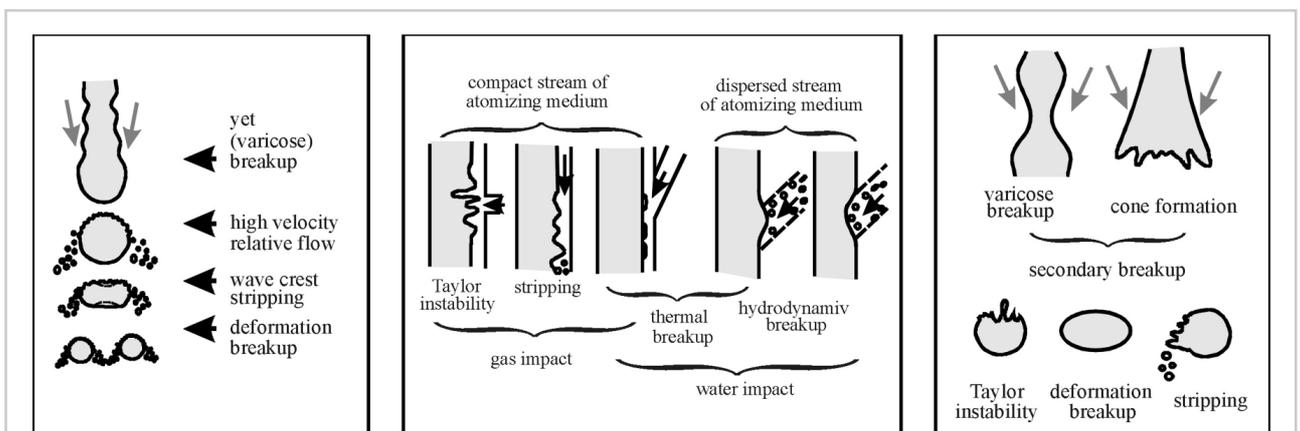


Fig. 10.8. Various stages of the pour out stability of molten streams (shadow) taking place during the self-quenching processes when preparing metallic ribbons. It shows the general character of possible interferences of stream imbibitions with surrounding media (air, surface). A cooling fluid may also be purposefully incorporated, usually inserted to break up the stream to obtain preferred droplets, which can be a desired semi-final product capable for further processing upon its densification to form bulk things by high pressures.

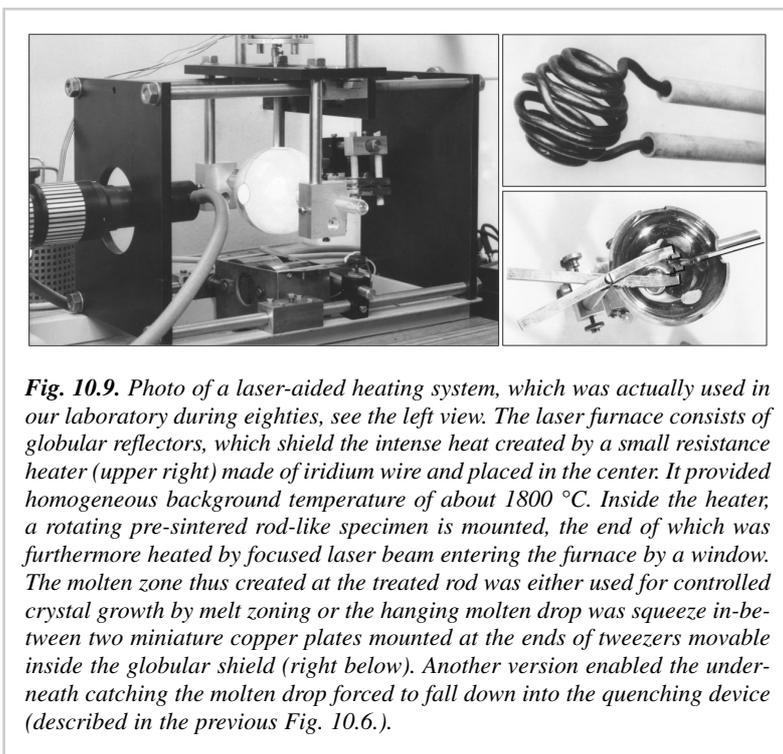


Fig. 10.9. Photo of a laser-aided heating system, which was actually used in our laboratory during eighties, see the left view. The laser furnace consists of globular reflectors, which shield the intense heat created by a small resistance heater (upper right) made of iridium wire and placed in the center. It provided homogeneous background temperature of about 1800 °C. Inside the heater, a rotating pre-sintered rod-like specimen is mounted, the end of which was furthermore heated by focused laser beam entering the furnace by a window. The molten zone thus created at the treated rod was either used for controlled crystal growth by melt zoning or the hanging molten drop was squeeze in-between two miniature copper plates mounted at the ends of tweezers movable inside the globular shield (right below). Another version enabled the underneath catching the molten drop forced to fall down into the quenching device (described in the previous Fig. 10.6.).

ment, as compared with conventional methods. Certainly, the thermal effect of laser radiation need not be limited to the surface only as, for example, CW CO₂ laser of 10 kW power output can be used to weld and cut steel up to 25 mm thickness as well as get applicable for crystal zone melting (compare Fig. 10.9.). In the thin film deposition, the laser heating find application evaporation, acceleration of electrolytic coating process, chemical vapor deposition (LCVD) based on chemical reaction initiated by laser radiation, and in photo-deposition of metals by photolysis. For the description of radiation with matter, we usually do not include phenomena where radiant energy impinging on the surface of a solid does not cause any significant evaporation or boiling that might lead to the creation of plasma over the surface. We assume that wavelengths ranging from ultraviolet to infrared interact with free electrons, which can be accelerated by external electromagnetic fields to a much larger degree than bound electrons, which is efficient particularly for metals. The penetration depth (or absorption length), d , is the distance below surface at which the radiant energy density drops to reciprocal exponential of its original value. There is a direct proportionality between the square roots of wavelength, λ , providing that if d is of the order of 10 nm it does not significantly vary from the visible to the infrared range. However, a different situation is met in semiconductors and insulators, where the reflectivity, R , (defined as the reflected-to-incident energy ratio) plays more important role. For example, for ruby (0.694 μm), neodymium (1.06 μm), iodine (1.315 μm) and CO₂ (10.4 μm) lasers, the reflectivity of metals falls usually in the neighborhood of 0.9 while for semiconductors rises between 0.96–0.99. Therefore we can use about 10% of the incident energy for the metallic samples but only few per-

cent for semiconductors. On one hand, the small penetration depth in metals (~ 10 nm) implies that the radiation has only a localized effect and heat is quickly distributed due to its high conductivity. On the other hand, d 's for semiconductors are substantially larger, often reaching into range of meters, so that these substances are factually transparent for the radiation in question.

In order to increase effectively the efficiency of the energy transfer from the beam of radiation to the material, and to increase the reproducibility and manageability of technological processes, the surfaces of materials is modified in to increase its absorption. It can be done mechanically (roughening, black painting) or coated by spraying, dipping, electrolysis, deposition or chemically treated (oxidation, phosphating, graphitization, carbide or nitride alloying). Substantial change of absorptivity takes place in the vicinity of the melting point. For example, for a CO₂ laser and steel surface at the power density below about 10⁴ W/cm² on the irradiated surface, we deal with normal heat treatment with

temperatures below the melting point. In the moment we exceed this value of irradiation melting-down of the surface takes place and the absorptivity significantly increases. The efficiency of the heat transfer is thus rapidly increased and the temperatures start to rise until a state of a dynamic equilibrium is attained. This steady state is given by physical and geometrical parameters of heated system including the translation speed (feed rate) of the beam. It means that for a sufficiently large sample, far from its edge, the temperature became constant in time and will migrate with the beam shifting. A substantial feature becomes the inherent flow of the melt in the melted-down regions and a particular type of wrinkling observed on the solidified surface. It is illustrated in the Fig. 10.10., where the upper part (1) shows the view from above and

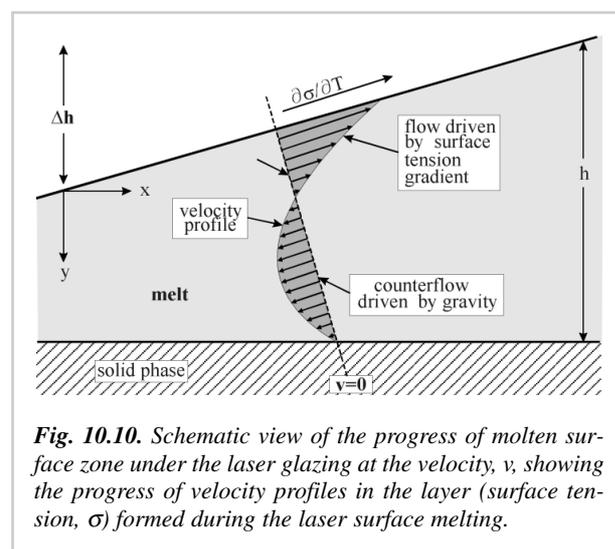


Fig. 10.10. Schematic view of the progress of molten surface zone under the laser glazing at the velocity, v , showing the progress of velocity profiles in the layer (surface tension, σ) formed during the laser surface melting.

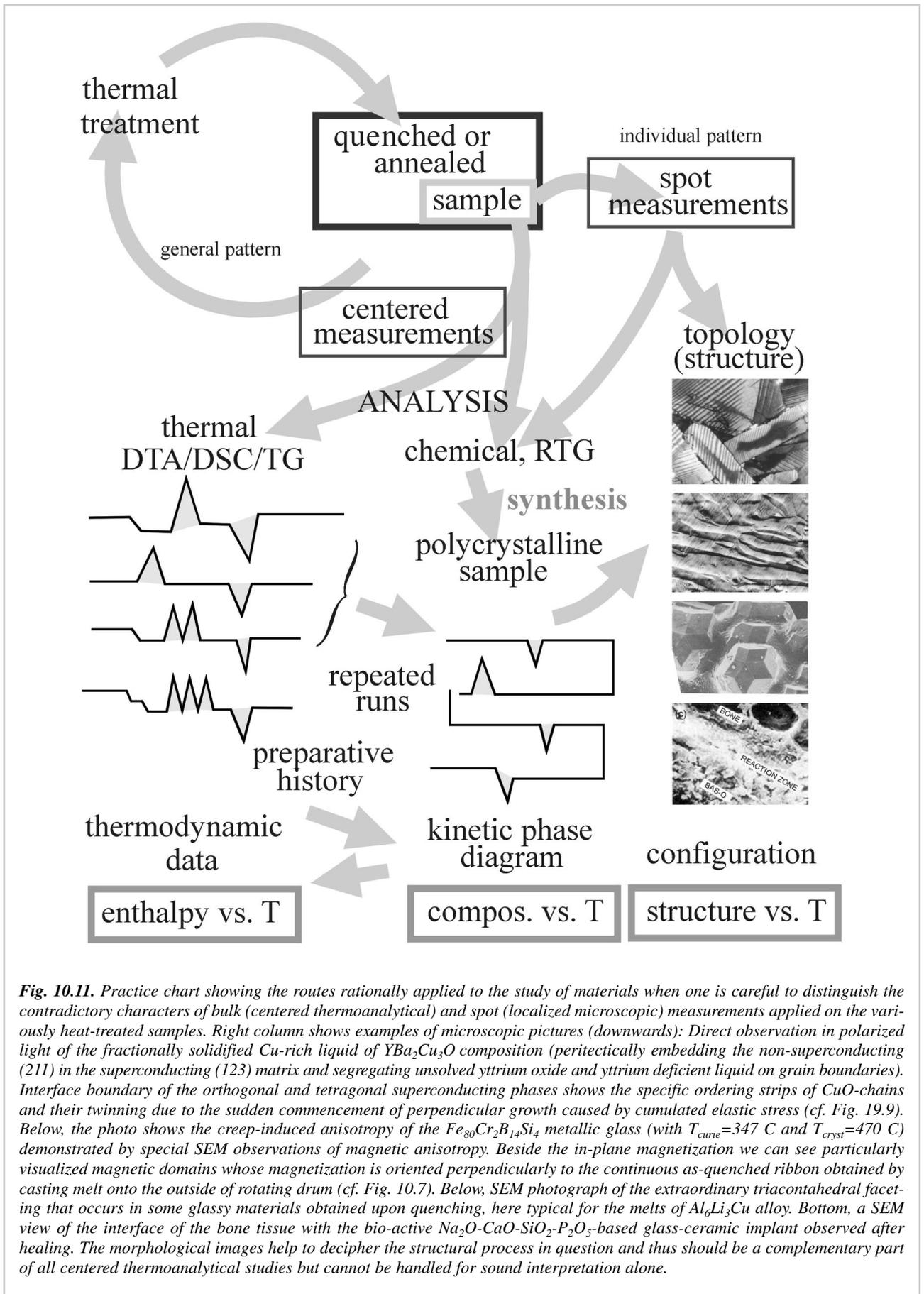


Fig. 10.11. Practice chart showing the routes rationally applied to the study of materials when one is careful to distinguish the contradictory characters of bulk (centered thermoanalytical) and spot (localized microscopic) measurements applied on the variously heat-treated samples. Right column shows examples of microscopic pictures (downwards): Direct observation in polarized light of the fractionally solidified Cu-rich liquid of $\text{YBa}_2\text{Cu}_3\text{O}$ composition (peritectically embedding the non-superconducting (211) in the superconducting (123) matrix and segregating unsolved yttrium oxide and yttrium deficient liquid on grain boundaries). Interface boundary of the orthogonal and tetragonal superconducting phases shows the specific ordering strips of CuO-chains and their twinning due to the sudden commencement of perpendicular growth caused by cumulated elastic stress (cf. Fig. 19.9). Below, the photo shows the creep-induced anisotropy of the $\text{Fe}_{80}\text{Cr}_2\text{B}_{14}\text{Si}_4$ metallic glass (with $T_{\text{curie}}=347\text{ C}$ and $T_{\text{cryst}}=470\text{ C}$) demonstrated by special SEM observations of magnetic anisotropy. Beside the in-plane magnetization we can see particularly visualized magnetic domains whose magnetization is oriented perpendicularly to the continuous as-quenched ribbon obtained by casting melt onto the outside of rotating drum (cf. Fig. 10.7). Below, SEM photograph of the extraordinary triacotahedral faceting that occurs in some glassy materials obtained upon quenching, here typical for the melts of $\text{Al}_6\text{Li}_3\text{Cu}$ alloy. Bottom, a SEM view of the interface of the bone tissue with the bio-active $\text{Na}_2\text{O-CaO-SiO}_2\text{-P}_2\text{O}_5$ -based glass-ceramic implant observed after healing. The morphological images help to decipher the structural process in question and thus should be a complementary part of all centered thermoanalytical studies but cannot be handled for sound interpretation alone.

when the part below (2) is a section perpendicular to the sample surface and parallel to the feed direction of the beam. A dip is formed at the spot where the laser beam, traveling to the left, impinges so that the melt flows to the right (behind the beam front), piles up, gradually cools down and eventually forms a ridge. The cross-sectional cut C is seen in part (3) – the overall formation of the trace is sufficiently clearly documented by parts (2) and (3).

Wrinkling of the surface relief is always irregular, since the interaction forces responsible for flowing in the melt give rise to flow fluctuations that manifest themselves as shape irregularities after cooling down. It is a nice example of fractal geometry played by consonance of heat and viscous flows so that it is worth of thorough description, which fits the scope of the book (cf. Chapters 13 and 15). The dip below the beam front is due to the combined effect of several factors. The front face of the melted-down region warms up so rapidly that the gas atmosphere over the surface does not have time to expand sufficiently quickly, giving the rise to a pressure wave that strongly depresses the melt surface just in the region of the front. Besides, the melting is accompanied by a temperature gradient that propagates radial from the center of the beam. The temperature of the melt under the beam is the highest and the surface tension is the lowest. Moving from the beam's center against the feed direction, the melt temperature decreases and the surface tension increases. The temperature gradient of the surface tension pulls the surface layer out of the beam's center against the feed direction towards more distant regions. The difference between the melt levels at the beam's center and in distant regions, however, gives rise to the gravitational flow under the surface layer of the melt. In the steady state, the surface flow of the melt due to the gradient of surface tension, is just balanced by the reverse gravitational flow in the lower layers, due to dip below the beam surface. In view of the larger temperature gradient and fast solidification due to the rapid heat transfer towards the bulk, after the passage of the beam this steady state deformation will eventually freeze into the shape of a wrinkled relief. The significance of convection in the process of melting of the surface layer consists in mixing up all components, so that the final composition of the layer can be very homogeneous. Diffusion in the melt plays a smaller role than convection, cf. Fig. 10.

As an example let us see what happened after the irradiation with pulsed laser beam of duration $\tau = 10$ ns and energy density of 1 J/cm^2 . Assuming 10% absorptivity the heat spreads down to a depth of $d = \sqrt{\Lambda \tau}$, where Λ is the temperature diffusivity. In the case of metals the value of d would reach about $0.1 \mu\text{m}$ and the mean increase of the enthalpy constant corresponding to this layer represents several kJ/cm^3 , which would be sufficient to melt down at least a part of material. The temperature gradient is of the order of 10^8 K/cm (i.e., 10^3 K along the distance of 10^{-5} cm), which corresponds to the heat flux in the neighborhood of 10^8 W/cm^2 emitted by the melt into the bulk after absorption of one pulse. At the end of the pulse, the cooling rate may be as high as 10^{11} K/s . This simple

estimate has demonstrated the order of magnitude of extreme values of affected layer thickness, temperature gradient and changes. These values are lower for CW lasers; in this case the cooling rate attains about 10^6 K/s at the feed rates of the order of $\mu\text{m/s}$.

The temperature can be simply calculated for a beam circular cross section of radius, r , and total power, P , of the uniform distribution of its density impinging and a planar surface of a plate of the infinite thickness. Then $T_{\text{max}} \cong P \varepsilon / (r \Lambda)$, where ε and Λ are the absorptivity of the surface and thermal diffusivity, and the average temperature is about 0.85 of its maximum value. It follows that the characteristic temperatures can be expressed as a product of two factors, namely P/r and ε / Λ , the first being dependent only on the laser unit, the other only on the material, which can be used to solve the reverse problem: i.e., what a required power density is necessary for given material. For example, for iron ($T_m = 1535 \text{ C}$), $\varepsilon \sim 10\%$, $\Lambda = 0.4 \text{ W/(K cm)}$ and use of 500 W CW-CO_2 laser, it is $2.35 \cdot 10^5 \text{ W/cm}^2$. The choice of actual irradiation regime is a matter of compromise among the number of requirements, often conflicting, i.e., halving the irradiation radius the required duration of exposition drop to a value about twenty times smaller, which means that the temperature field spreads to smaller depth in that shorter time. If we want to reach the same temperature at double the depth, we have to lower the feed rate to about one half. With decreasing power density, the final cooling rate for any melt-down depth always drops by more than two orders of magnitude.

In this way the critical cooling rates (in K/s) were determined for several melted metals, e.g., Ni (10^{10}), $\text{Fe}_{80}\text{B}_{11}$ (10^6), Ge (10^5), $\text{Ni}_{62}\text{Nb}_{38}$ (10^3), or $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ (10^3). Improved wear resistance of the irradiated surface of as-cast iron is due to homogenization and fast solidification resulting into primary austenite and ledeburite, both not allowed to exist when equilibrated at room temperature. Sometimes it is sufficient to harden material by surface phase transformation in solid state where the surface relief remains unchanged, thus obviating the need for further operations like smoothing the surface by grinding.

e) Controversial character of bulk and spot observations

Very important but often neglected problem is the mutual, somehow controversial existence of two basic kinds of observation, which are thus difficult to correlate. One is based on the indirect average measurement of the mean property of a whole sample, which is executed by the standard thermophysical and thermoanalytical measurements (e.g., DTA, DSC, XRD, thermogravimetry, dilatometry or magnetometry). The other is the appearance method consisting of visualized local-measurements directed at a precise spot on the sample surface or its intentional fracture, which is a traditional morphology measurement (such as light or electron microscopy). Both approaches have their loyal defenders and energetic rejecters often depending to what are their subject instrument and the direction of study. Though measurements on larger (more voluminous) samples are more sensitive to a mean property determination, particularly when repre-

sented by thermal (DTA, DSC), mass (TG) or magnetization measurements, they always involve undefined temperature (and mass gradients) in its bulk (Fig. 11.). Such gradients are often unnoticed or later observed as disagreeable changes of the result fine structure because the total sample size is simplistically defined by single values of temperature (in the same way as weight or magnetization). Even miniaturization of such a sample is not always a recommendable elucidation due to the undesirably increasing effect of the property of its surface over that of bulk although a specially shaped sample holders were devised to help the problem, cf. preceding Fig. 9.6. The averaged type of measurements are often sharply criticized when employed as the input data for the verification of kinetic models, which are based on specific physico-geometrical premises related to the idealized morphology pictures.

On the other hand, we can recognize the advantage of the spot measurements, which actually reveal a real picture of the inner structure, but we have to admit that the way how we see it, that is the entire selection of insight windows and their multiplicity, is often in the hands of the observer and his experience as to what is more and less important to bring to his view and then observe in more details. Therefore, such a morphological observation, on the contrary, can be equally questioned as being based on a very localized and almost negligible figure, which provides the exposed-surface pattern representing thus almost insignificant part of the sample. Moreover, it is observed under conditions much different from those occurring at the entire experimentation. Furthermore, considerable changes of the observed surface can occur not only as a result of the actual structure of the sample (and its due transformation) but also owing to the mechanical and chemical treatments. The preparation of the microscopically ready-to-observe sample, as well as the other effects attributable to experimental condition of the entire observations is often neglected. There is no any appropriate selection or recommendation; we have to restore our understanding and final attitude accounting on both aspects – limiting viewpoints having little networking capacity.

There are not many reliable reports showing the direct impact of the measuring finger ('gadget'), i.e., the way that we actually 'see' the sample (by, e.g., light or electron beam). Let us look at the scanning electron microscope analysis (SEM), which is one of the oldest methods using the focused electron beam having energy typically from 1 to 30 kV and a diameter from 5 nm to some micrometers. There can be seen a striking similarity with the previously discussed laser, which can equally be used as both, the measuring or the energy-source tool. SEM just disposes with the different energy source so that it is obvious that the interaction of the charged particles involved (electrons) can reveal the changes in

both the structure and the chemical composition of the sample under investigation. [44], cf. Fig. 12. It is assumed that about 40–80% of the power delivered into the excited volume is transformed into heat. Heat is generated in the excited pear-shaped volume below the surface and its quantity is determined by the irradiation parameters (such as accelerating voltage), the primary current, the beam diameter and by the material parameter abbreviated as 'f', which is defined as the fraction of the primary electron energy absorbed in the sample. The quantity $(1 - f)$ represents back scattered or secondary electrons. For the evaluation of temperature increase the same equation for thermal conductivity can be employed as shown in the previous sections. The temperature rise in the center of the probe was calculated for the case of a hemispherical homogeneous source in a semi-infinite homogeneous sample with its outer surface kept at room temperature [39] yielding relation $\Delta T \sim U I / \Lambda r_0$ where ΔT , U , I , Λ and r_0 are the maximum temperature rise in the center of the probe, electric voltage, current, thermal conductivity of the sample and the probe radius, respectively.

It is evident that a direct temperature measurement in the excited volume is possible only at very high currents of the electron beam. Moreover, it is impossible to study the temperature field created inside and outside the bombarded volume. The masterminded idea was to use a material that can change its structure with the temperature assuring that this change is instant, irreversible and observable with a sufficient resolution. Glass, glass-ceramics, or magnetic materials with visualized domains can serve for that purpose. The experimental result approved the calculated temperature field together with the SEM picture at the sample scale for glass-ceramics exposed to

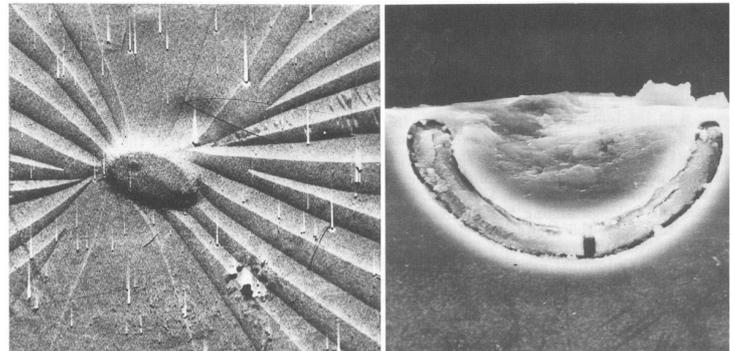


Fig. 10.12. Two illustrative examples of the surface damage caused by electron beam action during SEM at intensity of 10^{-6} A. Left: photograph of the metallic glass (composition $Fe_{40}Ni_{40}B_{20}$ with $T_{curie} \cong 350$ C and $T_{cryst} \cong 400$ C), showing the re-crystallized area (middle dark spot) as a result of electron beam impact (diameter 1μ) which is surrounded by yet remaining magnetic domains striation (characteristic for annealed as-cast ribbons, cf. previous Fig. 12.11.). Right: oxide glass (composition $60SiO_2-10Al_2O_3-10MgO-10Na_2O$, with $T_{cryst} \cong 780$ C and $T_{melt} \cong 1250$ C) revealing the crystallized region along the concave interface as well as the re-solidified area in the inner part as a result of the electron beam impact (diameter 10μ). The occurrence of melting is proved by disappearance of liquation spots characteristic for the originally phase separated glass. Courtesy of V. Hulínský and K. Jurek (Prague, Czechia).

a stationary beam of 200 μm diameter, accelerating voltage 50 kV and the absorbed current 7560 nA. Coming from the pot edge of the SEM image we can see the following areas, dark area of melted diopside crystals, this area continuously grades into the larger area containing large diopside crystals that become denser and smaller with the increasing depth. The next area contains individual rods of pyroxene that convert to spherulites near the lowest part of the crystallized volume.

The *a priori* fear that any SMA investigation may result in the sample over-heating is not tangible as the small exposed region permits very strong cooling by thermal conduction to the bulk. Nevertheless, the experimenter must be aware of the potential risk associated with the electron bombardment of the viewed sample surface, which, moreover, is exposed to vacuum providing little heat transfer to the surroundings. The maintenance of yet acceptable surface temperature by good heat sink to neighboring parts is the only securing parameter for realistic measurements, certainly not avoiding possible creation of certain (even mild) temperature gradients (which we ceaselessly face in all other type of measurements).

f) Particularities of temperature modulation

For the superimposed temperature transitions, two fundamental concepts are accessible: either the temperature modulation or the repeated temperature scanning [46,47]. In the temperature modulation, the amplitude of the temperature oscillation is generally small and response of the sample to this perturbation by temperature oscillation is observed. The experimental response can be the measure of heat flow, sample mass, etc. The responses are usually analyzed by *Fourier* analysis, and are separated into 'in-phase' and 'out-of-phase' responses, though their physical meanings are discussed from various points of view (see Chapter 11). The repeated temperature scanning, on the other hand, allows the sample heating and/or cooling in a large temperature range necessary to observe the sample behavior by this temperature fashion. Such amplitude of temperature oscillation lies, however, in a wider range, say from 50 °C and 200 °C. Until now, the sample mass changes are under such a mode of investigation. By extracting data of the mass and the mass change rate at a given temperature, we can get a relation between the mass and the mass change rate; the resulting curve is equivalent to that obtained by a commensurate isothermal run. Thus we can get equivalent isothermal curves at multiple different temperatures. Another application of this method is observation of non-stoichiometry, in which we can obtain *Lissajous* figures (see Chapter 14) by plotting the mass versus the temperature.

However, the essential point in both these methods is the same. When the property, under observation by thermo-analytical methods, depends only on the temperature, we get a hold of a single curve in the conventional plot of the property versus the temperature (*Lissajous* figure) and we do not observe 'out-of-phase' component in the response. This single curve obtained is independent on temperature control modes, such as constant-rate heating, sample-controlled thermal analysis or other temperature modulation

varieties. The sample behavior becomes dissimilar, when the property become dependent on the temperature and if the time gets involved in the kinetic effects, such as in relaxation, etc.. In this case, it takes a certain time for the sample to reach the stable (or equilibrium-like) state, and due to this kinetic time-obstruction, we find out a new, ellipsoid-like cyclic curve and we also observe the out-of-phase response. It can be said that the out-of-phase response and the ellipsoid-like cyclic curve (in the characteristic *Lissajous* figure) are observed when the sample property is dependent on its previous thermal history (namely known as hysteresis). One example is the glass transition often observed for organic and inorganic polymers by means of tm-DSC and another example is the case of non-stoichiometry detected by repeated temperature scanning. In the latter case, the large amplitude of temperature oscillation is preferable for detecting the effect by enlarging the change.

Observing these phenomena at very low frequencies (or at very low rates of heating and/or cooling), we do not perceive the out-of-phase response (nor the ellipsoid-like cyclic curve but a single curve) because enough time is given to the sample to relax reaching its stable state. In contrast with this, at very high frequencies or at very high rates of heating and/or cooling the change in the observed property cannot be detected, because no time to change is allowed to the sample adjustment. At a frequency in which the rate necessary to reach to the stable state is comparable to the frequency or the rate of heating and/or cooling, we observe maximum effect or the maximum out-of-phase response. Thus, the appropriate fine-tuning of frequency dependence is very important to get fitting insight to the sample behavior. For instance, it helped to elucidate that in the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ system three types of oxygen at three different crystalline sites are involved, which distinguish its non-stoichiometry (cf. Chapter 19). This was found as a consequence of associated kinetics because the frequency dependencies differ from each other.

To identify chemical reactions by the temperature oscillation, a similar but somewhat different viewpoint is needed. For simple chemical reactions, in which a single elementary process is involved, the rate of chemical reaction depends only on the temperature and the state of conversion. Thus, we can obtain a single isothermal-equivalent curve for the given temperature. For the other type of chemical reactions, which involve multiple elementary processes of different temperature dependence, the rate of chemical reaction is also restricted by the sample previous thermal history. Therefore, we cannot obtain a single equivalent to isothermal curve, as the heating mode is different from that under cooling. Interesting illustrations can be found for various depolymerization (or unzipping) of macromolecules (polymers). In these reactions, radicals are often formed by some elementary processes at weak links, at chain ends or at random sites in the main chain, and the radical is annihilated by radical recombination or disproportionation. The rate of mass loss caused by unzipping is proportional to the radical amount, and the radical concentration reaches to a constant in steady state, where the rate of radical annihilation becomes equal to the

rate of radical formation; the constant radical concentration in the steady state is dependent on the temperature. Thus this reaction proceeds by a first order reaction because the radical amount is proportional to the sample mass in the steady state. Supposing that time to reach to the steady state is comparable to the frequency or the rate of heating and cooling, the out of phase response would be observed and we would observe that equivalent isothermal curve. Evidently, on cooling it would be different, which stems from the time delay to reach the steady state.

The concept and theoretical considerations of the sample behavior, which responds to the temperature oscillation is, thus, quite similar to the sample behavior responding to other oscillation, such as polarization of dielectrics to alternating electric field and deformation of viscoelastic substances to dynamic mechanical stress, and these would also be applicable to other thermoanalytical methods, such as thermomechanical analysis, etc. The essential point is the existence of stable (or equilibrium) state and the disposition to reach stability. For example, let us mention cyclic voltammetry, in which electric current by electrode reaction is plotted against

applied voltage, while the voltage is repeatedly scanned over a wide range. When we observe dehydration and hydration process under constant water partial pressure by wide-range temperature oscillation, we would get a similar cyclic curve of the mass or the mass change rate versus the temperature, and the curve would become frequency dependent.

In order to describe as well as consider the oscillating behavior, the *Euler* equation and other methods of the determination of unknown parameters is necessary assuming the steady state of oscillatory behavior (*Fourier* analysis and *Lissajous* figures). However, it should be noted that these mathematical methods are regularly based on the linearity of processes so that any decrease in the amplitude and shift of the phase angle (inevitably occurring during propagation of the temperature wave along the instrument and into the sample), may cause errors. Therefore moderately thin specimens are preferably attentive to the sample low thermal diffusivity (polymers and powders) and the quality of thermal contact between the specimen and the instrument (cf. Chapter 5).

¹ Reactive milling has opened yet new ways for the realization of amorphization of standard crystalline structures without application of heat, i.e., by the disintegration of crystals below certain limiting size ($< \mu\text{m}$). The same technique is applicable to intensify and modify a range of solid-state reactions and the associated alloy syntheses, particularly for many high-melting intermetallics difficult to prepare by conventional processing [e.g., K. Wiczorek-Ciurowa, K. Gamrat, M. Parylo, Yu. G. Shirokov, *J. Thermal Anal. Calor.* 70(2002)165 and 237]. Mechanical activation or disintegration is usually carried out in high-energy devices such as vibratory, planetary or attritor mills. Simultaneously, actions of stroke and friction cause, besides comminution, changes of physico-chemical properties of ground materials, which also involve the excess energy accumulation. As a consequence, favorable conditions are formed to precede chemical reactions and physical processes, that normally require high-temperatures, and which can thus occur without externally applied heat. The energy transfer is governed by many parameters such as milling speed, ball size and their distribution. It is obvious that high kinetic energy of the balls is favorable for ease of mechanical alloying processing, which optimal intensity requires a mass excess of balls in comparison to milling material, usually in the ratio 1:50. Milling time become important factor in achieving the desired results, for Fe-Cu metastable alloy is in excess of 50 hrs while for TiAl_3 ordinary alloy formation goes down to mere 4 hrs.



CHAPTER ELEVEN

11. Thermal analysis and calorimetry

a) Systematic of calorimetry

Calorimetry is a direct and often the only way of obtaining the data in the area of thermal properties of materials, especially at higher temperatures. If the calorimeter is viewed as a certain 'black box', whose input information are thermal processes and the output figures are the changes in temperature or functions derived from these changes. The result of the measurement is an integral change whose temperature dependence is complicated by the specific character of the given calorimeter and of the measuring conditions. The dependence between the studied and measured quantity is given by a set of differential equations, which are difficult to solve in general case. For this reason, most calorimetric measurements are based on calibration. A purely mathematical solution is the domain of a few theoretical schools [1,48,49] and will not be specified herewith in more details.

If the heat, Q , is liberated in the sample, a part of this heat is accumulated in the calorimetric sample-block system (see Fig. 1) and causes an increase in the temperature. The remaining heat is conducted through the surrounding jacket into the thermostat. The two parts of the thermal energy are closely related. A mathematical description is given by the basic calorimetric equation, often called *Tian* equation [50].

$$Q' = C_p T'_B + \Lambda (T_B - T_J) \quad 10.1$$

where the prime marks the time derivative. The principal characteristics of a calorimeter are the calorimeter capacity, C_p , its heat transfer (effective thermal conductivity), Λ , and the inherent heat flux, q' , occurring at the interface between the sample-block, B , and surrounding jacket, J .

The temperature difference, $T_B - T_J$, is used to classify calorimeters, i.e., diathermal ($T_B \neq T_J$), isodiathermal ($T_B - T_J = \text{constant}$ and $d(T_B - T_J) \rightarrow 0$), adiathermal ($T_B \neq T_J$) and $\Lambda \rightarrow 0$, adiabatic ($T_B = T_J$), isothermal ($T_B = T_J = \text{const.}$) and isobaric ($T_B - T_J \rightarrow 0$). The most common version of the instrument is the diathermal calorimeter where the thermal changes in the sample are determined from the temperature difference between the sample-block and jacket. The chief condition is, however, the precise determination of temperatures. With an isodiathermal calorimeter, a constant difference of the block and jacket temperatures is maintained during the measurement, thus also ensuring a constant heat loss by introducing extra heat flux to the

sample from an internal source (often called microheater). The energy changes are then determined from the energy supplied to the source. If the block temperature is maintained constant, the instrument is often called a calorimeter with constant heat flux. For low Q' values, the heat loss can be decreased to minimum by a suitable instrument construction and this version is the adiabatic calorimeter. Adiabatic calorimeter suppresses heat losses by maintaining the block and jacket temperatures at the same temperature. Adiabatic conditions are more difficult to assure at both higher temperatures and faster heat exchanges so that it is preferably employed at low temperatures, traditionally using *Dewar* vessel as insulating unit.

Eliminating the thermal gradients between the block and the jacket using electronic regulation, which, however, requires sophisticated circuits, can attain the lowest heat transfer and a more complex setup. For this reason, the calorimeters have become experimentally very multifaceted instruments. With compensation "quasiadiabatic" calorimeter, the block and jacket temperatures are kept identical and constant during the measurement as the thermal changes in the sample are suitably compensated, so that the block temperature remains the same. If the heat is compensated by phase transitions in the bath in which the calorimetric block is immersed, the instrument are often termed transformation calorimeter. Quasi-isothermal calorimeters are again instruments with thermal compensation provided by electric microheating and heat removal is accomplished by forced flow of a liquid, or by the well-established conduction through a system of thermocouple wires or even supplemented by *Peltier* effect. The method in which the heat is transferred through

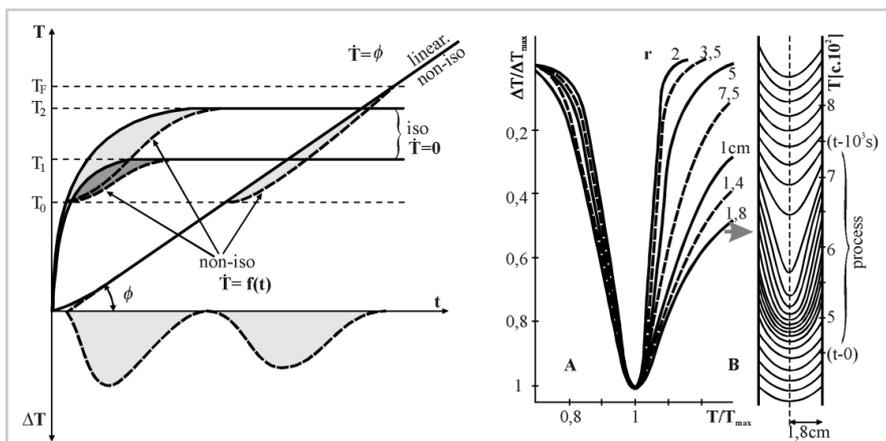


Fig. 11.1. Some aspects of DTA-based effects. Left, the sketch showing the development of a DTA peak under idealized and authentic temperature profiles of the sample in isothermal and nonisothermal regimes. The DTA peak is determined as a response of the sample temperature being different from the programmed temperature of the sample surroundings due to the heat sink. The temperature differences actually resemble the traces of both the isothermal and normal DTA record. The dashed lines mark the real temperature change in the sample due to both the externally applied heating and the internally absorbed (or generated) heat of reaction (shaded). The solid lines express the idealized temperature changes habitually assumed to be representative enough even for the sample temperature and identical to the thermally controlled surroundings. Right, the set of normalized DTA peaks, calculated for a real material placed as variously diameter samples, illustrate the actual profiles of temperature gradients in a cylindrical sample (with a limiting diameter of 18 mm) due to the thermal gradient developed during an ongoing process.

a thermocouple system is often called *Tian-Calvet* calorimetry. A specific group consists of isoperibolic calorimeters, which essentially operate adiabatically with an isothermal jacket. Temperature gradients do not exceed a few degrees and the separation of the block from jacket (a vacuum or low-pressure air gap) should ensure that the heat transfer obeys the Newton's cooling Law. There are other version such as the throw-in calorimeter where the sample is preheated to high temperatures and then dropped into a calorimetric block, and combustion calorimeter where the sample is burned in the calorimetric block (often under pure oxygen atmosphere). A separate field forms enthalpiometric analysis, which includes liquid flow-through calorimeters and thermometric titrations lying beyond this brief introduction.

b) Classification of thermoanalytical methods – heat balance

Theoretical treatments of DTA/DSC have been published at various levels of sophistication. The most complex analyses have usually been geared to the details of particular instrumentations so that they bring too specific knowledge for a generally oriented reader. There are two most common lines of attacks:

- (i) homogeneous temperature distribution in the calorimetric samples [25] and
- (j) complete incorporation of the effects of temperature gradients and heat fluxes [51], cf. Fig. 11.1. Our approach here will be, first, to give a more transparent treatment of DTA/DSC based on the presentation of Gray, [52] and Šesták and his coworkers [53,54].

The popular technique of differential thermal analysis (DTA) belongs among the indirect dynamic thermal techniques in which the change of the sample state is indicated by the temperature difference between the sample and geometrically similar inert reference held under identical experimental conditions. The method of heating and cooling curves, long popular in metallurgy, paved the way to its development by inserting the comparing site. Further sophistication was achieved by further incorporation of a sample-attached microheater. The advantage of this widely used method is a relatively easy verification of differences in thermal regimes of both specimens and so the determination of zero trace during the test measurements, currently replaced by inbuilt computer programming.

Fig. 11.2. shows a schematic of the DTA/DSC standard arrangement used in the customary sphere of dynamic calorimetry. The sample and reference compartments can be in contact with the common block, B, which is at temperature T_B , through the respective thermal resistances. The actual sample (S) and reference (R) are in thermal contact with the two respective holders/cells through the relevant thermal resistances again, which, however, are often assumed to be effectively zero, i.e., the temperatures of the sample and reference are equal to those of the

respective holders. The methods of analysis can be characterized by envisaging the basic flux, q'_s , to take place between the sample investigated and its environmental jacket, J, that is $q'_s = \Lambda_s (T_s - T_J)$, where Λ is the effective thermal conductance (which is the inverse of the respective thermal resistance). In some high-temperature systems, the heat transfer may occur through radiative as well as conductive paths. In the twin arrangement the standard sample heat exchange is also accompanied by additional fluxes between the reference sample and its environment, $q'_R = \Lambda_R (T_R - T_J)$, and between the sample and the reference, $q'_\Delta = \Lambda_\Delta (T_S - T_R)$. It then holds for the change in the sample enthalpy that $\Delta H'_S = q'_s + q'_\Delta + Q'_S$ and for the reference sample $\Delta H'_R = q'_R + q'_\Delta + Q'_R$, where Q' is the compensation heat flux which is to be supplied by the excess microheater (often built into the measuring head). The scheme of all participating thermal fluxes in the twin crucible arrangement is shown in Fig. 2. In the result, we can derive basic equations for the individual setups:

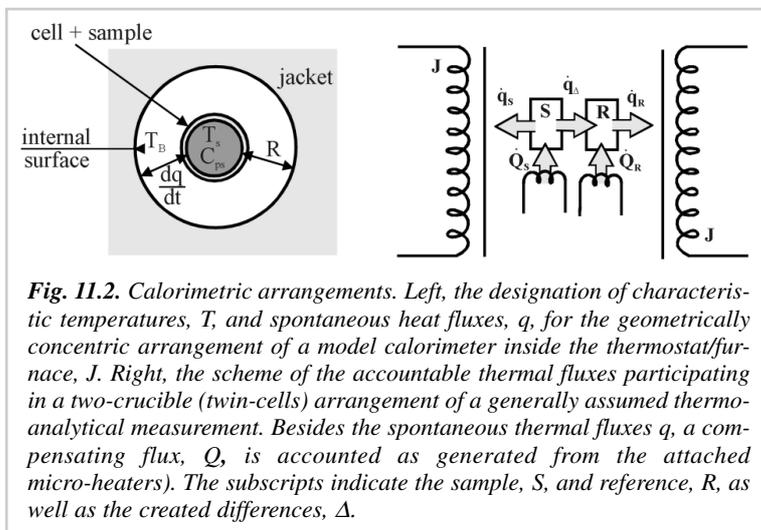


Fig. 11.2. Calorimetric arrangements. Left, the designation of characteristic temperatures, T , and spontaneous heat fluxes, q , for the geometrically concentric arrangement of a model calorimeter inside the thermostat/furnace, J. Right, the scheme of the accountable thermal fluxes participating in a two-crucible (twin-cells) arrangement of a generally assumed thermoanalytical measurement. Besides the spontaneous thermal fluxes q , a compensating flux, Q , is accounted as generated from the attached micro-heaters). The subscripts indicate the sample, S, and reference, R, as well as the created differences, Δ .

1) For the determination of heating and cooling curves the solution leads to the single-crucible method, where the temperature of the sample, T_S , reads as

$$T_S = \Delta H_S / \Lambda_S \alpha' + C_{pS} / \Lambda_S T'_S + T_J \quad 10.2$$

2) For the classical differential thermal analysis (DTA), where the sample and reference are placed in the same block and the radiation transfer of heat, is neglected, we obtain

$$\Delta T = [- \Delta H_S \alpha' + (C_{pS} - C_{pR})\phi + C_{pS} \Delta T' - \Delta \Lambda (T_R - T_J)] / (\Lambda_S + 2\Lambda_\Delta) \quad 10.3$$

where $\Delta \Lambda = \Lambda_S - \Lambda_R$ and $T'_J = \phi = T'_S - \Delta T'$. This equation can be simplified by introducing the assumption that $\Delta \Lambda = 0$ (i.e., the both sites in the crucible block are identical). If $\Delta \Lambda$ also equals zero, then the DTA arrangement involves the common case of two separate crucibles providing the most widespread instrumentation following

$$\Delta T = [- \Delta H_S \alpha' + (C_{pS} - C_{pR})\phi + C_{pS} \Delta T'] / \Lambda_S \quad 10.4$$

where the overall coefficient of heat transfer Λ_S is called the DTA apparatus constant ($= K_{DTA}$) which is conveniently determined by the calibration of the instrument by the compounds of known properties or by direct use of electric heat pulses. We can proceed to specify similarly the equations for analogous measurement of both the spontaneous thermal fluxes by the single crucible method, the differences of the external thermal fluxes or even the heat-flux differential scanning calorimetry (often called differential *Calvet* calorimetry) as follows from Fig. 2.

3) However, the method of power-compensating differential scanning calorimetry (DSC) bears a special importance calling for a separate notice as it exhibits a quite different measuring principle. In the thermal balance the compensating thermal flux, Q' , appears to maintain both crucibles at the same temperatures ($T_S \cong T_R$) so that the traditional difference, ΔT_{DTA} , is kept at minimum (close to zero) and thus serves for the regulation purposes only. Then we have

$$\Delta Q' = -\Delta H_S \alpha' + (C_{pS} - C_{pR})\phi + \Delta \Lambda (T - T_J). \quad 10.5$$

All the equations derived above can be summarized within the following schema using the general summation of subsequent terms, each being responsible for a separate function:

$$\text{enthalpy} + \text{heat} + \text{inertia} + \text{transient} = \text{measured quantity}$$

It ensues that the effects of enthalpy change, heating rate and heat transfer appear in the value of the measured quantity in all of the methods described. However, the inertia term is specific for DTA, as well as for heat-flux DSC, and expresses a correction due to the sample mass thermal inertia owing its heat capacity of real material. It can be visualized as the sample hindrance against immediate 'pouring' heat into its heat capacity 'reservoir'. It is similar to the definite time-period necessary for filling a bottle by liquid (easy to compare with 'caloricum' as an outdated fluid theory discussed in Chapter 3, the philosophy of which is inherent in our mathematics). This somehow strange effect is often neglected and should be accentuated because the existence of thermal inertia shows its face as the definite distinction between the two most popular and commercially available methods: (*heat-flux*) *power compensating DSC* and *heat-flux (measuring) DSC*. Though the latter is a qualitatively higher stage of calorimetry as matured from DTA instrumentation, it remains only a more sophisticated DTA. It factually ensures a more exact heat transfer and its accurate determination, but it still must involve the heat inertia term in its evaluation, in the same way as the classical DTA does.

If the heat transfers, between the sample/reference and its holders are nonzero and imbalanced the area under the peak remains proportional to the enthalpy, ΔH , but the proportionality constants includes a term arising from the definite value of Λ_{SR} so that $\Delta H \cong \Lambda_S [1 + 2(\Lambda_{SR}/\Lambda_S)]$. The coupling between the sample and reference cells in

the disk-type-measuring heads can be significant and such links should not be neglected as done above. Similarly, the central mode of balanced temperature measurements gives another modified solution. A useful model [55] was suggested on basis of analogy between thermal and electric resistances and capacities.

c) DSC and DTA as quantitative instruments

The idea of DSC arrangement was first applied by *Eyraud* [56] and further developed by *O'Neill* [57]. Whereas *Eyraud* accomplished the internal microheating by passing the electric current directly through the mass of the sample composed of the test material mixed with graphite powder as an electric conductor. *Speros* and *Woodhouse* [58] already employed a classical platinum spiral immersed in the sample. Modern commercial instruments employs microheaters attached to the surface of the sample cells. One of the first, more detailed descriptions of DSC theory and its applicability was given by *Flynn* [59], who introduced the notion of time constant of temperature program cropping up from the difference in the microheater power and the interface sample conductivity. It is assumed that DSC operates in a stationary program, with a constant increase in the jacket temperature and with differences in the heat drop, the heat capacities and the masses of the two DSC cells being constant and reproducible functions of temperature.

In [49] the DSC equation is usefully modified by assuming that $Q'' \cong (T'_B - T'_S)\Lambda$, to encompass the form

$$\Delta H_S = -Q' - C_{pS} Q''/\Lambda + (C_{pS} - C_{pR}) T'_B \quad 10.6$$

and assuming that the electronic control system maintains the temperature of both the sample and reference cells at the temperature of the block, T_B , by controlling the power applied to their respective microheater. This portrays well that the power developed in the sample cell is the contribution of the terms placed on the right-hand side: the first term is related to the directly measured signal, the second to the first derivative of the measured signal and the third to the heat capacity difference between the sample and reference cells. Because the thermal resistance ($1/\Lambda$) appears as a coefficient in front of the second DSC term (while in the DTA equation it serves as the whole proportionality constant for the measured signal), it results in the ability of DSC instruments to reduce the resistance, thereby decreasing the time constant without decreasing its sensitivity. On the other hand, in DTA equipment there is a trade-off between the need for a large resistance for higher sensitivity but a low time-constant ($\tau = C_{pS}/\Lambda$) for high resolution. A small resistance ensures that the lag of the sample temperature behind that of the sample holder is minimized.

Several studies comparing the advantages and disadvantages of the heat-flux and power-compensating DSC methods were conducted, showing not essential differences. The lower values of enthalpies sometimes obtained from the heat-flux measurements were found to be due to the base line correction as a result of algorithm used by computer. However, parameter-space-induced errors,

which are caused by changes in the time constant of the sample arising from changes either in the heat exchange coefficient or in the heat capacity of the sample, are less significant in the power-compensating DSC.

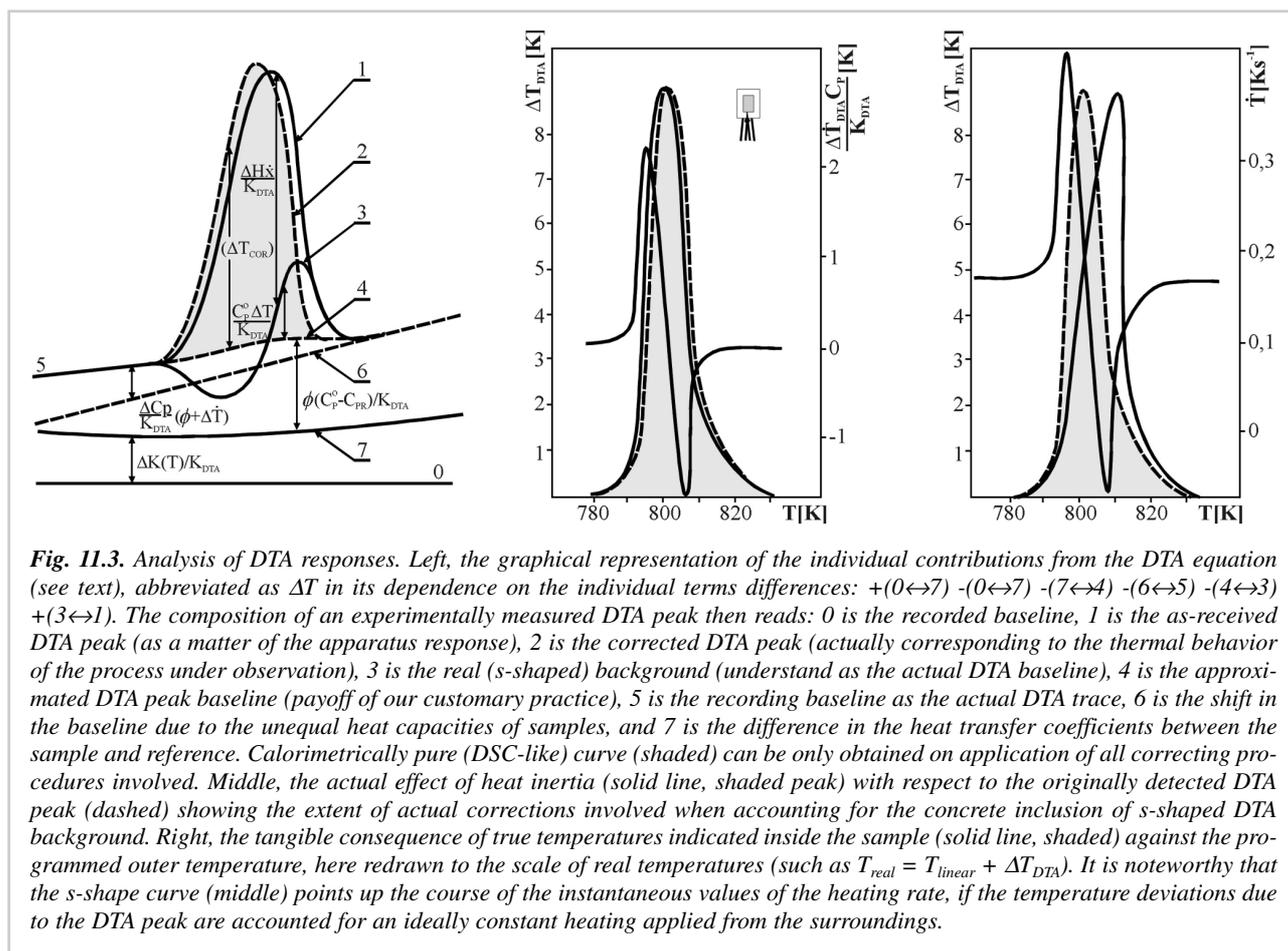
The temperature modulated DSC (often abbreviated as TMDSC) has aroused attention as a rather new technique that was conceived in the early 90's and immediately patented and commercialized. The temperature signal is here modulated as a sinusoidal wave and is superimposed over the traditional monotonous curve of heating. This technique offers the possibility of deconvoluting the signal into an in-phase and an out-of-phase response, which can be used to calculate heat flows or heat capacities. It was preceded by experiments performed by early eighties [60,61] and is actually a consequential development of the so-called ac-calorimetry [62].

It would be difficult to survey all possible and existing applications of DSC, which is one of the most commonly used calorimetric methods. Among these, we can mention the determination of impurities, evaluation of phase transformations of the first and second orders, determination of heat capacities and heat conductivities, reaction kinetics, study of metastable states and glasses, determination of water clusters, thermal energy storage, etc.

The traditional method of DTA has deeper roots and it has been described elsewhere [63,64]. DTA applications were first based on experience and semi-quantitative eval-

uations so that the early articles, e.g., [65], should be noticed for using a computer in the verification of the effects influencing the shape of DTA peak. The DTA peak area was verified to be proportional to the heat of reaction (in the ΔT vs. t coordinates) and found dependent on the heating rate and distorted by increasing crucible diameter. It is, however, almost independent of the positioning of the thermocouple junction within the sample (it affects the apex temperature).

Through the commercial perfection and instrument sophistication the most DTA instruments reached the state of a double non-stationary calorimeter in which the thermal behavior of the sample (T_S) and of the reference material (T_R), placed in the thermally insulated crucibles, is compared. The relatively complicated relationship between the measured quantity, $\Delta T = T_S - T_R$, and the required enthalpy changes of the sample, ΔH , has been the main drawback in the calorimetric use of DTA. Doubts about the quality of the enthalpy measurement by DTA stem from the fact that the changes in ΔT are assumedly affected by many freely selectable parameters of the experimental arrangement. So the suitable formulation of DTA equation, neither too complicated nor too simple, was the main objective for the progress of methodology. In our opinion the most important study was that done by *Faktor* and *Hanks* in 1959 [25], which was used as a basis for our further refinement in defining thus the complete DTA equation [1,53,54],



$$\Delta T = [\Delta H_S \alpha' - (C_{p_{oS}} - C_{p_{R}})\phi - \Delta C_{p_S} (\phi + \Delta T') - C_{p_{oS}} \Delta T' + \Delta K(T)] / K_{DTA} \quad 10.7$$

where the term $C_{p_{oS}}$ is a modification of C_{p_S} as $(C_{p_o} + \Delta C_p \alpha)$, the collective thermal transfer term $\Delta K(T)$ is the sum of the individual heat transfer contributions on all levels (conduction as well as radiation) and the so-called DTA instrument constant, K_{DTA} , is the temperature dependent parameter, characteristic for each instrument and showing how the overall contributions of heat transfers change with temperature. The detailed graphical representation of individual terms is illustrated in Fig. 10.3a.

There are four main requirements for the correct DTA measurement:

- 1) *Attainment of a monotonous increase in the temperature* (preferably $T = \phi = \text{const.}$). If included in the apparatus software, there is danger that the perfectly linearized baseline could become an artifact of computer smoothing so that it is advisable to see the untreated baseline too.
- 2) *Correct determination of the peak background*, i.e., the method of the peak bottom line linearization (either joining the onset and outset temperatures or extrapolating the inwards and outwards baseline against the normal of the peak apex, cf. Fig. 4). Actual s-shaped background is symmetrical (both deviations are equal) and for $\Delta C_p \rightarrow 0$ does not affect the determination of the peak area.
- 3) *Appropriate determination of characteristic points*, as the onset, outset and tip of peaks, based on a suitable approximation of the base line and extrapolation of peak branches.
- 4) *Experimental resolution of the temperature dependence of the DTA instrument constant*, which is often inherent in the software of the instruments commercially available.

It should be re-emphasized that during any DTA measurements the heating rate is changed due to the DTA deflection itself see Fig.10.3b. Actually, as soon as completely controlled thermal conditions of the sample were achieved, the entire DTA peak would disappear. Fig. 10.3b well demonstrates the disagreement between non-stationary DTA traces for a real sample and its equilibrium-adjacent rectification when accounting for corrections due to the heat inertia discussed above and those caused by the inherent changes in heating rate.

e) DTA calibration and the use of defined electrical pulses

Calibration of a DTA involves adjustment of instrumental electronics, handling and manipulation of the data in order to ensure the accuracy of the measured quantities: temperature, heat capacity and enthalpy. Temperature sensors such as thermocouples, resistivity thermometers or thermistors may experience drifts that affect the mathematical relationship between the voltage or resistance and the absolute temperature. Also, significant differences between the true internal temperature of a sample with poor thermal conductivity and the temperature recorded by a probe in contact with the sample cup can

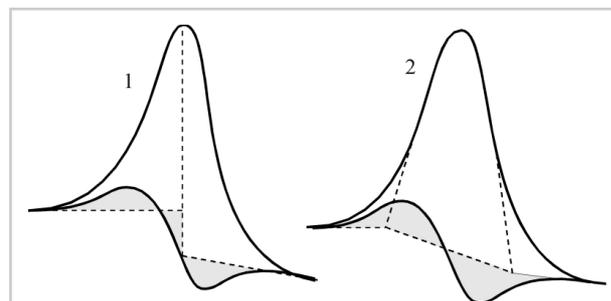


Fig. 11.4. Two customary methods for the linear approximation of the DTA peak background (which are in agreement with the ICTAC recommendation). The shaded area shows the difference between the interpolated values and actual background.

develop when the sample is subjected to faster temperature scans. The important quantity measured in DTA experiments is the ΔT output from which enthalpy or heat capacity information is extracted. The proportionality constant must thus be determined using a known enthalpy or heat capacity – the power-compensated DSC requires lower attentiveness as it works already in units of power. The factors such as mass of the specimen, its form and placement, interfaces and surface within the sample and at its contact to holder, atmosphere link and exchange, temperature sink, and other experimental effects influence the magnitude of the power levels recorded in DTA (and DSC) instruments, recently often hidden in computerized control.

One of the most straightforward pathways to formulating a relationship between the measured and actual temperatures is the use of standard substances with defined temperatures of certain transformations connected with a suitable thermal effect (peak). This procedure was extensively studied during seventies by the Standardization Committee of ICTA and chiefly directed towards explaining discrepancies in the published data and towards selecting and testing standards suitable for DTA. In cooperation with the US national Bureau of Standards there were published and made available four certified sets of the DTA temperature standards covering the temperature region of about 1000 degrees.

Most common calibration substances involve transitions and/or melting (in °C) and they can include: O_2 (boiling point, -182,96), CO_2 (sublimation point, -78,48), cyclohexene (-87 & 6.5), Hg (solidification point, -38,86), dichlorethane (-35), H_2O (melting point, 0.0), diphenylether (27), o-terphenyl (56), biphenyl (69), H_2O (boiling point, 100), benzoic acid (solidification point, 122,37), KNO_3 (128), In (solidification, 156.63), $RbNO_3$ (164 & 285), Sn (232), Bi (solidification, 271,44), $KClO_4$ (301), Cd (solidification, 321,11), Zn (solidification, 419,58), Ag_2SO_4 (426), CsCl (476), SiO_2 -quartz (573), K_2SO_4 (583), Sb (solidification, 630,74), Al (solidification, 660,37), K_2CrO_4 (668), $BaCO_3$ (808), $SrCO_3$ (925), Ag (solidification, 961,93), ZnS (1020), Au (solidification, 1064,43), Mn_3O_4 (1172), Li_2TiO_3 (1212) or Si (1412) (italic figures note the fixed definition points of

the *International Practical Temperature Scale*). For more extended figures, including associated enthalpy data, see Tables in the appendix as transferred from ref. [1]). The deviation of a well-done determination in ordinary DTA-based laboratory can usually vary between 2 to 6 °C (not accounting the higher temperature measurements usually executed above 900 °C). Nonetheless, calibration procedures became a standard accessory of most commercial software associated with marketable apparatuses and thus given instrumental sets of calibration substances. The both involved processes of transition and melting, however, limit the range of application in various fields because both processes (as well as materials involving salts, oxides and metals) have a different character fitting to specific calibration modes only (material of sample holders, atmosphere, sample size and shape, etc.). Further, other inconsistency arising from different heat absorption of the radiation-exposed surface (sample and its holder), quality of adherence between the sample and inner walls of the holder, etc., must be taken in account. Often a distinctive adaptation such as sample compression or even blending with grains of well-conducting inert admixtures (noble metals Ag, Au, Pt, Ir or inert ceramics Al_2O_3 , ZrO_2), special cutting (or even holder-encapsulation by) layers and ribbons, or favored blacking of the exposed surfaces by fine-powder platinum can improve the quality of calibration (as well as the exactness of consequent measurement, which, certainly, must be done in the exactly same manner as the calibration).

Even more complicated is the guarantee of quantitative determinations by calibrating peak areas to represent a defined amount of enthalpy change. The same test compound did not exhibit sufficiently correct results, so that no ICTA recommendation was issued. In the laboratory

scale, we can use certain compounds and their tabulated data, but the result is questionable due to the various levels of the data accuracy. It is recommendable to use the sets of solid solution because they are likely to exhibit comparable degree of uncertainty, such as Na_2CO_3 - CaCO_3 or BaCO_3 - SrCO_3 systems [66] or various sesquioxides (manganese spinels) [67]. The temperature of the cubic-to-tetragonal transformation of MnCrO_3 - Mn_3O_4 increases linearly with increasing manganese content, from about 200 C up to 1172 C for pure Mn_3O_4 , which was successfully employed as a high-temperature standard in ref. [68] see Appendix.

The use of the Joule heat effect from a resistance element on passage of electric charge is the preferable method for an 'absolute' calorimetric calibration. It certainly requires a special setup of the measuring head enabling the attachment of the micro-heater either on the crucible surface (similarly to DSC) or by direct burying it into the mass of (often-powdered) sample. A combination of both experimental lines (substances and pulses) may provide a successful result as shown in Fig.10.5. In this case, we use a series of rectangular pulses generated by an electronic circuit [69] assuring the same amount of delivered heat (0.24 J) by automatic alteration of paired inputs of voltage and current¹.

We also used a rectangular heat stroke for experimental verification of the DTA equation. The resulting curves of the input and output signals are also shown in Fig. 10.b. The responding signal is washed out due to thermal phenomena involved but the effect of thermal inertia is clearly seen and can be separated by the application of the DTA equation. This mathematical correction factually decreases the degree of rectangularity distortion. The remaining misfit is due to the thermal gradients (cf.

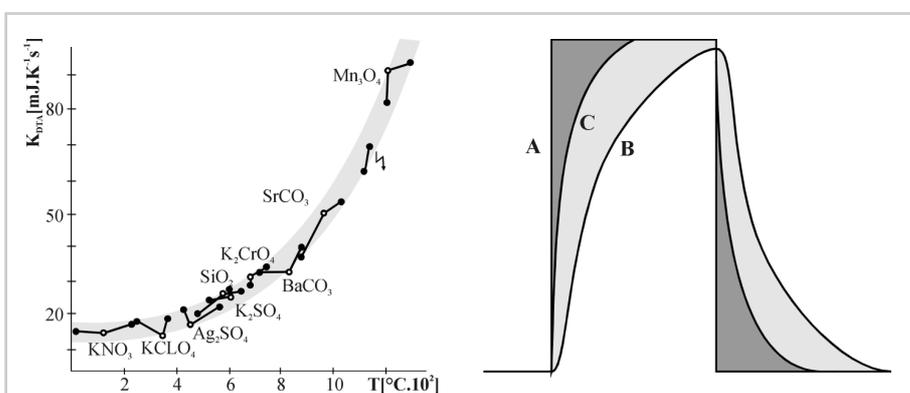


Fig. 11.5. – Use of the generator of defined heat pulses. Left, an example of a combined calibration plot for a set of DTA measurements using the heats of transformation (of the ICTAC recommended substances), supplemented with the heat of pulses obtained by electric resistive flush-heating applied before and after each transformation (the related calibration points are connected by a line and the substance specified by formulae). Right, the analysis of a response peak showing the assessment of a rectangular thermal pulse (A) (launched by electric flush-heating into the sample bulk using the micro-heater placed inside the material under study) in comparison with the actual response by DTA instrument (B). Upon the numerical application of DTA equation, a corrected DTA peak is then obtained (C). The shaded areas illustrate the effect of the sample thermal inertia and the remaining dark shaded areas reveal the probable effect of thermal gradients remaining within the sample body due to the excess unequilibrated heat.

Fig. 1) and inherent impediment in the heat transfer.

In addition, for a relatively longer frontal part of the response peak we can make the direct determination of overall data of the mean heat capacity involved, C_p and the global heat transfer coefficient, Λ . Factually, it is a traditional technique known as a *ballistic method* often applied in calorimetry when measuring amplitude ΔT_{\max} and the peak area A_{\max} for prolonged time ($t \rightarrow t_{\infty}$), which can also be easily modified for DTA measurement. Then we can determine the time constant of the apparatus, $\tau = A_{\max} / \Delta T_{\max}$, and knowing the rate of heat input, Q' , (by, e.g., feeding a constant current) the instrumental heat transfer coefficient can be determined as $\Lambda = Q' / \Delta T_{\max}$. The time constant can also be found from the

decaying curve associated with the sample cooling (the tail of DTA peak) after the termination of heating. By linearization of the standard *Tian* equation it yields, $\tau = (t - t_0)/(\ln T_0 - \ln T) = \cotan \omega$, where ω is the angle of the straight line obtained by plotting $\ln T_t$ against t .

Another type of a triangular pulse has negligible frontal part but the tail is similarly valuable for determining the time constant of apparatus. However, this 'saw-tooth' pulse may become a welcome tool for possible calibration of reaction dynamics, which would be a desirable instrument regarding a better determinability and characterization of the kinetics of processes.

For experimental practice, it is interesting to compare the sensitivity of DTA and DSC for a given experimental arrangement from which a certain value of the heat transfer coefficient follows. It can be seen from Fig. 10.6. that the magnitude (and also the area) of a DTA peak is inversely proportional to the magnitude of heat transfer [1,59]. With a good thermal conductivity, the DTA peak actually disappears, whereas it becomes more pronounced at low thermal conductivity. On the other hand, a change in heat transfer should not affect the magnitude of a DSC peak, provided that the work is not carried out under extreme conditions. It is obvious that a substantial change of heat transfer can change the character of DSC measurement, which is encountered in practice in temperature regions where the temperature dependence ceases to be linear (conduction). Therefore most DSC instruments does not exceed working limit of about 800 C (the approximate onset of radiation as the cubic type of heat transfer).

f) Practical cases of applications

Phase diagrams

A successive DTA/DSC investigation of the samples of different compositions provides us with a series of traces useful for exploratory determination of a phase boundary, see Fig. 11.7. It, however, requires certain expertise in a conscientious process of a gradual refinement of the positioning of characteristic points, such as eutectic, peritectic or distectic, which are most important for the final determination of the shape of the phase diagram. Their position can be determined as the intercept of suitable extrapolation preferably fitted from both sides, usually by plotting the areas of successive peaks of fusion or solidification versus composition [70]. If such a plot has axes calibrated to the peak areas, it can reveal the enthalpy change associated with the extrapolated maximum peak area. However, it should be noticed that in the region between the solid and liquid phases the less is the solid phase melted per time unit, the steeper is the liquid phase curve. Therefore the DTA/DSC peaks of samples whose composition differs little from that of the eutectics are strongly concave, showing thus less sensitivity than those of the compositions far apart. Although it

seems easy to construct a phase diagram merely based on DTA/DSC curves, it is rarely a case of very simple or ideally behaving systems. Monitoring the reactions of solids mixtures and solutions (particularly powders in ceramic oxide systems), a complex pattern is often obtained exhibiting an assortment of the desired (equilibrium-like phenomena) together with delayed or partially occurring reactions (hysteresis due to nucleation, transport, etc.). One of the most misleading phenomena is the plausible interference of metastable phases, i.e., side effects due to the partial or full detection of extrapolated phase boundaries (cf. Figs. 7.7. and 7.8.) down into lower-temperature (often metastable) regions. Therefore it is always necessary to combine practical continuous heating/cooling TA measurements with complementary data on high-temperature equilibrated samples investigated in-situ (by high-temperature XRD) or after sufficiently effective quenching or by other techniques of magnetic, electric or structural investigation.

DTA/DSC data can be of a variety of assistance such as in the glass viscosity prediction and associated evaluation of glass stability through ready-available non-isothermal data. It is based on the determination of the temperature range of glass transformation interval, T_g , and its relation to the so-called *Hruby* coefficient [71] (cf. Fig. 7.11).

A more sophisticated correlation provides interrelation between the experimental activation energy, E_{DTA} , and those for shear viscosity, E_η , on the basis of the relative constant width of T_g , (i.e., difference between the onset and outset temperatures). It reveals a rough temperature dependence of the logarithm of shear viscosity on the measured temperature, T , using the simple relation $\log \eta = 11.3 + \{4.8/2.3 \Delta(1/T_g)\}(1/T - 1/T_g)$ [72], etc., the detailed discussion of which is beyond the scope of this text.

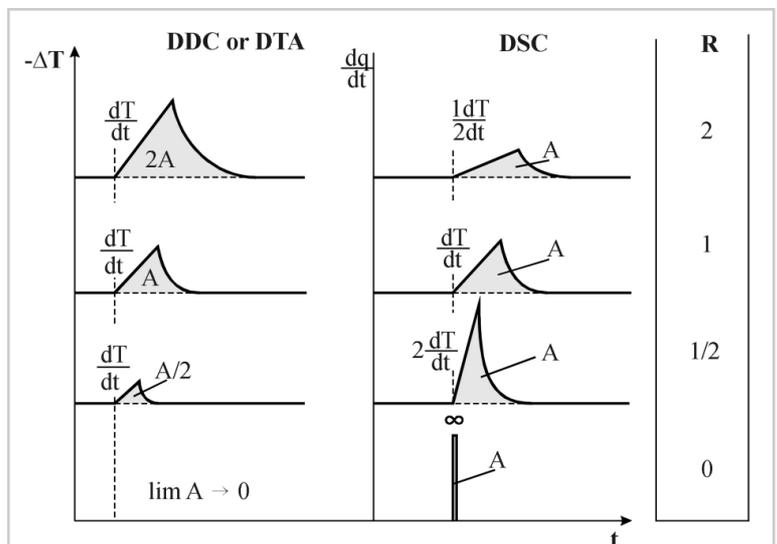
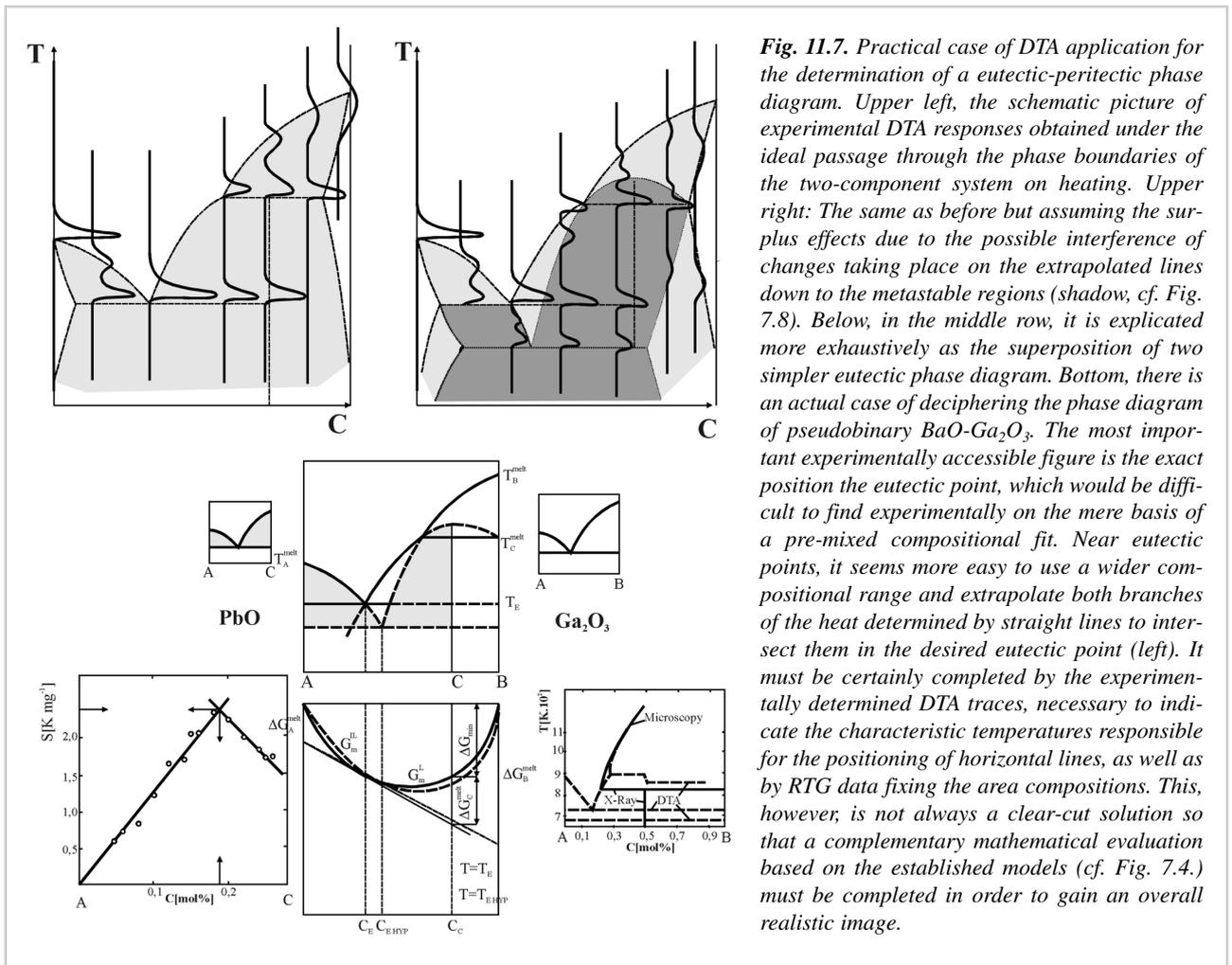


Fig. 11.6. Schematic comparison of the reciprocal sensitivity of DSC and DTA methods indicating an analogous thermal process under comparable experimental conditions when the heat transfer coefficient is the only varied property. It points up the level of acceptability and possible degree of replacement of DSC and DTA.



Certainly, we can anticipate a future progress in the derived methods. Among many others there belong the development of a laser flush apparatus for simultaneous measurements of thermal diffusivity and specific heat capacity (Shinzato [73], Netzsch commercially available instrument) or the localized micro-thermal analysis (Price [74]). Practical applications in materials science matured, for example, searching for non-stoichiometry in high- T_c superconductors (Ozawa [75]), defining glass transitions in amorphous materials (Hutchinson [76]) or fitting heat capacity for the spin crossover systems (Simon *et al* [77]).

Heat capacity

A classical example of the specific heat determination [78] was carried out emphasizing the ratio method [79]. The first measurement is done with empty crucibles (the base line run) while in the second measurement a standard material of the known specific heat (synthetic sapphire) is employed in the same crucible, see Fig. 11.8. In the third run the sample being analyzed is put into the

same crucible, which provides the necessary data for the determination of the requested sample heat capacity, $C_{p,\text{sam}}(T)$, through the ratio of $m_{\text{cal}} \{V_{\text{sam}}(T) - V_B(T)\}$ versus $m_{\text{sam}} \{V_{\text{cal}}(T) - V_B(T)\}$ multiplied by $C_{p,\text{cal}}(T)$, where respectively m_{cal} and m_{sam} are the mass of calibrating substance (cal) and sample (sam), and $V_B(T)$, $V_{\text{cal}}(T)$ and $V_{\text{sam}}(T)$ are the measured

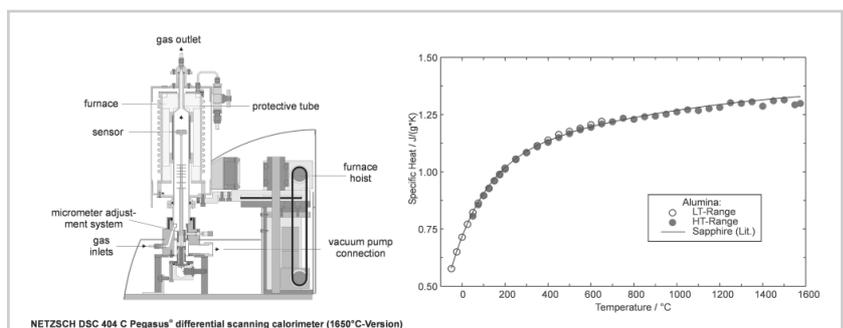


Fig. 11.8. Schema of the high temperature instrument (Netzsch DSC 404 C Pegasus, version up to 1650 °C). Right, the calibration curve of specific heats obtained on α -alumina samples between -50 and 1600 °C using platinum crucibles with lids under an inert atmosphere. Courtesy by J. Blumm and E. Kaisersberger (Netzsch, Germany).

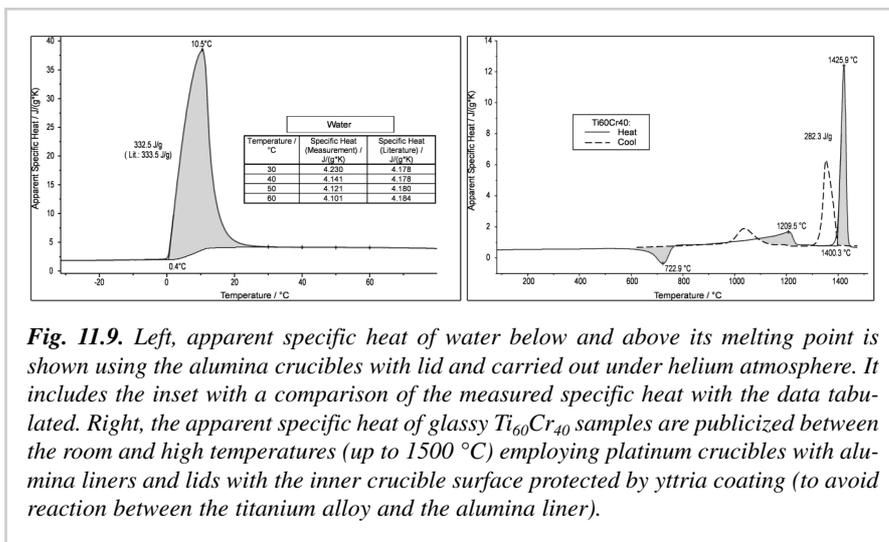


Fig. 11.9. Left, apparent specific heat of water below and above its melting point is shown using the alumina crucibles with lid and carried out under helium atmosphere. It includes the inset with a comparison of the measured specific heat with the data tabulated. Right, the apparent specific heat of glassy $Ti_{60}Cr_{40}$ samples are publicized between the room and high temperatures (up to 1500 °C) employing platinum crucibles with alumina liners and lids with the inner crucible surface protected by yttria coating (to avoid reaction between the titanium alloy and the alumina liner).

of whole set of the sample with its holder and the first term serves as a correction for the larger changes of C_s with temperature relative to that of reference, C_R . As long as the change in the difference between reference and sample temperatures becomes negligible ($\Delta T' \cong 0$), that the heat capacity is directly proportional to flux rate. The sample temperature is usually calibrated with the onsets of the melting peak of two or more melting-point standards and the value of K_{DSC} must be established as a function of temperature by performing a calibration run, typically with sapphire

differences in thermocouple voltages between the sample and reference (B), and the differences observed during calibration (cal) and sample measurement (sam).

Concrete outputs are shown in Fig. 11.9. Left, the measurement of the apparent specific heat of water is depicted, being specific for its positioning within a sensitive temperature region ($-35 < T < 80$ C), normally difficult to ascertain. The melting point is clearly detected at 0 C and the heat of fusion overlaps the specific heat between 0 and 30 C (its value is close to the literature data). The accuracy of the measured specific heat between 30 and 60 C is below 2%. Another extremely sensitive case is the specific heat determination of partially amorphous titanium- chromium alloy due to its extreme sensitivity to oxidation requiring a particularly purified atmosphere of argon. The both heating (solid) and cooling (dashed) curves were recorded exhibiting that on heating the measured specific heat was slightly lower compared to the cooling run. Outside the transition ranges, a good agreement was achieved between heating and cooling runs².

g) Temperature modulated mode

Rather high-speed measurements of the sample heat capacity are a characteristic feature of DSC methodology. It is based on a linear response of the heat-flow rate, q' , to the rate of change in temperature, T' , which is proportional to the temperature difference, ΔT . For a steady state with negligible temperature gradients it follows that the product of sample mass, m , and its specific heat capacity, C_p , is ideally equivalent to the ratio of q'/T' . It can be practically expressed according to Wunderlich [81,82] as $K_{DSC} \Delta T/T' + C_s \Delta T'$, where C_s stands for the specific heat capacity

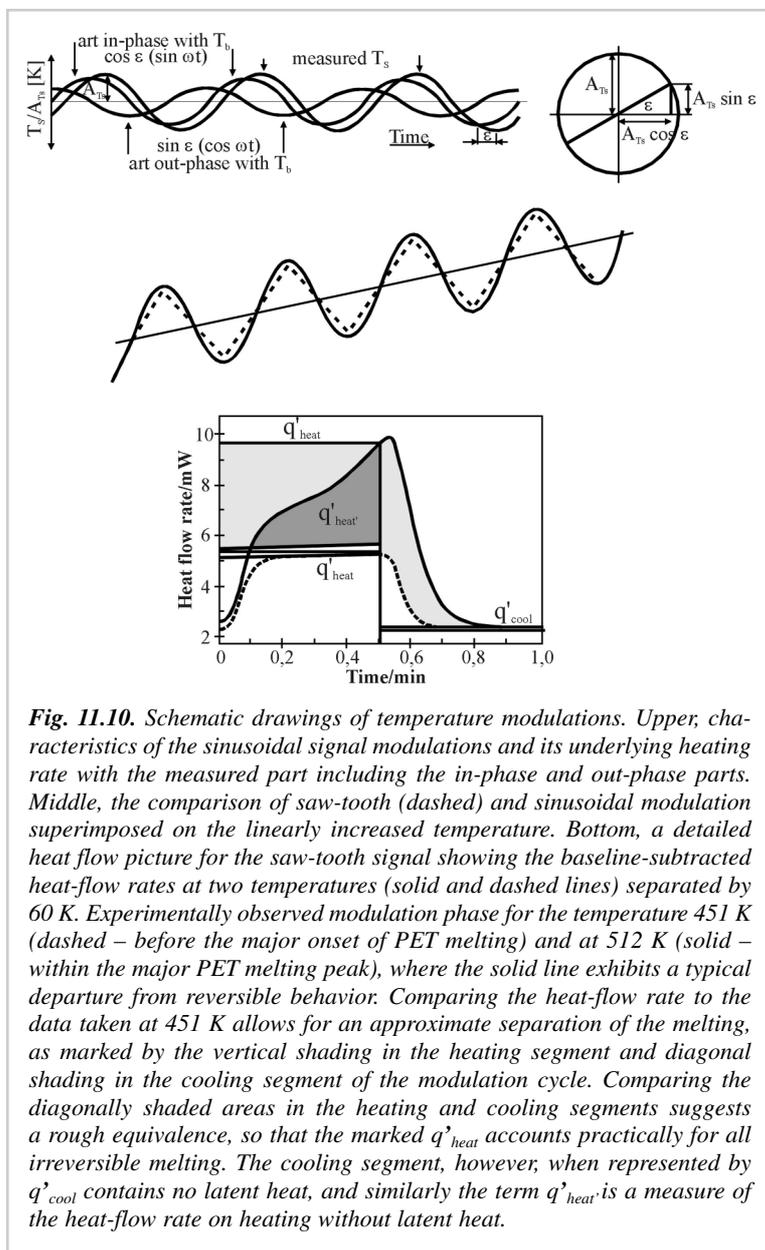


Fig. 11.10. Schematic drawings of temperature modulations. Upper, characteristics of the sinusoidal signal modulations and its underlying heating rate with the measured part including the in-phase and out-phase parts. Middle, the comparison of saw-tooth (dashed) and sinusoidal modulation superimposed on the linearly increased temperature. Bottom, a detailed heat flow picture for the saw-tooth signal showing the baseline-subtracted heat-flow rates at two temperatures (solid and dashed lines) separated by 60 K. Experimentally observed modulation phase for the temperature 451 K (dashed – before the major onset of PET melting) and at 512 K (solid – within the major PET melting peak), where the solid line exhibits a typical departure from reversible behavior. Comparing the heat-flow rate to the data taken at 451 K allows for an approximate separation of the melting, as marked by the vertical shading in the heating segment and diagonal shading in the cooling segment of the modulation cycle. Comparing the diagonally shaded areas in the heating and cooling segments suggests a rough equivalence, so that the marked q'_{heat} accounts practically for all irreversible melting. The cooling segment, however, when represented by q'_{cool} contains no latent heat, and similarly the term q'_{heat} is a measure of the heat-flow rate on heating without latent heat.

as the sample. The same is true in the case of saw-tooth modulation where the heating and cooling segments are long enough to reach the steady state in-between switching. If needed, it is also possible to insert occasional isothermal segments between the modulations as to monitor the base-line drift of the calorimeter.

In the true, temperature-modulated DSC, the experiment is carried out with an underlying change of temperature, which is represented by sliding average over one modulation period. The sample temperature and heat-flow is changing with time, as dictated by the underlying heating rate and the modulation, and are written as $T_S(t)$ and $q'(t)$. The measurement of C_p remains simple as long as the conditions of steady state and negligible gradients can be maintained. If the sample response is linear, the sliding averages over one modulation period of T_S and q' , abbreviated as $\langle T_S \rangle$ and $\langle q' \rangle$, yield identical curves as for the standard DSC. A simple subtraction of these averages from their instantaneous values yields the 'pseudo-isothermal (reversing) signal'. For the sinusoidal modulation, the quasi-isothermal analysis is known as it provides for the heat capacity the following expression:

$$(C_S - C_R) = A_\omega / A_\phi \sqrt{1 + \{C_R \omega / K_{DSC}\}^2} \quad 10.8$$

where A_ω and A_ϕ are the modulation amplitude of the heat-flow and that of the heating rate ($A_{T_S} \omega$), respectively. The frequency ω is given in rad^{-1} ($\omega = 2\pi/p$, where p is the modulation period in seconds). It can be seen that if the reference calorimetric holder is an empty pan/cell, then $(C_S - C_R) = m C_p$ and so A_ϕ represents the maximum amplitude of the rate of temperature change without the effect of underlying constant heating. If the calibration and measurements are performed at frequency ω using the same reference site, the square root becomes constant and can be made part of a calibration constant.

It is clear that the conditions of steady state and negligible temperature gradients within the calorimetric sites are more stringent for this dynamic version (TMDSC) than for the standard DSC. In fact, with a small temperature gradient set up within the sample during the modulation, each modulation cycle has smaller amplitude of heat-flow rate, which depends on the unknown thermal conductivities and resistances. A negligible temperature gradient within the sample requires thus the sample calorimeter to oscillate in its entirety. It also requires almost negligible thermal resistance between all parts of calorimeter, such as thermometer, sample holder and the sample itself. The phase lag between the heater and the sample must be entirely controlled by the thermal diffusivity of the path to the sample. As soon as any shift and a change in maximum amplitude develop during the modulation, it is impossible to appropriately handle the analysis under the above-mentioned equations and the relationships becomes more complicated. We know well that even at the standard DSC setup we are not completely aware of the 'truly entire' sample temperature conditions and super-

imposed "complication" of temperature further modulation makes our restricted knowledge yet less complete. It even stirs up some concern whether the dynamic techniques can provide an adequately realistic picture and not only a virtual, mathematical or artifact-like image convincingly evaluated at our best will.

A definite progress was made recently by studying TMDSC with the simpler saw-tooth modulations [81]. Providing that the *Fourier* equation of heat flows holds, the solution for the different events in the DSC attitude are additive. Steady state, however, is lost each time when a sharp temperature change occurs, i.e., T'' attains a real value. An empirical solution to this problem was to modify the description by introducing a kind of 'time constant', τ , dependent not only on the heat capacity of samples and cooling constants but also on the mass, thermal conductivities, interface hindrances, etc. So that $(C_S - C_R) = A_\omega / A_\phi \sqrt{1 + \{\tau \omega\}^2}$ where τ depends on the calorimeter type and all possible cross-flows between the samples and holders. Its real manifestation can be assessed by the inverse plot of the uncorrected heat capacity against the square of frequency. It is true for longer frequencies only, say > 200 s, while for the shorter frequencies, reaching down to 5 s, τ and remains a continuous function of ω . Naturally, to conduct a series of measurements at many frequencies for each temperature represents a considerable increase in the effort to establish the required data, but it can be eased by application of different frequencies at a single run.

For the analysis with the standard DSC method, the initial data after each change in the heating must be discarded until a steady state is reached. Hence, if the heating/cooling segments are too short to attain the equilibrium-like state and thus minimize temperature gradients within the sample, the evaluation does not give useable results. It may be possible, however, to extrapolate the immediate conditions to a certain state of steadiness or, of course, to modify the modulation mode as to find the steady-state situation experimentally.

In the current TMDSC approach, the non-reversible contribution of the latent heat can only be assessed indirectly by subtracting the irreversible heat capacity from the total one or by analyzing the time domain. Any error in reversing as well as total heat capacity will then be transferred to the non-reversing heat capacity. The analysis using the standard DSC method allows a direct measurement of the non-reversing heat capacity by determining the difference in the heat capacities at their steady state. We can call this quantity as the imbalance in heat capacities so that $(m C_{p_{\text{imbal}}}) = (q'/T')_{\text{heat}} - (q'/T')_{\text{cool}}$. The advantage of the imbalance measure is that it is a directly measurable quantity of the non-reversible contribution and avoids, under the requested conditions, the contribution of potential errors. The irreversible heat-flow rate can be calculated by separating q'_{heat} into its reversible, underlying and irreversible contributions (q'_{rev} , q'_{under} and q'_{irrev}) which can provide relation $q'_{\text{irrev}} = m C_{p_{\text{inal}}} / (1/q'_{\text{heat}} - 1/q'_{\text{cool}})$ if the irreversible parts are equal.

APPENDIX I

Enthalpy Changes during Fusion of Some Compounds not Containing Oxygen

Compound	Melting point [°C]	C_p and ΔC_p of solid phase at T fusion [J mol ⁻¹ K ⁻¹]		ΔH fusion in [KJ mol ⁻¹] tabulated in			ΔH procedural values in [KJ mol ⁻¹] determined by DTA	
				(G)	(K)	(B)	(H)	(L)
Hg	-39	28.55	—	—	—	2.33 ⁺⁺	—	—
Ga	30	26.64	0.1	—	—	5.59	—	—
In	157	30.35	-0.8	3.27	3.27	3.29 ⁺⁺	3.3	3.3
Sn	232	30.76	1.0	7.02 ⁺⁺	7.16	7.03	7.5	7.2
Bi	272	29.84	-6.6	10.87	10.88 ⁺⁺	11.3	10.1	10.9
Cd	321	29.55	-1.8	6.2	6.41 ⁺⁺	6.2	5.8	6.3
Pb	327	29.42	-1.2	4.77	4.83 ⁺⁺	4.78	4.0	4.7
Zn	420	29.60	-1.8	—	7.29	7.33	—	6.9
CuCl	430	62.9	-4.1	10.24	10.26	—	—	10.9
Te	450°	35.11	-2.6	17.5	17.5	17.5	18.8	17.6
InSb	525	56.41	-5.6	49.4	—	50.66 ⁺⁺	48.1	48.6
AgI	558	56.52	-2.1	9.42 ⁺	9.42	9.42	—	8.8
	(147 trans.)	(66.75)	(10.2)	(—)	(—)	(6.15)	(—)	(—)
Sb	631	30.90	-0.4	19.85	19.81 ⁺⁺	19.89	17.4	20.2
Al	660	33.76	2.0	10.72	10.80 ⁺⁺	10.72	10.5	10.9
GaSb	707			61.13 ⁺	—	—	—	58.2
KBr	734	68.35	-1.6	—	25.54	25.54	—	25.7
NaCl	801	63.51	-6.2	28.18 ⁺	28.05	28.18	—	27.7
Ag ₂ S	830	82.77	-10.4	—	—	7.87	—	—
	(176 trans.)	(82.6)	(-1.1)	(—)	(3.97 ^x)	(3.94)	(—)	(—)
	(676 trans.)	(83.91)	(1.1)	(—)	(—)	(0.5)	(—)	(—)
InAs	942	54.79	-5.1	61.1 ⁺	—	77.04	—	61.9
Ge	940	28.78	1.2	36.84 ⁺⁺	36.84	36.97	38.6	34.3
Ag	961	31.95	-1.6	11.64	11.1-	11.3	11.3	11.4
Na ₂ AlF ₆	1012	355.8	40.6	113.4°	111.8	107.3	116.7°	—
	(565 trans.)	(305.2)	(-23.1)	(—)	(9.3)	(8.5)	(—)	(—)
	(880 trans.)	(280.5)	(75.4)	(—)	(—)	(3.8)	(—)	(—)
AlSb	1060	56.38	-2.7	—	—	82.06	—	—
Au	1064	33.38	2.4	—	12.77	12.56	—	12.9
Cu	1083	29.94	-1.5	13.02 ⁺⁺	12.98	13.27	13.3	13.0
FeS	1195	65.71	-5.5	—	—	32.36	—	—
	(138 trans.)	(69.33)	(-3.5)	(—)	(4.4 ^x)	(2.39)	(—)	(—)
	(325 trans.)	(72.85)	(15.8)	(—)	(—)	(0.5)	(—)	(—)
Si	1412	29.22	-2.0	—	—	50.24		
CaF ₂	1418	125.8	25.7	—	—	29.73		
	(1151 trans.)	(103.4)	(-19.6)	(—)	(—)	4.77		
Ni	1459	36.21	6.9	—	—	17.48		
Co	1495	37.79	2.75	—	—	16.2		
	(427 trans.)	(31.1)	(-4.85)	(—)	(—)	(4.52)		

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APPENDIX II

Enthalpy Changes for Phase Transformations of Selected Oxide Compounds

Compound	Phase transformation [°C]	C_p and ΔC_p in [J mol ⁻¹ K ⁻¹] at transf. T		ΔH tabulated values [in kJ mol ⁻¹]			ΔH procedural values determined by DTA, [in kJ mol ⁻¹]				DSC meas. [GR]
				[B]	[R]	[G]	Old ICTA test (variance)	[M]	[N]	DDR test ^x	
KNO ₃ (s ₂ →s ₁)	128	108.59	-12.0	5.11	5.44	—	13.6 (± 86%)	—	5.60	6.11	5.0
	(128)	(—)	(—)	(—)	(2.34)	(—)	(—)	(2.93)	(—)	(—)	(2.52)
Na ₂ SO ₄	249	162.96	-10.69	10.82	—	—	—	—	—	—	—
	(707)	(198.69)	(—)	(0.34)							
KClO ₄	299.5	162.36	—	13.77	13.77	—	32.7 (±85%)	13.82	18.55	17.04	1434
Na ₂ CrO ₄	421	198.3	12.5	9.59	—	—	—	—	—	—	—
Ag ₂ SO ₄	430	178.83	—	15.7	7.95	—	43.1 (±110%)	17.58	18.59	—	16.12
Na ₂ CO ₃	450	192.27	48.8	0.69	—	—	—	—	—	—	—
SiO ₂ (quartz)	573	75.49	1.9	0.73	0.63	0.63	0.9 (±99%)	0.81	0.59	—	0.39
K ₂ SO ₄	583	203.32	14.62	8.96	8.12	—	—	8.79	8.71	6.15	5.63
Li ₂ SO ₄	586	195.3	6.5	27.21	28.47	—	—	—	—	—	—
K ₂ CrO ₄	666	194.18	-1.6	13.73	10.26	—	8.2 (±22%)	7.45	9.42	7.85	6.92
Bi ₂ O ₃ (s ₁ →s ₂)	727	136.34	-10.2	57.12	—	—	—	36.84 ⁺	39.8 ⁺	—	29.56 ⁺
BaCO ₃	810	138.79	-16.1	18.84	19.68	—	25.7 (±59%)	18.0	22.15	19.57	18.71
	(968)	(154.91)	(-8.4)	(2.93)							
ZnSO ₄	754	154.66	—	19.68	—	—	—	—	—	—	—
PbSO ₄	866	195.08	10.9	17.17	17.0	—	—	—	—	—	—
SrCO ₃	925	131.59	-10.8	19.68	—	—	15.9 (±65%)	17.17	18.50	—	—
ZnS	1020	57.28	-1.3	13.4	—	—	—	—	—	—	—
Mn ₃ O ₄	1 172	210.05	—	20.93	18.84	18.84	—	—	16.74	—	—
CaSiO ₃	1 190	191.51	1.1	7.12	—	—	—	—	—	—	—
Li ₂ TiO ₃	1212	161.61	-3.48	11.61	—	—	—	—	—	—	—
Ca ₂ SiO ₄	1420	214.12	9.78	4.44	1.47	—	—	—	—	—	—
	(675)	(191.51)	(1.3)	(3.27)	(3.22)	—	—	—	—	—	—

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¹ Back at the beginning of the seventies, we put in use a generator of defined heating pulses. A commercial but slightly modified DTA measuring head was equipped by electric heating element consisting of a platinum wire (diameter 0.1 mm) coil with the total electric resistance of 1.5 Ohm, which was immersed in the material studied (sample). The pre-selected amount of heat was 1/4 Joule, easy adjustable by simple selection of input voltage and current pairs, which provided rectangular heat pulses with reproducibility better than 3% and independent of temperature effects. Connecting wires (0.5 mm) were assorted in different ways (e.g., through a capillary lead aligned or even joined with the temperature measurement), which was necessary to respect both the given setup of the measuring head and the guaranty to satisfy the least drop on the incoming voltage. Alternatively, we also used a DTA measuring head modified to accommodate three independent cells enabling the measurement of mutual temperature differences. Beside some other advantages it showed that application of electric pulses into the reference material (thus actually simulating an endothermic process with regard to the sample) had a minimal effect on accuracy. In order to match a more authentic course of a real process we modified our electric circuit to produce the triangular heating pulses, which was found suitable for a better resolution of some kinetic problems. Resulting calibration was very reliable up to about 700 C, which was in agreement with the experience of DSC builders, where the temperature limit is roughly the same. The attachment of externally controlled heat pulsater verified the suitability

for such, at that time, advanced solution for improved electric calibration, which also helped to better analyze the peak response necessary to authorize importance of the partial heat contributions, cf. Fig. 10b. It was only a pity that no commercial producer, neither ICTAC, became active in their wider application conservative with the application of the ICTAC calibration substances. It would be much easier if a computerized unit were used and built into commercial instruments.

¹ There is a wide sphere of applicability of DTA/DSC technique, which is regularly described in satisfactory details in the individual apparatus manuals or other books [M.E. Brown "Introduction to Thermal Analysis: techniques and applications" Chapman Hall, London 1988; J.Boerio-Goates, J.E. Callen "Differential Thermal Methods" in "Determination of Thermodynamic Properties" B.W. Rossiter, R.C. Beatzold (eds.), Wiley, New York 1992]. The usage can be sorted in to two classes: (i) the measurements applicable under the ordinary apparatus' set up (e.g. impurity measurements [E.E. Marti, *Thermochim. Acta* 5 (1972) 143]) and (j) the methods based on the modified instrumentation (e.g. high-pressure studies [Y. Sawada, H. Henmi, M. Mizutami, M. Kato, *Thermochim. Acta* 121 (1987) 21] or differential hydrothermal analysis [V. Šatava, *J. Amer. Cer. Soc.* 58 (1975) 357]). Let us mention here only one of the earliest application of DTA/DSC, which is aimed to the rapid determination of the impurity (of mostly organic compounds) without the requirement for using a reference material [W.P. Brenann, M.P. DeVito, R.I. Fayans, A.P. Gray "Overview of the Calorimetric Purity Measurements" and J.P. Elder "Purity Analysis by Dynamic and Isothermal Step DSC" in "Purity Determinations by Thermal Analysis" R.L. Blaine, C.K. Shoff (eds.), Amer. Soc. Test. Mater., Philadelphia 1984]. The procedure is based on the thermodynamic relationship for the depression of the melting point by the presence of impurities, x_{im} , assuming ideal solution, immiscibility and the constant enthalpy of fusion, ΔH . It provides that $x_{im} = \Delta H/R(1/T_{im} - 1/T_o)$ where x_{im} and T_{im} are the impurity mole fraction and the melting temperature of impure material and T_o is the melting temperature for pure material. Because $T_{im} \cong T_o$ it simplifies as $x_{im} = \Delta H/(RT_o^2)(T_o - T_{im})$ yielding for the fraction, $F = x_{im}/x_2$, of the sample melted at temperature T (given by the ratio of the composition of the sample x_{im} to the composition of the equilibrated liquid x_2) the relationship: $F = RT_o^2 x_{im}/\{\Delta H(T_o - T)\}$. This relation is then used in the convenient form of $T = T_o - (x_{im}RT_o^2)/\Delta H (1/F)$ furnishing the plot of the sample temperature (T) versus the reciprocal of the fraction melted ($1/F$) which straight line has a slope equal to $(-x_{im}RT_o^2)/\Delta H$ and intercept T_o . Values of the fraction melted at various temperatures are obtained from a series of partial integration of the DTA/DSC peak, where $F(T) = \Delta H(T)/\Delta H_f$. This sort of the *van't Hoff* plot shows often a nonlinearity, which is attributed to the underestimation of the fraction melted in the early part of the melting process. The movement of dH/dt curve away from the base line is customarily so gradual that it is sometimes difficult to estimate the exact beginning of the melting. Preselecting few reference points in order to determine a suitable correction factor [D.L. Sondack, *Anal Chem.* 44 (1972) 888] can eliminate this arbitrariness. Another limitation is the factual formation of solid solutions [W. Brostow, M.A. Macip, M.A. Valerdi, *Mater. Chem. Phys.* 10 (1984) 31] as well as the precarious applicability of the method to determine ultra small impurity levels. Because the technique is measuring small differences in pure materials, appropriate care during the preparation of the specimen is critical.



CHAPTER TWELVE

12. Nonisothermal kinetic by thermal analysis

a) Fundamental aspects of kinetic evaluations

Thermoanalytical (TA) data are of a macroscopic nature as the measured (overall) occurrence (in the sense of observation) is averaged over the whole sample assemblage under study (cf. Chapter 10). In spite of this fact, the experimentally resolved shape of TA curves has been widely used as a potential source for the kinetic appreciation of elementary solid-state reactions taking place within the sample (bulk or interfaces) [1,53,82,83]. The shape of the TA curve (cf. Fig. 9.2.) is then taken as the characteristic feature for the reaction dynamics and is then mathematically linked with the analytical form of model functions, $f(\alpha)$, (cf. Chapter 8). We, however, should remind that these diagnostic-like formulas are derived on the basis of the simplified physical-geometrical assumptions of the internal behavior (movement) of reaction interfaces (see Fig. 8.5.) displaying thus a norm character only.

The basic relationship $\alpha' = k(T) f(\alpha) = Z \exp(-E/RT) f(\alpha)$, given by the previous equation 8. 8, provides the root for most traditional evaluation procedure, i.e., for all *differential methods* of kinetic data determination when the logarithmic form is applied:

$$\{- \ln [\alpha'/f(\alpha)]\} = \text{const.} - (E/R) \{1/T\}. \quad 12.1$$

Associated kinetic analysis is carried out by two possible ways, either to find directly a linear dependence between the functions in {brackets} or to further differentiate (Δ) the above relation. The latter is possible only if the function $f(\alpha)$ is suitably substituted. The replacement is frequently done by applying a simple relation, $(1-\alpha)^n$, representing the so called *reaction order* model, see the previously listed Table 8.I. As a result it provides a simple plot of the kind $\{(\Delta \ln \alpha' / \Delta \ln (1-\alpha))\}$ vs. $\{\Delta 1/T / \Delta \ln (1-\alpha)\}$, which can be used for the direct determination of the most common kinetic constants, that are the activation energy, E (slope) and the reaction order, n (intercept) [84].

Because of the simplified form of the function $f(\alpha)$ applied, the plot provides only apparent kinetic parameters, E_{app} and n_{app} , related to the true values by the ratio, $E_{\text{app}}/E = - [f(\alpha_{\text{max}})/f'(\alpha_{\text{max}})] n_{\text{app}}(1 - \alpha_{\text{max}})$, where f is the appropriate function and f' is its derivative [85,86]. In general, such differential methods of the kinetic data determination are very sensitive to the quality of experimental data, especially to the determination of instantaneous rates, α' , and the related differences, Δ . For this reason, and in view of the inaccuracy of this determination in the initial and final reaction stages, they are not so extensively used. However, on rearrangement and upon assuming constant values of α and/or α' , the following ratio is found useful for another direct estimation of E from several parallel measurements by the so-called *iso-conversional* and *iso-rate* cross sections, as introduced by *Ozawa* and *Flynn* [87,88]

$$\begin{aligned} (\alpha = \text{const} \Rightarrow) \Delta \ln \alpha' / \Delta (1/T) &= E/R \\ = \Delta \ln Z f(\alpha) / \Delta \ln (1/T) (\Leftarrow \alpha' = \text{const}) & \quad 12.2 \end{aligned}$$

Another, rather popular method of kinetic data analysis is based on expressing the maximum value (index max) on the dependence of α' vs. T , for which it holds

$$\alpha'' = 0 = \alpha'_{\text{max}} [E/RT_{\text{max}} / Z / \phi \exp(-E/RT_{\text{max}}) df(\alpha)/d\alpha] \quad 12.3$$

where Z is the preexponential factor and R the gas constant.

The result provides simple but useful dependence, often called *Kissinger plot* and known since 1959 [89], which in various modifications approvals shows the basic proportionality

$$\ln (\phi/T_m) = (E/R) (1/T_m). \quad 12.4$$

More mathematical results, such as direct estimation of E from a single point, i, using equation, $E = T_i^2 R \alpha' / [f(\alpha) g(\alpha)]$ [90], etc. can be found. For a more detailed analysis of the mathematics involved in deriving the individual methods of evaluation, see numerous review articles and books, such as ref. [1,91-95].

The differential mode of evaluation can even match up with the true experimental conditions when non-uniform heating and actual temperatures are considered. Hence, we ought to introduce the second derivatives, T'' , which lead to an equation in the complex form [96]:

$$\{\alpha'' T^2 / \alpha' T'\} = df(\alpha)/d\alpha / f(\alpha) \{T^2 \alpha' / T'\} + E/R. \quad 12.5$$

However, it is almost impossible to compute this relation to a satisfactory precision because of its extreme sensitivity to noise, which requires enormously high demands on the quality of input data, so that it did not find its way to wider practical applications.

So-called *integral methods* of evaluation became recently more widespread. They are based on a modified, integrated form of the function $f(\alpha)$, which is determined by the following relation:

$$\begin{aligned} g(\alpha) &= \int_{\alpha_0}^{\alpha} d\alpha / f(\alpha) = \int_{T_0}^T k(T) dT / \phi \\ &= (ZE)/(\phi R) \exp(-E/RT) \pi(x)/x = (ZE)/(\phi R) p(x) \quad 12.6 \end{aligned}$$

where ϕ is the constant heating rate applied, $\pi(x)$ is an approximation of the temperature integral (often used in the intact representation as the $p(x)$ function [1,95,97] where $x = E/RT$). There are many approximations of this temperature integral arising from the simplest $\pi(x) = 1/x$ and $(1-2/x)/x$ (based on the expansion) to more accurate $= 1/(x+2)$ and often sufficient $(x+4)/(x^2 + 6x + 6)$ (based on the rational approximations). It should be emphasized, however, that the determination and sufficiently precise calculation of the $p(x)$ function should be seen as a marginal problem although it has led to exceptionally wide publication activity. Despite its accuracy accounts it can be shown that the nature tends to simple solutions, because in most kinetic calculations the effect of the actual value of $\pi(x)$ is often neglected. This actually implies that $k(T)$ is considered as a constant and, instead of complex integration, is simply put in front of the inte-

gral, namely, $\int k(T) dt \cong k(T) \int dt$, which is often hidden behind complicated mathematics.

The frequent practice of evaluation by the individually derived methods is then done by plotting $\ln g(\alpha)$ vs. the range of functions of temperature, arising from its logarithm $\ln T$ [98] over T (or better ϑ as a given temperature) [99] to its reciprocal $1/T$ [100-102], which are respectively employed in the relation to the $\pi(x)$ approximations applied. They differ in the multiplying constants, which, by itself, is a definite evidence for a certain extent of inherent inexactness of such integral way of modeling.

It is worth highlighting that already a plain application of logarithmic function brings not only the required data smoothing but also introduces a higher degree of insensitiveness. Therefore, the popular double-logarithmic operation effectively paralyses the discriminability of individual kinetic models and our associated desire to attain linear proportionality acts sometimes in the role of a plot 'drawn on rubber-stretch paper'.

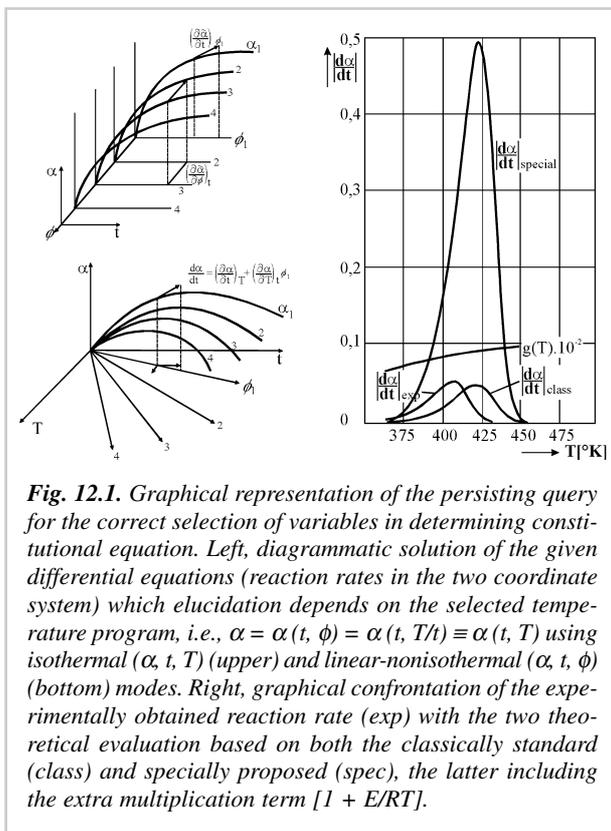


Fig. 12.1. Graphical representation of the persisting query for the correct selection of variables in determining constitutional equation. Left, diagrammatic solution of the given differential equations (reaction rates in the two coordinate system) which elucidation depends on the selected temperature program, i.e., $\alpha = \alpha(t, \phi) = \alpha(t, T/t) \cong \alpha(t, T)$ using isothermal (α, t, T) (upper) and linear-nonisothermal (α, t, ϕ) (bottom) modes. Right, graphical confrontation of the experimentally obtained reaction rate (exp) with the two theoretical evaluation based on both the classically standard (class) and specially proposed (spec), the latter including the extra multiplication term $[1 + E/RT]$.

To get a better insight, let us divide these integral methods into three groups according to the method of plotting $\ln g(\alpha)$ against either of three above-mentioned functions of T ($\ln T, T$ or $1/T$) [103,104] giving thus the respective slopes of $\tan \varpi$. Consequent estimation of E depends on the respective values of RT_m ($\tan \varpi - 1$), $RT_m^2 \tan \varpi$ and $(R \tan \varpi - 2RT)$. The approximation used can be tested [105] using the asymptotic expansion of a series with a dimensionless parameter replacing E . It was shown that the latter dependence is twice as good as that of the former two dependencies. In this way, we can confirm the numerical results of several authors who

found that the plain dependence of $\ln g(\alpha)$ vs. T yields E with an error of about 15% at best, whereas the $\ln g(\alpha)$ vs. $1/T$ plot can decrease the error by half. This is relative to the entire series given by set of T 's and $1/T$'s. Another important characteristic of integral methods is the *overlapping* of the $\ln g(\alpha)$ functions for two or more different reactions mechanism, for example, the models describing diffusion (*Jander*) and phase boundary reaction [1], etc.

The above evaluation methods can be approximately systemized as follows:

Variables	Model function	Rate constant	Name of method	Comprehension
α, T	$g(\alpha)$	$p(x)$	integral	low discriminability
α, α', T	$f(\alpha)$	$k(T)$	differential	high sensitivity
$\Delta\alpha, \Delta\alpha', \Delta T$	$\Delta f(\alpha) \Rightarrow m, n$	$k(T) \Rightarrow E$	difference -differential	greater sensitivity
$\alpha, \alpha', \alpha'', T, T'$	$df(\alpha)/d\alpha f(\alpha)$	$k(T), dk(T)/dT$	double -differential	too high sensitivity

It is worth noting that the incommutably plain passage between integral and differential representation *must be reversible* under all circumstances, though it may recollect the dilemma of early-argued problem of the equality of isothermal and non-isothermal rates [106,107] (as already mentioned in Chapter 8.). This brainteaser, which was recently opened to renewed discussion [108] somehow readdress the query, what is the true meaning of partial derivatives of time-temperature dependent degree of conversion $\alpha = \alpha(t, T)$ mathematically leading to obvious but curiously interpreted $\alpha' = (\partial\alpha/dt)_T + (\partial\alpha/dt)_T T'$, which is the lesson of mathematics applied to the mutual derivation and integration of the basic kinetic equation.

Notwithstanding, some authors thus keep still convinced that apparently 'isothermal' term $(\partial\alpha/dt)_T$ has the significance of the isothermal reaction rate and the additional term $(\partial\alpha/dt)_T T'$ is either zero or has a specific 'non-isothermal' meaning. Recent treatments [108] recall this problem by applying the re-derivation of the integral form of kinetic equation 12.6. (cf. Chapter 8). It is clear that this equation was derived upon integration of basic kinetic equation 8. 8, so that any reversing mathematical procedure must be compatible with the original form of differential equation because α depends on t through the upper limit of integral only. Hence, any extra-derived multiplying term $[1 + E/RT]$ [108,109] is somewhat curious and misleading, see Fig. 12.1, and leads to incorrect results. We have to keep in mind that the starting point of the standard isokinetic hypothesis is the independency of the transformation rate on its thermal history. Therefore the transformed fraction calculated upon the integration must be clearly dependent on the whole $T(t)$ path and any further assumption of the coexistence of an $\alpha(T, t)$ function, dependent on the actual values of time and temperature, is fully incompatible with this formulation.

In fact, this can serve as a good example of an inappropriately posed question where an incorrect formulation of constitutional equations is based purely on

a mathematical treatment (which can appear physically problematic and sightless) instead of the required application of logical analysis first. This approach was once unsuccessfully applied in kinetic practice [110,111] and is not necessary to repeat that no doubts can be raised concerning the mathematical rules for the differentiation of implicit functions.

b) Formal kinetic models and the role of an accommodation function

It is clear that the experimental curves, measured for solid-state reactions under thermoanalytical study, cannot be perfectly tied with the conventionally derived kinetic model functions (cf. table 8. I), thus making impossible the full specification of any real process due to the complexity involved¹. The resultant description based on the so-called apparent kinetic parameters, deviates from the true portrayal and the associated true kinetic values, which is also a trivial mathematical consequence of the straight application of basic kinetic equation 8.8. Therefore, it was found useful to introduce a kind of pervasive description by means of a simple empirical function, $h(\alpha)$, containing the smallest possible number of constant. It provides some flexibility, sufficient to match mathematically the real course of a process as closely as possible. In such case, the kinetic model of a heterogeneous reaction is assumed as a *distorted* case of a simpler (ideal) instance of homogeneous kinetic prototype [112, 113]. It is mathematically treated by the introduction of a multiplying function $\underline{a}(\alpha)$, i.e., $h(\alpha) = f(\alpha) \underline{a}(\alpha)$, for which we coined the term [112] ‘accommodation function’ and which is accountable for certain ‘defect state’ (imperfection, in the same way as that of interface during the new phase formation, cf. Chapter 7.).

It is worth mentioning that $\underline{a}(\alpha)$ cannot be simply replaced by *any* function, such as that of time, e.g., $f(t) = t^{p-1}$, because in this case the meaning of basic kinetic equation would alter yielding a contentious form, $\alpha' = k_i(T) t^{p-1} f(\alpha)$. This mode was once popular and serviced in metallurgy, where it was applied in the form of the so-called *Austin-Rickett* equation [114]. From the viewpoint of kinetic evaluation, however, it is inconsistent as this equation contains two variables of the same nature but in different connotation so that the kinetic constant $k_i(T)$ is not a true kinetic constant. As a result, the use of both variables, α and t , provides incompatible values of kinetic data, which can be prevented by simple manipulation and re-substitution. Practically, the *Austin-Rickett* equation can be straightforwardly transferred back to the standard kinetic form to contain either variable α or t on its own by, e.g., a simplified assumption that $\alpha' \cong t^{p-1}$ and $\alpha \cong t^{p/p}$ and $\alpha' \cong \alpha^{(1-1/p)} \cong \alpha^m$.

Another case of mathematical inter-convertibility is the JMayK model function, $(1-\alpha)[-ln(1-\alpha)]^p$, which can be transferred to another two parameter form of eq. 12.7, as both functions $(1-\alpha)$ and $[-ln(1-\alpha)]^p$ can be expanded in infinite series, recombined and converted back to the multiple of functions α^m and $(1-\alpha)^n$.

It follows that the so-called *empirical kinetic model function* can be generally described by all-purpose, three-

exponent relation, first introduced by (and often named after the authors as) Šesták and Berggren (SB) equation [115], or

$$h(\alpha) = \alpha^m (1 - \alpha)^n [-ln(1 - \alpha)]^p. \tag{12.7}$$

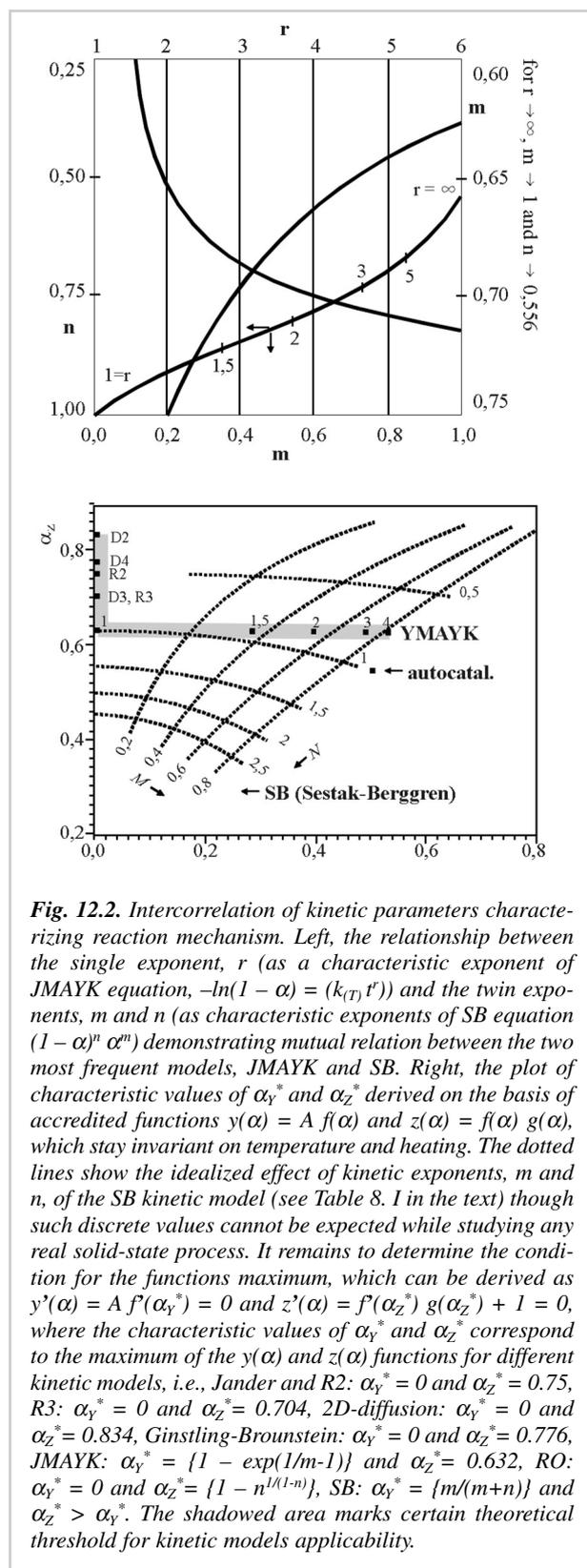


Fig. 12.2. Intercorrelation of kinetic parameters characterizing reaction mechanism. Left, the relationship between the single exponent, r (as a characteristic exponent of JMayK equation, $-\ln(1 - \alpha) = (k_T t^r)$) and the twin exponents, m and n (as characteristic exponents of SB equation $(1 - \alpha)^n \alpha^m$) demonstrating mutual relation between the two most frequent models, JMayK and SB. Right, the plot of characteristic values of α_Y^* and α_Z^* derived on the basis of accredited functions $y(\alpha) = A f(\alpha)$ and $z(\alpha) = f(\alpha) g(\alpha)$, which stay invariant on temperature and heating. The dotted lines show the idealized effect of kinetic exponents, m and n , of the SB kinetic model (see Table 8. I in the text) though such discrete values cannot be expected while studying any real solid-state process. It remains to determine the condition for the functions maximum, which can be derived as $y'(\alpha) = A f'(\alpha_Y^*) = 0$ and $z'(\alpha) = f'(\alpha_Z^*) g(\alpha_Z^*) + 1 = 0$, where the characteristic values of α_Y^* and α_Z^* correspond to the maximum of the $y(\alpha)$ and $z(\alpha)$ functions for different kinetic models, i.e., Jander and R2: $\alpha_Y^* = 0$ and $\alpha_Z^* = 0.75$, R3: $\alpha_Y^* = 0$ and $\alpha_Z^* = 0.704$, 2D-diffusion: $\alpha_Y^* = 0$ and $\alpha_Z^* = 0.834$, Ginstling-Brounstein: $\alpha_Y^* = 0$ and $\alpha_Z^* = 0.776$, JMayK: $\alpha_Y^* = \{1 - \exp(1/m-1)\}$ and $\alpha_Z^* = 0.632$, RO: $\alpha_Y^* = 0$ and $\alpha_Z^* = \{1 - n^{1/(1-n)}\}$, SB: $\alpha_Y^* = \{m/(m+n)\}$ and $\alpha_Z^* > \alpha_Y^*$. The shadowed area marks certain theoretical threshold for kinetic models applicability.

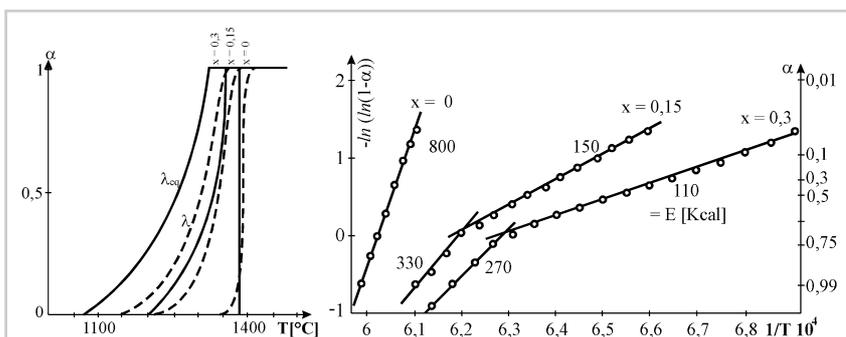


Fig. 12.3. Formal kinetic account of the complex dissociation process of solid-state solutions of hematite-type (*h*) to spinels (*sp*), $Mn_xFe_{3-x}O_{9/2} (h) \rightarrow Mn_xFe_{3-x}O_4 (sp) + 1/4 O_2$. Left, the profiles of the equilibrium backgrounds (solid) and the corresponding kinetic advancements (dashed). Right, formal kinetic evaluation using the logarithmic (JMAYK) model equation with the marked Mn-stoichiometry (x) and values of apparent activation energies (E). The breaks on the linear interpolation (at $x \cong 0.15$ and 0.3) indicate the instant where the equilibrium background reaches its final value ($\lambda_{eq} = 1$) terminating thus its interference with the kinetics ($\alpha = \lambda/\lambda_{eq} = \lambda$).

It is practically applicable as either form, Šesták - Berggren equation, $\alpha^m (1 - \alpha)^n$, and/or modified JMAYK equation, $(1 - \alpha)^n [-\ln(1 - \alpha)]^p$ (related to its original form, $-\ln(1 - \alpha) = (k_T t)^r$, through the exponents p and r , i.e., $p = \{1 - 1/r\}$).

It is broadly believed that an equation, which would contain as many as three variable exponents (such as m , n and p), would be capable of describing any shape of a TA curve. In reality, however, such model equability is *over-determined* by using all three exponents at once and thus the model is factually competent to describe almost ‘anything’ [116]. Therefore only the single exponents, such as m , (classical reaction order) or p , (traditional JMAYK equation with $n=1$) or the two appropriately paired exponents are suitable for meaningful evaluation such as the classical model of self-catalyzes ($m=1$ and $n=1$), which is thus a special case of the general SB equation. The right and proper complementary couples are only $(m+n)$ or $(m+p)$, whilst the pair $(n+p)$ exhibits an inconsistent role of two alike-functions, which are in a self-supporting state discussed above.

It is worth noting that the most common pair, $(n+p)$, further abbreviated as the SB-equation, involves a special case of the autocatalytic equation, where $n=1$ and $m=1$. This equation subsists the generalized use of a basic logistic function, $x(1 - x)$, which is exploited to depict the case of population growth in Chapter 13. It consists of the two essential but counteracting parts, the first responsible for *mortality*, $x \cong \alpha^m$, (i.e., reactant disappearance and the product formation) and the other for *fertility*, $(1-x) \cong (1 - \alpha)^n$ (i.e., a kind of products’ hindrance generally accepted as an ‘autocatalytic’ effect). The non-integral exponents, m and n , play thus a role similar to circumstances, which are represented by the true fractal dimensions² [112,117].

As in the case of phase-boundary-controlled reaction, the conventional kinetic model describing the diffusion-controlled reactions is ideally based on the expression of geometrical constraints of the movement of reaction interface (cf. Fig. 8.6). Extension of the reaction geometry

to non-integral values is again a common and plausible way to formalize the empirical kinetic model functions [119,120]. As already mentioned in Chapter 8., these models, derived for the phase-boundary-controlled reactions (abbreviated R_n) and for the random nucleation and growth (JMAYK abbreviated as A_m), can easily be formalized with non-integral (fractal) dimensions, such as $R_n = 1 \leq n \leq 3$ and A_m , with $n=1, 0.5 \leq m \leq 4$, see Fig. 12.2. Employing the non-integral values of the dimension $1 \leq n \leq 3$, we obtain the relation $r/r_0 = (1 - \alpha)^{1/n}$, where r and r_0 are the radii of the reactant particles at $t = 0$ and $t = t$. The non-integral values are described by reactions on a fractal domain, the hallmarks of which are anomalous order and time-dependent reaction rate constants.

These anomalies stem either from incompatibility of ideal geometrical models with real reaction morphology (cf. Fig. 8.6) and from the non-randomness of the reactant distribution. For the diffusion-controlled reactions the non-integral kinetic exponents can be assumed from the proportionality of the rate of volume shrinkage to the amount of diffused substances at certain time and under the constant concentration gradient along the direction of diffusion. i.e., $\alpha = \underline{k} / [\pm x - (1 - \alpha)^{2/n-1}]$ where \underline{k} is the apparent rate constant and exponent n varying $1 \leq n \leq 2$ ($x=1$), $n=2$ ($x=0$) and $2 \leq n \leq 3$ ($x=-1$). This relation is taken as the kinetic rate equation for the diffusion-controlled reaction with geometrical fractals [121,122] corresponding to the conventional parabolic law.

It should be noticed that SB equation, with both non-integral exponents, $(n+m)$, is capable to mathematically fit almost any type of thermoanalytical curves, supporting thus indistinctive representation of a reaction mechanism, which would well correlate to the fractal image of true reaction morphology (cf. Fig. 10.11). It provides the best mathematical fit, but gives little information about the modeled mechanism. On the other hand, the goal of most studies is more pragmatic, i.e., the reportable determination of a specific reaction mechanism, which would correlate to one of the confident physical-geometric models even though there is no concurrence of observable morphology between the true reaction image observed and the theoretical ‘view’ symbolized by the model assumed, cf. Chapter 10. It may provide certain, even idealized, information but, factually, it does not keep in fully distinguishing touch with the reaction reality.

The decision what tactic is the best to select is entirely in the hands of experimenters and theoreticians and their individual attitude how they want to present and interpret their results. It certainly depends of what would be the result’s further destiny (application); citing Garn “materials and reactions themselves do not know any of our mathematical simulations” [92]. This chapter is obviously incapable of including the exceptionally extensive litera-

ture so far published on non-isothermal kinetics [1, 92–95] and thus is powerless to incorporate all peculiarities involved. Only a very small fraction of the adequate literature is cited herewith and the thermoanalytical public is still waiting for a comprehensive book to be published on this motivating topic.

c) Peculiarities of non-isothermal models

Apparent values of activation energies E

For an appropriate derivation of kinetic parameters the previously shown procedures should always be reconsidered for and fitted to a *real* thermoanalytical application in order to become authentically relevant to actual state of non-isothermal conditions (cf. next Chapter 16) and the type of process under study. In many cases we are supplied with the ready-to-use commercial programs, available as the accessories of most marketed instruments so that we have to take care about the *apparent* values thus received. Individual and often sophisticated programs involve their own peculiarities, which we do not want to comment or deal with more extensively but all such individualities must be judged by users themselves.

First, we need not pay attention to a more detailed temperature-dependence of the integration of basic nucleation-growth equations. It has been already approved that the standard, and so far widely applied procedures, yield very similar dependences comparing that, which is found with the application of more complicated derivations involving all variables and functions [1,123]. The results effectively differ only by a constant in the pre-exponential terms depending to the numerical approximations employed in the integration. This means that the standard form of JMAYK equation can be used throughout all non-isothermal treatments.

A simple preliminary test of the JMAYK applicability to each studied case is worth of mentioning. The simple multiple of temperature, T , and the maximum reaction rate, $d\alpha/dt$, which should be confined to the value of 0.63 ± 0.02 , can be used to check its appropriateness. Another handy test is the value of shape index, i.e., the ratio of intersections, b_1 and b_2 , of the in inflection slopes of the observed peak with the linearly interpolated peak baseline, which should show a linear relationship of the kind $b_1/b_2 = 0.52 + 0.916 \{(T_{i1}/T_{i2}) - 1\}$, where T_i 's are the respective inflection-point temperatures [124,125].

Conventional analysis of the basic JMAYK equation shows that the overall values of activation energies, E_{app} , usually determined on the basis of DTA/DSC measurements, can be roughly correlated on the basis of the partial energies of nucleation, E_{nucl} , growth, E_{growth} and diffusion, E_{diff} . It follows that $E_{app} = (a E_{nucl} + b d E_{growth}) / (a + b d)$, where the denominators ($a + b d$) equal the power exponent, r , of the integral form of JMAYK equation and the coefficients b and d indicate the nucleation velocity and the growth dimension. The value of b corresponds to 1 or 1/2 for the movement of the growth front controlled by chemical boundary (chemical) reaction or diffusion, respectively. For example, the apparent values can be read as [1,125–127]:

		Chemical, $b=1$	Diffusional, $b=1/2$
Instantaneous nucleation (<i>saturation</i>)	1-D growth	$r=1;$ E_{growth}	$r=0.5;$ $E_{diff}/2$
	2-D growth	$r=2;$ $2 E_{growth}$	$r=1;$ E_{diff}
	3-D growth	$r=3;$ $3 E_{growth}$	$r=1.5;$ $3 E_{diff}/2$
Constant rate (<i>homogeneous nucleation</i>)	1-D growth	$r=2;$ $(E_{growth} + E_{nucl})$	$r=1.5;$ $(E_{diff}/2 + E_{nucl})$
	2-D growth	$r=3;$ $(2 E_{growth} + E_{nucl})$	$r=2;$ $(E_{diff}/2 + E_{nucl})$
	3-D growth	$r=4;$ $(3 E_{growth} + E_{nucl})$	$r=2.5;$ $(3 E_{diff}/2 + E_{nucl})$

The value of E_{app} can be easily determined from the classical *Kissinger* plot (eq. 12.4) for a series of peak apexes at different heating rates irrespective of the value of exponent, r .

Adopting the heat-dependent concentration of nuclei [128], we can employ a modified plot in the form of $\ln(\phi^{(e+d)}/T_{apex})$ versus $(-d E_{growth}/RT_{apex})$ applicable to the growth of bulk nuclei where the number of nuclei is inversely proportional to the heating rate ($a \cong 1$). This is limited, however, to such crystallization where the nucleation and growth temperature regions are not overlapping. If $E_{nucl} = 0$ then E_{app} simplifies to the ratio $(d E_{growth} + 2\{a + d - 1\}E T_{apex}) / (d + a)$ where $E_{growth} \ll 2\{r + d - 1\}R T_{apex}$.

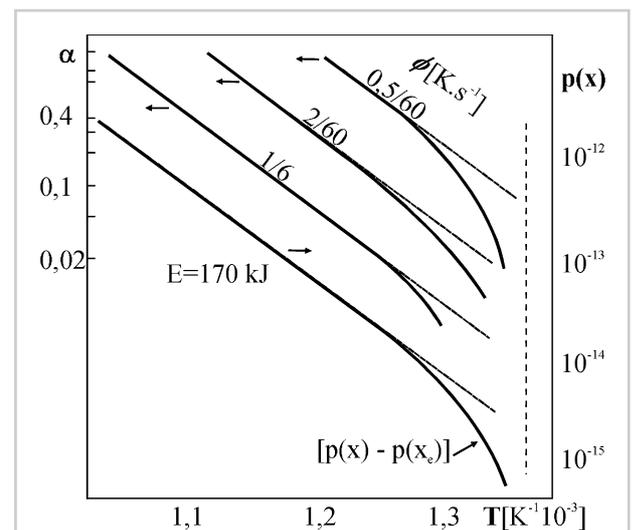


Fig. 12.4. The effect of heating rate, ϕ , on the integral kinetic evaluation of a process, which proceeds in the vicinity of equilibrium temperature of decomposition, T_{eq} , effecting thus the value of the function $p(x)$ used for approximation. It is illustrated on the case of one of the most problematic study – the decomposition of CaCO_3 . If the kinetic plot is markedly curved for small values of α (proximity to equilibrium), the extent of linear region used for the determination of E may significantly shrink as a result of decreasing capability of the sample state to equilibrate when departing too fast ($>\phi$) from its proximity conditions near equilibrium. At a certain stage (ϕ_{crit} effective $\{p(x)-p(x_{eq})\}$) all curves become bandy making possible to find an almost arbitrary fit, which often provides a wide spectrum of non-characteristic constants (e.g., typical expansion of E -values).

With the decreasing particle size, the number of surface nuclei gradually increases, becoming responsible for the peak shape. The particle-size-independent part of E_{app} can be explained by the nucleus formation energy, which is a function of the curved surface. Concave and convex curvature decreases or increases, respectively, the work of nucleus formation. Extrapolation of E_{app} to the flat surface can be correlated with E_{growth} for $a=1$ and $d=3$, being typical for silica glasses. It is, however, often complicated by secondary nucleation at the reaction front exhibited by decreasing E_{app} with rising temperature for the various particle zones. The invariant part of E_{app} then falls between the microscopically observed values of E_{growth} and E_{nucl} , the latter being frequently a characteristic value for yet possible bulk nucleation for the boundary composition of the given glass. Particular effect due to the addition of various surface dopants can be found for nano-crystallizing metallic glasses to fine-metallic nanocomposites which is different from the conventional nucleation-growth and is often characterized by values of the exponent, $r (<4)$.

Assuming that the as-quenched glass has a number of nucleation sites equal to the sum of a constant number of quenched-in nuclei, T_{apex}^o , and that, depending on the consequent time-temperature treatment, T_{apex} , the difference between the apex peak temperatures for the as-quenched and nucleated glass becomes proportional to the number of nuclei formed during thermal treatment. The characteristic nucleation curve can then be obtained by plotting $(T_{apex} - T_{apex}^o)$ against temperature, T , or even simply using only DTA/DSC peak width at its half maximum. The situation becomes more complicated for less-stable metallic glasses because the simultaneous processes associated with primary, secondary and eutectic crystallization often taking place not far from each other's characteristic composition. Another complementary technique is thus required to elucidate the kinetics.

Effect of the environment – near equilibrium studies

Often neglected but one of the most important cases we should recall is the subsumption of differences arising from the effect of *changing the equilibrium background* of the process (see Chapter 8, Fig. 8.3). It is illustrated on the example of various processes taking place for the tetragonal-cubic phase transformation of spinels, $Mn_xFe_{3-x}O_4 (t) \rightarrow Mn_xFe_{3-x}O_4 (c)$ see Fig. 3. The simple kinetic analysis of plotting the model relation against reciprocal temperature revealed that the change of the slope, often ascribed to the change of reaction mechanism, is just caused by switching between the part of the process proceeding under changing equilibrium background and the remainder invariant part controlled by the process itself [129].

As mentioned above, for the generally assumed transformations, the most frequently applied isothermally derived theory is directly applied to non-isothermal kinetic evaluations. The detailed analysis dictates, however, that such a non-isothermal generalization is only possible along the lines of the 'isokinetic' hypothesis, i.e., the invariance of the rate equation under any thermal conditions. It

was shown [123,130–132] that the non-isothermal derivation includes the use of the integral of Arrhenius exponential, i.e., the above mentioned $p(x)$ function, the suitable approximation of which leads to the change of the pre-exponential factor maintaining thus the residual model function unchanged. Thanks to that coincidence, all functions mentioned in the Chapter 8 are applicable for straightforward application to non-isothermal conditions.

Another obstruction may be seen when employing the temperature program, which is proportional to the reciprocal temperature, i.e., $dt = \phi d(1/T)$. In this case the function $p(x)$ simplifies as the difference dT is replaced by $d(1/T)$ so that $p(x) \sim (ZE/R\phi) [(-E/R)(1/T - 1/T_o)]$, which would be no complication but, on contrary, it would allow more straightforward kinetic appraisal. Although such temperature regulation is rare, it would essentially facilitate the kinetic data calculation, requiring, however, another systematics. It would be feasible, depending just on the manufacturers, to consider the unproblematic extension of their digital programmers to be applicable for another, newly specified case of kinetic investigations [1].

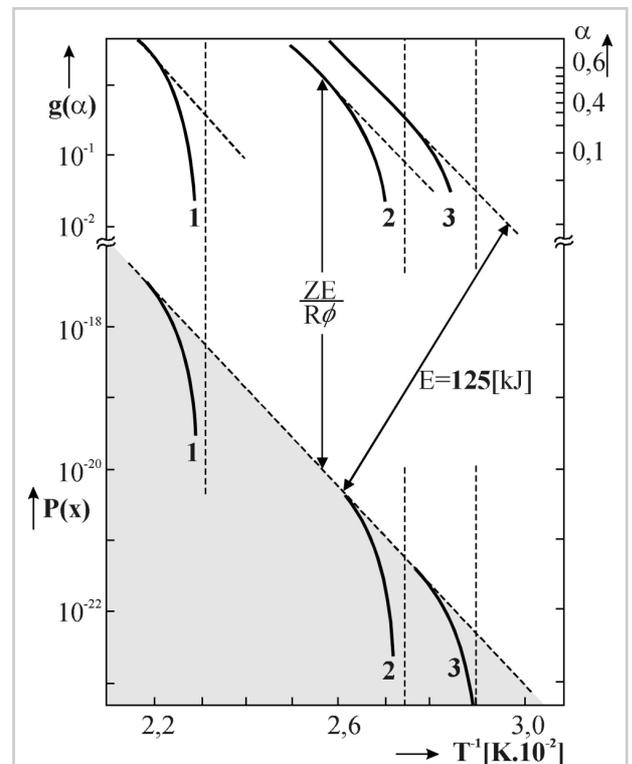


Fig. 12.5. The example of kinetic integral evaluation by simple plotting $\ln g(\alpha)$ versus $1/T$ using experimental data for the dehydration of sulphate hemihydrate, $CaSO_4 \cdot 1/2H_2O$, which dehydrates close to the equilibrium. The following vapor pressures, (1) $\sim 10^2$, (2) $\sim 2,5$ and (3) $\sim 0,6$ kPa were applied during the experiment. At the bottom figure the real shape of function $p(x)$ is marked as solid lines, whose linear extrapolation (dashed lines) yields the real value of activation energy, which simplified approximation is thus problematical and often misleading in search for the adequate characteristic values (cf. previous Fig. 12.4.).

Another special case of non-uniform heating is the cyclic heating introduced by *Ordway* in the fifties [133] and actually applied by *Reich* [134] to determine kinetic parameters under isoconversional conditions. If the temperature changes stepwise from T_i to T_{i+1} then it holds that $E/R = (\ln \alpha_i / \alpha_{i+1}) / (1/T_i - 1/T_{i+1})$. If the temperature is varied in harmonic cycles, then for the two mentioned temperatures the rate of the change can be obtained by constructing a straight line through the apices of sine waves. This method is analogous to work with several heating rates, but does not require the sample replacement. It also links with the modulated methods of thermoanalytical calorimetry, discussed in the preceding Chapter 11.

Proximity to equilibrium often plays, however, an important role in the beginning of a reaction where the driving force is minimal. In such a case some integration terms in eq. 12.6 cannot generally be neglected. The resulting function $[p(x) - p(x_0)]$ and the associated general plot of $g(\alpha)$ vs. $1/T$ dependences become non-linear. This effect can be illustrated on the decomposition of CaCO_3 , Fig. 4, the dehydration of sulphate hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$), see Fig. 5 [135] where too low heating results in most of the dehydration process taking place close to equilibrium and the non-linear dependence can be linearized only with large errors. The apparent E value that is determined is usually larger than the actual E value; its correct value must be obtained by extrapolation of curves plotted either for different pressures, illustrated later, or for different heating rates, to get away from the access of overlapping equilibrium, cf. Fig. 4.

A further complication is brought about by considering the effect of the reverse reaction, e.g., in the well-known *Bradley* relationship [1,136], i.e., replacing in eq. 12.6 the standard rate constant, $k_{(T)}$, by the term $k_{(T)}[1 - \exp(\Delta G/RT)]$. The ΔG value then actually acts as a driving force for the reaction and, thermodynamically, has the significance of the Gibbs energy, i.e., for $T \rightarrow T_{\text{eq}}$, $\Delta G \rightarrow 0$ and $\alpha \sim f(\alpha) k(\Delta G/RT)$ whereas $T \gg T_{\text{eq}}$, $\Delta G \rightarrow \infty$. Integration yields a complex relation of $[p(y-x) - p(y_{\text{eq}} - x_{\text{eq}})]$ where additional variable, y , depends on $\Delta G/RT$, the detailed solution of which was given in our previous work [136].

Further complication can be expected when the process being studied has a more complex nature, involving several reaction steps each characterized by its own different mechanism and activation energy [137-139]. The work of *Blažejowski* and *Mianowski* [140] showed that thermogravimetric curves can be modeled by an equation relating to logarithm of the conversion degree as a function of temperature. It follows from the *van't Hoff's* isobar, which determines the dissociation enthalpy, ΔH_{dis} , that this quantity is proportional to the ratio of $\ln \alpha / \{(1/T) - (1/T_p)\}$. Providing that the equilibrium state is reached at constant ΔH_{dis} the relation $\ln \alpha = a_0 - a_1/T - a_2 \ln T$ becomes applicable using three a 's as approximate constants.

In some special cases, where we must account for auxiliary autonomous variables (cf. eq. 8.7. discussed in the preceding Chapter 8), the thermal decomposition can proceed in a mixed-control kinetic status. In such a case,

both diffusional and chemical processes simultaneously control the overall reaction course with the same strength. Moreover, we have to account, at the same time, for the effect of partial pressure, p_r , of a reactant gas. *Malewski* [141] derived a more complex equation than that given in Table 8.I., which, however, has a multifaceted form such as

$$1 - (2/3) \alpha - (1 - \alpha)^{2/3} + s [1 - (1 - \alpha)^{1/3}] = k_r t. \quad 12.8.$$

The complex parameters, $k_r = 2 v_m \Delta p D / R^2_0$ and $s = 2 D / (R_0 k_{(T)})$, are composed of standard quantities of D , $k_{(T)}$, v_m , R_0 , and Δp , which express, besides the classical degree of decomposition, α , the diffusion coefficient, the reaction rate constant for a chemical reaction, the molar volume of the substrate, the radius of reacting sphere-shaped grains and the difference between the equilibrium partial pressure of volatile reactant and its external ambient pressure ($p_r - p_0$), respectively. The apparent activation energy, E_{app} , is then given by rather complicated equation, or

$$E_{\text{app}} = [R T^2 D (d \ln k_{(T)} / dT) + R_0 k f R T^2 (d \ln D / dT)] / (k_{(T)} R_0 f + D) + R T^2 (d \ln \Delta p / dT) \quad 12.9.$$

where $f = \{1 - (1 - \alpha)^{1/3}\}$ and which can be simplified for a negligible external reactant gas pressure ($p_r \cong 0$) to the equanimity related to the activation energies of chemical

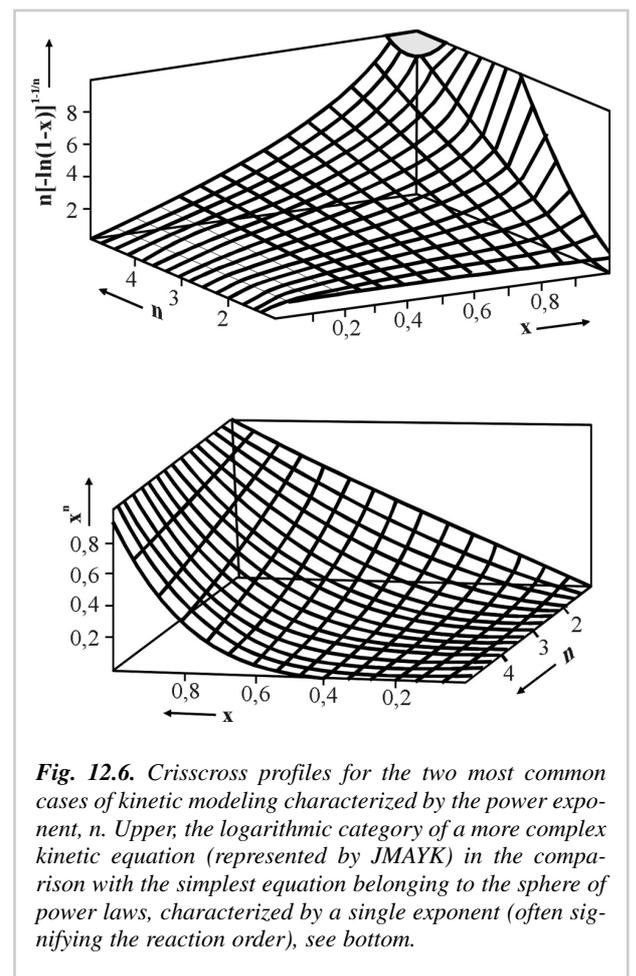


Fig. 12.6. Crisscross profiles for the two most common cases of kinetic modeling characterized by the power exponent, n . Upper, the logarithmic category of a more complex kinetic equation (represented by JMAK) in the comparison with the simplest equation belonging to the sphere of power laws, characterized by a single exponent (often signifying the reaction order), see bottom.

reaction, E_k , and diffusion, E_D , through $E_{app} = (s E_k + 2 f E_D)/(2 f + s) + \Delta H$. The model has been approved upon the study of the thermal decomposition of Co_3O_4 within the 2–20 kPa range of the oxygen pressure.

Yet another approach was recently proposed by *Schiraldi* [142] who criticized the use of monomial functions (or their combinations) and suggested the elimination of any specific form of reaction mechanism (and associated Arrhenius-like behavior) from kinetic calculations. He proposed formal expressions that included thermodynamic constraints identifiable for any spontaneous process and thus described the reaction rate as a result of the effects of the thermodynamic driving force, identified with the drop of the *Gibbs* function, and of the medium hindrance.

d) Optimal evaluation procedures

Due to an inseparable variation of different $f(\alpha)$ [or $h(\alpha)$] functions within non-integral values of kinetic exponents, the kinetic data evaluation based on a single-run method always exhibits certain degree of ambiguity [143–145]. It can be eliminated if the characteristic value of activation energy, E , is already known (or determined *a priori*), e.g., through application of eq. 12.6. It was proposed by *Málek* that for such a diagnostic purpose it is very useful to define two special functions, $y(\alpha)$ and $z(\alpha)$,

which can easily be obtained by simple transformation of the experimental data [143,145,146], i.e., $y(\alpha) = (d\alpha/d\theta) = \alpha' \exp(x) = Z h(\alpha)$ and $z(\alpha) = (d\alpha/d\theta) \theta = h(\alpha) g(\alpha) = \pi(x) \alpha' T/\phi$ where $x=E/RT$ and $\theta = \int^t \exp(-E/RT) dt$. The product of the function $h(\alpha)$ and $g(\alpha)$ is a useful diagnostic tool for determining the most appropriate kinetic model function, in which all the functions have a maximum at a characteristic value of α_p . By plotting the $y(\alpha)$ function vs. α , both normalized within the interval $\langle 0,1 \rangle$, the shape of the function $h(\alpha)$ is revealed. The function $y(\alpha)$ is, therefore, characteristic of a given kinetic model, as shown in Fig. 7. We should call attention to the important aspect that the shapes of functions $y(\alpha)$ are strongly affected by the value of E . Hence, the value of *a priori* constant E is decisive for a reliable determination of kinetic models because of the correlation of kinetic parameters involved. Similarly we can discuss the mathematical properties of the function $z(\alpha)$. Its maximum is at α_p^∞ for all kinetic models and, interestingly, it does not practically depend on the value of E used for its calculation.

In order to see this behavior we have to modify the basic kinetic eq. 8.8 to the form of $\alpha' = h(\alpha) g(\alpha) \phi / \{T \pi(x)\}$, which can be differentiated $\alpha'' = [\phi / \{T \pi(x)\}]^2 h(\alpha) g(\alpha) [h'(\alpha) g(\alpha) + x \pi(x)]$ and set equal to zero, thus deriving once more the mathematical conditions of the peak as, $-h'(\alpha_p) g(\alpha_p) = x_p \pi(x_p)$. When x_p is infinite, we can put the limit $\{-h'(\alpha_p^\infty) g(\alpha_p^\infty)\}$ equal to unity, which can be evaluated numerically providing the dependence of α_p^∞ on the non-integral value of exponent n , illustrated for example for diffusion-controlled models in Fig. 7. It became apparent that the empirical diffusion model D_n is characterized as concave, having the maximum at α_{max} equal 0, using the $y(\alpha)$ function, and equal $0.774 \leq \alpha_p^\infty \leq$ (in the $z(\alpha)$ function). Table 8.I shows schematically the empirical kinetic model determination by means of $y(\alpha)$ and $z(\alpha)$ functions. By adding the empirical model functions based on the geometrical fractals, the empirical RO_n and $JMAYK_m$ functions can be related to the conventional kinetic model functions $f(\alpha)$ within the integral kinetic exponents. However, the $SB_{n,m}$ function has a true empirical (and fractal) character, which in turn makes it possible to describe all various type of shapes of thermoanalytical curves determined for solid-state reactions (just fulfilling $\alpha_{max} \neq 0$). The kinetic parameter ratio m/n is then given by a simple ratio $\alpha_{max}/(1 - \alpha_{max})$.

It is surprising that the mutual correlation of kinetic parameters as well as apparent kinetic models are often ignored even in the commercially available kinetic soft wares. Therefore we recommend a package which first includes the calculation of E from several sets of kinetic data at various heating rates. This value of E is used as input quantity to another program calculation the above defined functions of $y(\alpha)$ and $z(\alpha)$. The shapes of these functions then enable the proposal of the most probable kinetic model rates [147]. Then the pre-exponential factor Z and kinetic exponents m/n are calculated. The procedure can be repeated for all heating rates yielding several sets of kinetic data corresponding to various heating rates. If the model mechanism of the process does not change during whole thermoanalytical experiment, it approves its reli-

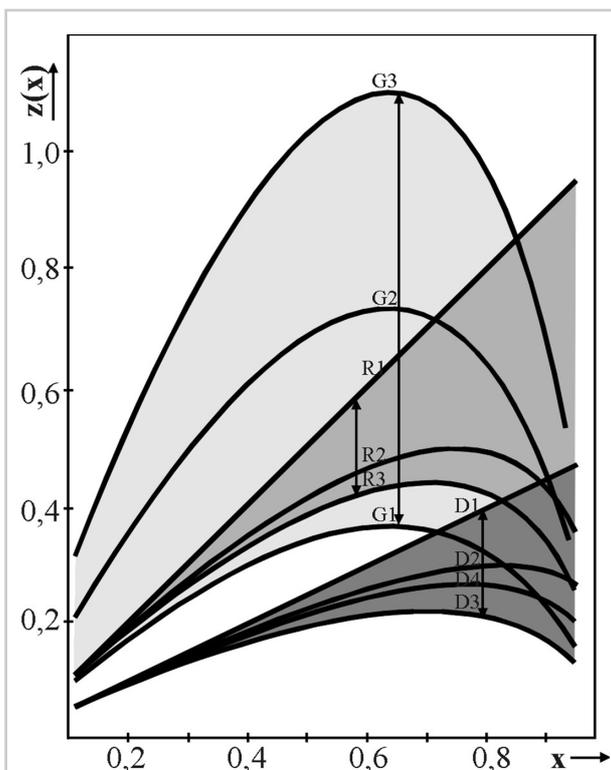


Fig. 12.7. Graph of the characteristic functions $z(\alpha) = f(\alpha) g(\alpha)$ plotted against α showing the individual types of the 'master plot curves' typical for the following kind of processes: nucleation-growth ($G1 \leftrightarrow G3$, light shadow range), phase-boundary (chemical, $R1 \leftrightarrow R3$, shadow range) and diffusional ($D1 \leftrightarrow D4$, dark shadow range). For the model illustration and mathematical expression see Chapter 8 and Fig. 8.6.

ability and the consistency of the kinetic model thus determined can be assessed by comparing experimental and theoretically calculated curves. Consequently, the isothermal-like $\alpha - t$ diagrams can be derived in order to predict the behavior of the studied system under isothermal conditions.

Accounting for the evaluation best reliability, we can see that the models of reaction mechanisms can be sorted into three groups, R, A and D, see Fig. 7 and probably it also gives the extent of determinability and model differentiability by integral calculation methods. *Ozao* and *Ochiai* introduced the model uncertainty due to the fractal nature of pulverized solid particles [109]. The area within the limits of side curves of each the given bunch of curves in Fig. 7 became extended (fuzzy) and the individual curves with integral exponents lose their dominance in favor of multiple curves (lying within each shaded area) with various non-integral exponents. This, again, supports the viewpoint that through the kinetic evaluation of a single non-isothermal curve we can only obtain information about the kind of process, i.e., assortment within the range of models R, A and D.

In the literature there have appeared multiple computer programs of rather sophisticated kinetic data evaluation, which we do not want to repeat. Among others, a simple numerical method was proposed using an arbitrary temperature-time relationship. The algorithm searches for E and rate constants by means of minimization of the average square deviation between the theoretically computed and experimentally traced curves on a scale of the logarithm of reduced time, which is expressed as the integral of the Arrhenius exponential. The standard eighteen models (cf. Table I) are included for the sequential analysis and arrangements of the roots of mean square deviations provide a good approximation of the original kinetic curves. [143,147].

e) Controlled rate and temperature oscillation modes of thermal analysis

We should also account for the resolution power of controlled rate thermal analysis (CRTA) enabling to control the transformation at such a low rate that the remaining temperature and pressure gradients through the sample are themselves low enough to avoid overlapping, often successive transformation steps. Therefore the term $k_{(T)} = Z \exp(-E/RT)/f(\alpha)$ is constant and its differentiating with respect to α , respecting the conditions of both minima, α_{\min} and α_{\inf} provides $dT/d\alpha = -T^2/ER \cdot f'(\alpha_{\min})/f(\alpha_{\min}) = 0$. The theoretical CRTA curves can be divided into three groups whose general shapes were illustrated previously in Fig.10.1. Thus, the general rules regarding the shape of an experimental curve α versus T can be formulated as follows [148]

- The mechanism of nucleation and subsequent growth of nuclei, i.e., JMAK model ($\alpha_{\min} = 1 - \exp\{1-n/n\}$) as well as empirical SB model ($\alpha_{\min} = m/\{m-n\}$) lead to the curves with temperature minimum.
- The boundary-controlled mechanisms as well as the reaction-order models give the shape without minima or inflexion points.

- The diffusion processes provide the curves with an inflexion point, the location of which is affected by the value of reduced activation energy, $x = E/RT$ (e.g., for classical *Ginstling-Brounshtein* model as $1 - \{(2 + 3x)/4x\}^3$).

The principle of activation energy calculation is to bring the rate of reaction to switch between two preset values – whose ratio, r , is conventionally chosen to lie within 1 to 4. About tens of jumps are usually performed to analyze one individual step. Each temperature jump allows determining a separate value of activation energy, since it provides a couple of temperatures obtained by extrapolation for exactly the same degree of reaction. Since the degree of reaction remains virtually unchanged during the rate-jump and furnishes that $f(\alpha)$ is not changed, we can assume that $E = (ln r RT_1 T_2)/(T_1 - T_2)$, where T_1 and T_2 are the sample temperatures just before and after a rate jump, unnecessary to know the entire reaction mechanism $f(\alpha)$. After evaluating the value of E by the jump method, a single CRTA curve is subjected to the determination of

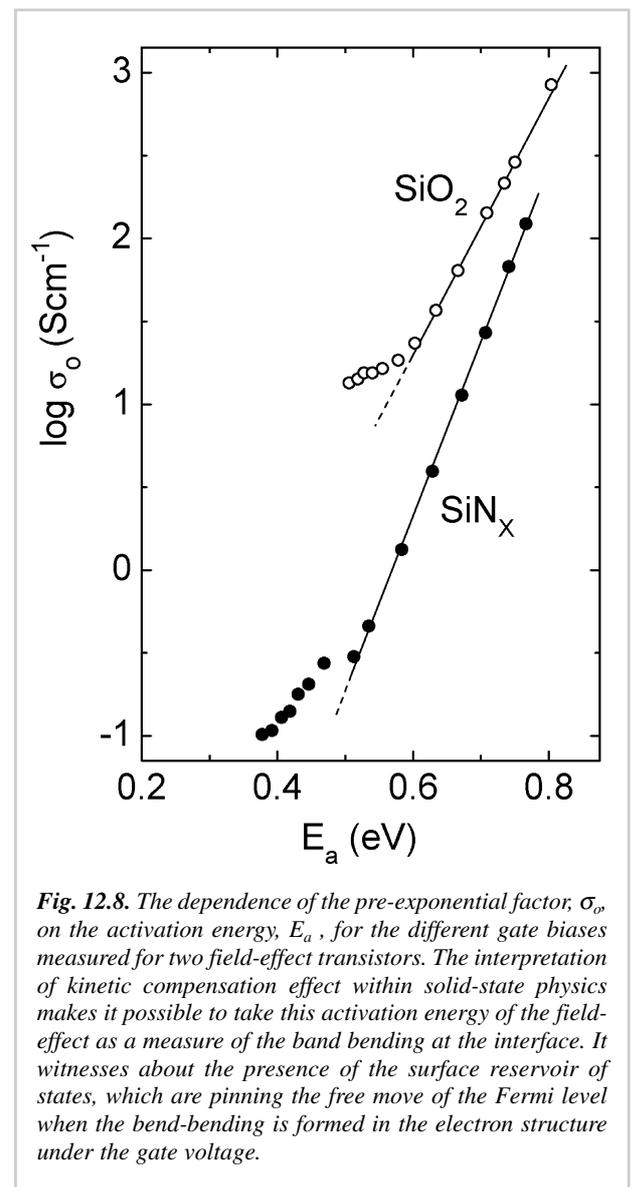


Fig. 12.8. The dependence of the pre-exponential factor, σ_0 , on the activation energy, E_a , for the different gate biases measured for two field-effect transistors. The interpretation of kinetic compensation effect within solid-state physics makes it possible to take this activation energy of the field-effect as a measure of the band bending at the interface. It witnesses about the presence of the surface reservoir of states, which are pinning the free move of the Fermi level when the bend-bending is formed in the electron structure under the gate voltage.

the α dependence as characterized by $f(\alpha)$ and the Arrhenius pre-exponential factor Z by following the kinetic equation in different forms.

An agreed approach for evaluating E is known as the temperature jump [149], only different in the controlling parameter, i.e., the transformation rate or temperature. From the viewpoint of kinetic analysis, the modulated temperature control introduced in the thermoanalytical technique [46,150] can be recognized as a sophisticated temperature control based on the temperature jump method, avoiding over- and undershooting during the jump. However, such a sudden change in the reaction rate or temperature may sometimes be a plausible source of further complications due to the influences of heat and mass transfer phenomena. It should always be borne in mind that the reliability of the kinetic results is determined not only by the methodology of the kinetic measurements and the consequent mathematical treatment, but also by the kinetic characteristics of the reaction under investigation.

f) Kinetic compensation effect

A wide variety of the physical, chemical and biological phenomena are traditionally described by means of the exponential law, $G_0 \exp(-E_a/kT)$, where the activation energy of a kinetic process, E_a , depends on the input parameter, \underline{a} , distinguishing the material system under study (for example, related to the history of the system investigated, such as quenching rate, variously imposed external fields of pressure, electric/magnetic/gravity etc). Here, T is the absolute temperature, k is the Boltzmann constant and G_0 is the pre-exponential factor (pre-factor). For this, so-called Arrhenius relation [150], there exists in many cases (especially within limited ranges of the input parameter \underline{a} and/or T) extra correlation between E_a and G_0 which is observed and called *thermodynamic compensation law* [151–153], or more often as the kinetic compensation effect [1,154] – commonly abbreviated as KCE. It holds that $\ln(G_0/G_{00}) = E_a/kT_0$, where G_{00} and T_0 (so-called iso-kinetic temperature) are assumed constants). The geometrical meaning of such a KCE correlation is quite obvious: the empirical dependences, fulfilling exponential relation and plotted in the so-called Arrhenius diagram ($\ln G$ vs $1/T$) are arranged in a bundle of straight lines with a single and common intersection point with the coordinates $1/T_0$ and $\ln G_{00}$. If the above formulae are simultaneously valid, the transformation to an equivalent form is admissible, $G = G_{00} \exp(-F/kT)$ and $F = E_a(1 - T/T_0)$. It is worth noticing that it is similar to the original relation but the G_{00} is a constant here and F is a linear function of temperature. The direct comparison with the Gibbs statistical canonical distribution leads to the conclusion that F should have the meaning of isothermal potential (isothermal free energy) which is adequate for the description of isothermal kinetic processes. From this point of view the validity of KCE is mathematically equivalent to the linear dependence of the free energy on the temperature and bears no essentially new physical content – it is a pure mathematical consequence [1] of the approximations used. It is evident that in many cases such a linear approximation can serve as a satis-

factory description of experimentally observed data, but it is often used to describe their material diversity.

Appearance of two new quantities, G_{00} and T_0 , may, however, be used for an alternative description and parameterization of a system involving kinetic processes. Taking in account the Helmholtz relation between the free energy coefficient and the entropy [1,153] it provides $(\partial F/\partial T)_a = S(a)$. We can immediately obtain the entropy changes related to the changes of input parameters \underline{a} in the form $S(a_1) - S(a_2) = (E(a_1) - E(a_2))/T_0$. The right side of this equation can be directly evaluated from the observed data without difficulties. The term on the left-hand side can be interpreted as a “frozen entropy” related to the parameter \underline{a} . It is an additional term contributing to the total entropy of a given material system, and may be expressed in a generalized form $S(a) = E_a/T_0$. Using the Einstein fluctuation formula [155], we can obtain for the relative change of the thermodynamic probability, W , of the system with respect to the input parameter \underline{a} the following relation: $\ln(W_1/W_2) = \{E(a_1) - E(a_2)\}/kT_0$. The right-hand side may thus serve as a measure of the rigidity and/or stability of the system with respect of the changes in \underline{a} . As such, it can be employed to draw up certain consequences to technological conditioning of the system preparation (chemical composition, cooling rate, annealing, mechanical history, external pressure, etc.).

The change of the “frozen entropy”, E_a/T_0 , characterizes, on the one hand, the internal configuration of the material system under study and, on the other hand, has a simultaneous meaning of the coefficient in the linear term of the free energy. Consequently, such a change of E_a/T_0 must be inevitably associated with the change of the reaction mechanism. We can exemplify it by the correlation between the activation energy of conductance and the corresponding pre-factor in the field effect transistor [156]. The sudden change of the plot for large gate biases (small E_a) corresponding to the electron transport just in the vicinity of the interface between the insulator (SiO_2 or SiN_x) and amorphous (glassy) semiconductor (a-Si) shows the switch in the conductivity mechanism, see Fig. 8.

In the field of chemical kinetics the KCE was first pointed out by Zawadski and Bretsznyayder [11,154] while studying the thermal decomposition of CaCO_3 under various pressure of CO_2 ($E_a \equiv P_{\text{CO}_2}$) but in the field of solid state physics it was often called the thermodynamic compensation rule [151], derived upon conductivity studies on various oxides [157]. Early studies pointed that non-linearity in the Arrhenius plots gives the evidence of a complex process [1,150,152], that the mathematical correlation of pre-factor and activation energy is inseparable [158] or the determination of the KCE is incorrect by mere linear regression of E_a vs. G_0 , because these quantities are mutually dependent being just derived from the original kinetic data. There were even attempts to relate the KCE to the geometrical shape of the χ -square function [159]. However, the KCE was mostly dealt with in the field of chemical kinetics being a frequent target of critique, but more often under attempt to be explained and solved both from various experimental [160–164] and

theoretical [162,163,165–167] points of view, as reviewed by *Koga* [152]. Among others, it was pointed out that the KCE can be affected by changes in the defect concentrations, is sensitive to the sample mass or may even results from a mere computational error [169]. Even separation of the false and true KCE by two sets of iso-kinetic temperatures was investigated distinguishing physicochemi-

cal factors and experimental artifact [170]. The most important, however, were mathematical treatments showing that the KCE is a *factual mathematical consequence of the formulae employed* – exponential rate constant $k_{(T)}$ [152,153,171] including the effect of distortion caused by mere application of incorrect or inappropriate kinetic model functions [166].

¹ Back in 1979, I published a series of thought-provoking questions [70,71] which may still stay partly unresolved:

- * Why has non-isothermal kinetics gained so unfavorable reputation? Is it due to experiments carried out mainly by thermoanalysts or is it liable to pay for the mode of historical introduction and simplified mathematics?
- * Where are the roots of possible misfits and which evaluation method is better? (integral vs. differential)
- * What do the kinetic parameters such as energy, E , and orders, n , m , mean? Are these terms generally applicable?
- * What about separability and non-constancy of kinetic data, what is the kinetic compensation effect?
- * Is the kinetic evaluation accuracy affected merely by the precision of experimental input data or is it further affected by the distinctiveness of mathematical treatment? (choice of method vs. calculation procedure)
- * Is the DTA technique suitable for kinetic data determination or is it too dependent on its experimental set up?
- * If there are so many troubles with gradients, would it be better to employ only isothermal or other stationary methods?
- * How compatible are kinetic and equilibrium data, should we thus account for the equilibrium background?
- * Can we ever separate the isothermal and non-isothermal reaction rates? (mathematically vs. physically)
- * Is it worth paying such attention to non-isothermal kinetics if it is a narrow region of scientific interest?
- * Will a sophisticated computing technique be of real help in solving problems or does it just solve only most painful numerical troubles? Would it create a ‘black-box’ technique with smooth zero lines and curves and with easy-to-publish data?

² For many multifaceted (i.e., complex fractal-like) systems, the instantaneous rate constant must be further specified as an evolutionary (time-dependent) coefficient, $k(T,t)$, conventionally represented by the product, $k(T)$ with t^h . Exponent-parameter, h , expresses thus the system ‘fractality’, which is for strictly homogeneous conditions (under vigorous stirring and without accounting on the effect of initial conditions) equal to unity. For a simple case of $[A+A]$ reaction in one-dimensional space, h is $1/2$, but actually it is given by $(h = 1 - d_s)$, where d_s is the so-called random-walk occurrence (spectral) dimension (see Chapter 13). Thus for both the $[A+A]$ reaction and the geometrical construction of porous aggregated (based, e.g., on triangles called *Sierpinski* gasket, see Chapter 13), h is around 0.32, because the typical values for d_s are 1.36 (gasket) or 1.58 (percolation). Assuming a more general exponent, n , for $[A]^n$, we can find for the ordinary diffusion-effected case $n = 1 + 2/d_s = 1 + (1 - h)^{-1}$ so that the expected value for n is 2.46 for a gasket, 2.5 for a percolation cluster and 3 for the standard homogeneous one-dimensional reaction, still retaining its bimolecular character in all above cases. Practically, we have to distinguish a connected fractal, such as reactants in the form of ‘dust’ or ‘colloids’ where the effective dimension is $h \cong 1/3$ (i.e., $0 < d_s < 1$, providing $3 < n < \infty$), and segregated reactants, which often con-jure self-organized reactions (*Belousov-Zhabotinski*, see Chapter 16), which are more complex for the description. It is worth noting that the effect of segregation is in concurrence with the almost unknown *Wenzel’s Law*. *Wenzel* stated in 1777 [C.F. Wenzel, *Lehre Verwandtschaftschaft* Koerper 8, Dresden 1977] that *for heterogeneous reactions holds that: the larger the interface, the faster the reaction*, that is, the rate per unit surface is reconcilable and the interface (and its character) thus backs any modeling as a self-similar fractal.

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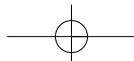
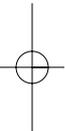
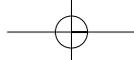
Volume four
**THERMAL DYNAMICS AND NON-EQUILIBRIUM
PHENOMENA**

Power law, fractals, chaos and information or how nature is smart

Oscillation modes and modern theories of state

Advanced evaluation of processes – disequilibria and dendritic growth

Principle of least action and self-organization of chemical reactions





CHAPTER THIRTEEN

13. Power law, fractals, chaos and information or how nature is smart

a) Stimulation responses and logarithmic dependencies

Most of our culture experience lies in the linearly perceived world. We are taught from early childhood to geometrically apprehend things, objects and their surroundings and to foresee them in the basic visible forms of lines (and aggravated blocks) and the associated circles (and spheres). There arises a question whether such an austere 'linear' education is satisfactorily intrinsic to our naturally sensed education (through the process of evolution, which materialized in the development of general responses of our organisms). We may become inquisitive if some other functions (obviously exhibiting a damping character) are even more natural (particularly when presumptuous how the organisms avoid the self-destruction processes due to incessant surfeit). Furthermore, we may benefit from our sensing the loveliness provided by the structure of nature available through various ways of sensation. For example, most of us have experienced eye vision (and its brain perception) of a forest. From a distance the forest may be noticed as a two-dimensional object, getting closer its three-dimensional imprint becomes more and more obvious, but on the actual entering the woods their complex structure can be felt as a beautiful mixture of bizarre patterns and forms, which are absolutely out of our standard cognition of linearity. Its curiosity has become the driving force for the recent development of alternative portraying of geometry and commensurate mathematics.

It is well known that every physiological property of sensation is related to some physical property of the corresponding stimulus. *Sensation* is the process by which our sensory systems gather information about the environment. *Perception* is the selection process of organization and interpretation of sensations. *Stimulus* is a form of energy that can excite the nervous system and the transformation of external stimulus into neural impulses is called *transduction*. The *absolute threshold* is the weakest stimulus that can be detected in a modality and the *relative threshold* is the smallest change in intensity that can be detected. In psycho-physical terms, intensity is related to the amount of stimulus energy falling on the sensory surface. If the original physical intensity, I , is low, even a very small change, Δ , is noticeable; however, if it is high, a relatively larger change is required. This principle is represented in *Weber's Law* where $\Delta/I = \text{constant}$. A more general principle relat-

ing the sensor intensity (response), S , to the stimulus dimension (measured in distance from the threshold), I , was introduced by *Fechner* and is presently known as *Weber-Fechner* [1] logarithmic law, $S = \text{const} \log I$. It shows the importance of a *logarithmic function*¹ as the operation introduced by nature in the biological necessity gearing up the sensation change to proceed more slowly having thus a certain self-protection role against damages due to sensation overloading.

An even more general psycho-physical law is the power law [2], named after *Stevens*, which states that $S = \text{const} I^N$, where N is the modality-dependent exponent (either power or root) and I is again the above-mentioned intensity of physical stimulus. The exponent N was estimated to equal 0,5 for brightness, 0.6 for loudness, 0.9 for vibration, 1.4 for heaviness and 1.6 for temperature. Some special cases of *Stevens Law* are worth noting: if the exponent N is less than unity, it complies with the above case of compressed stimulation, and when $N = 1$, it provides the case of the so-called 'length exception' to the *Weber-Fechner Law*, where every change in I produces an isomorphic change in S . The *Stevenson Law*, however, is applicable to all modalities, and all qualities within a modality, which takes place under any circumstances, and which is suitable to describe so-called 'operating cha-

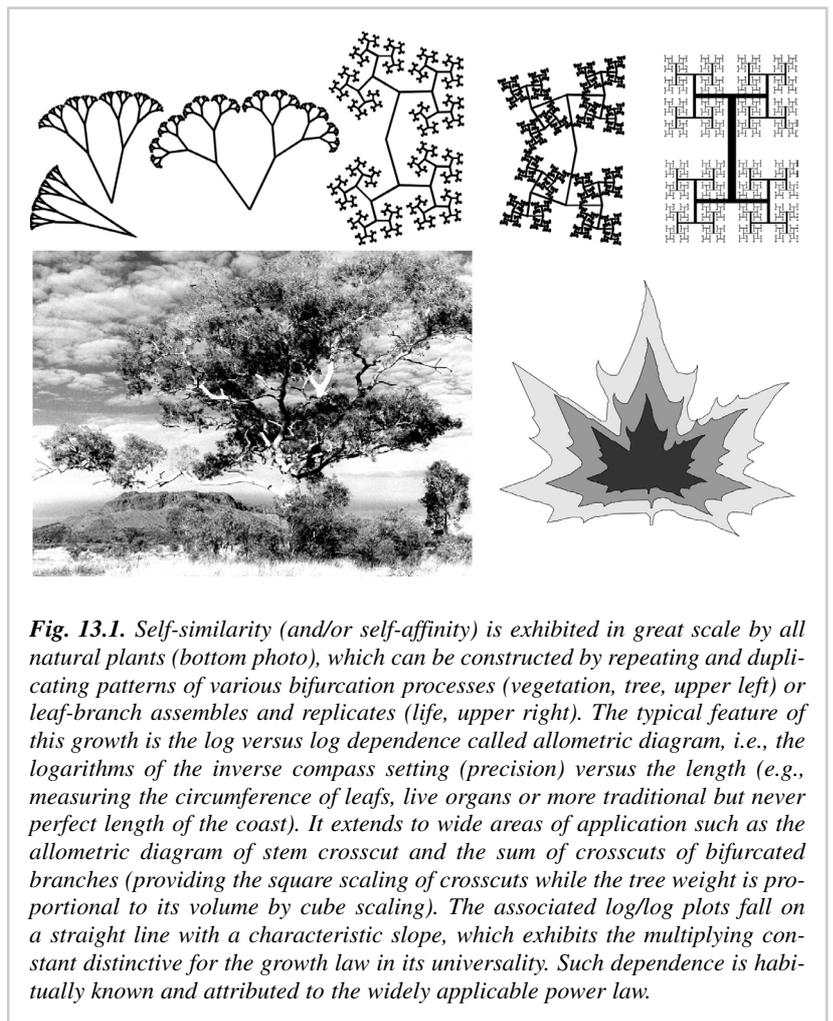


Fig. 13.1. Self-similarity (and/or self-affinity) is exhibited in great scale by all natural plants (bottom photo), which can be constructed by repeating and duplicating patterns of various bifurcation processes (vegetation, tree, upper left) or leaf-branch assemblies and replicates (life, upper right). The typical feature of this growth is the log versus log dependence called allometric diagram, i.e., the logarithms of the inverse compass setting (precision) versus the length (e.g., measuring the circumference of leaves, live organs or more traditional but never perfect length of the coast). It extends to wide areas of application such as the allometric diagram of stem crosscut and the sum of crosscuts of bifurcated branches (providing the square scaling of crosscuts while the tree weight is proportional to its volume by cube scaling). The associated log/log plots fall on a straight line with a characteristic slope, which exhibits the multiplying constant distinctive for the growth law in its universality. Such dependence is habitually known and attributed to the widely applicable power law.

acteristics'. This term has appropriated from the spheres of engineering, as *any* sensory transducer behaves similarly, which is true even for expanded stimulations, where $N > 1$ (as is in the 'pain' exception).

Any further analysis of detection needs more detailed ratiocination as to involve both the motivation and the expectancy. These considerations gave rise to signal detection theory, a modern form of psycho-physics, which takes into account both the sensitivity of the nervous system, and the goals and expectation of the observer. A stimulus, or a signal, is often presented against a background of noise and if the signal is just slightly more intensive than the noise then such situation injects considerable uncertainty into each trial. The observer's expectations are further manipulated by varying the proportion of catch trial, in which signal is actually off, as well as by his motivation if influenced by a payoff matrix – if no penalty for false alarms, the subject is liberally positive in accepting but become more conservative if the each error costs dearly.

There are many other experimental scales related to the damping role of our sensation such as *Pogson's Law* to evaluate the magnitude of stars, *Banfort's scale* of wind-strength or *Mercalli-Cancani* magnitude of earthquake². Important is the strength of the acoustic signal and particularly the music harmony³, which was revolutionize by turning from the original *natural tuning* (traditional since *Pythagoreans*, using the ratios of chords length from 1, 9/8, 5/4, 4/3, 9/2, 5/3, 15/8 to 2) to the equidistant interval division called *tempered tuning* [3] introduced by *Werckmeister* in 1691 and practically employed by *Bach* in his famous "48" piano composition in 1722. It reads for the frequency, $\log f = \log f_0 + m(1/12) \log 2$, and the staves of sheet music are thus separated in the logarithmic scale.

The associated logarithmic function even touches the sphere of psychology where a Czech priest *Šimerka* [4] made in the year 1882 an experimental record and analysis of confrontation and quarrels based on his confession practice. He proposed that the *strength of conviction*, *P*, and *number of reasons*, *D*, are logarithmically proportional as $P = \log(1 + D)$ showing the table of *D* versus *P* pairs: 0 – 0, 1 – 0.7, 2 – 1.1, 3 – 1.4, 10 – 2.4, 20 – 3.0 and 50 – 3.9. It follows that the most confident belief is for just one motive regardless if it is certainty or insinuation, defamation, journalese, publicity or politics while the cause multiplication does not improve the trustworthiness to

a great extent – only three times for as many as twenty reasons. Therefore the most important sphere became information which will be dealt with separately in further parts of this chapter [5,6].

The above discussed and naturally originated power laws, see Fig. 1, are very important for the approval of validity of the laws in physics, either derived theoretically or developed on the basis of experiments. All resulting relations stand for the functional dependence [7], *f*, between the *i*-quantities, *x*, characterizing the given phenomenon and numerical values, which depends on the selection of the *j*-units, *k*, independent to the character of law. For example, it reads that $x = f(x_1, x_2, x_3, \dots, x_i)$ so that $x_1^{k_1} x_2^{k_2} x_3^{k_3} \dots x_i^{k_i} = 1$, which is called the dimension analysis. It can be illustrated on the transport phenomena relating two alike processes, 1 and 2, of heat transfer applied for temperatures $T_2 = k_T T_1$, with generalized

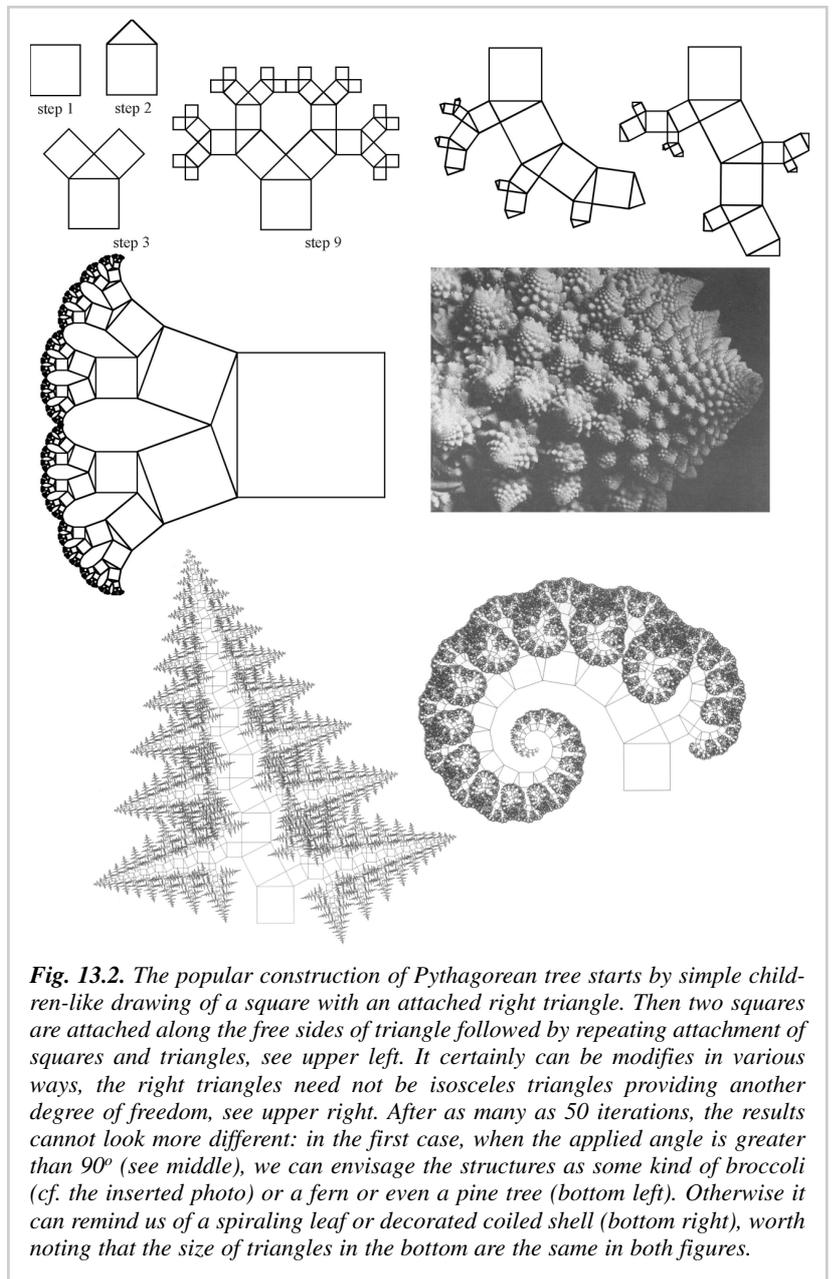


Fig. 13.2. The popular construction of Pythagorean tree starts by simple children-like drawing of a square with an attached right triangle. Then two squares are attached along the free sides of triangle followed by repeating attachment of squares and triangles, see upper left. It certainly can be modified in various ways, the right triangles need not be isosceles triangles providing another degree of freedom, see upper right. After as many as 50 iterations, the results cannot look more different: in the first case, when the applied angle is greater than 90° (see middle), we can envisage the structures as some kind of broccoli (cf. the inserted photo) or a fern or even a pine tree (bottom left). Otherwise it can remind us of a spiraling leaf or decorated coiled shell (bottom right), worth noting that the size of triangles in the bottom are the same in both figures.

time, k_t , distance, $k_x (=x)$ and heat diffusivity, k_a . It follows that $k_a k_t/k_x^2 = 1$, which makes it directly available in the form of two dimensionless numbers, which were earlier introduced by *Fourier* and *Biot* for the heat and mass transport as $F_o = k_a t/x^2$ and $Bi = \alpha x/\lambda$ (alternatively as $F_{om} = Dt/x^2$ and $Bi_m = \alpha_m x/D$, where D is the diffusion and α is thermal expansion coefficients). Another renowned number of that kind was devised by *Rayleigh* in the form, $R \equiv \alpha g \Delta T/(k_a \nu)$ [8] (cf. Chapter 4) where g , ΔT , k_a and ν are respectively gravitation acceleration, thermal gradient, thermal diffusivity and kinematic viscosity. Certainly, there are many other important dimensionless numbers, among others let us mention *Reynolds*, $Re = vx/\nu$ or *Prandtl*, $Pr = \nu/k_a$, both useful in the theory of motion of fluids.

b) Significance of limits and self-similarity

We learned in the chapter one that we live in the world that provides us a limited view within a certain horizon. The limits have always involved something mysterious about them, and it would be felt insufficient not to deal with them in more details although it somehow falls beyond the entire scope of heat but it links, however, with

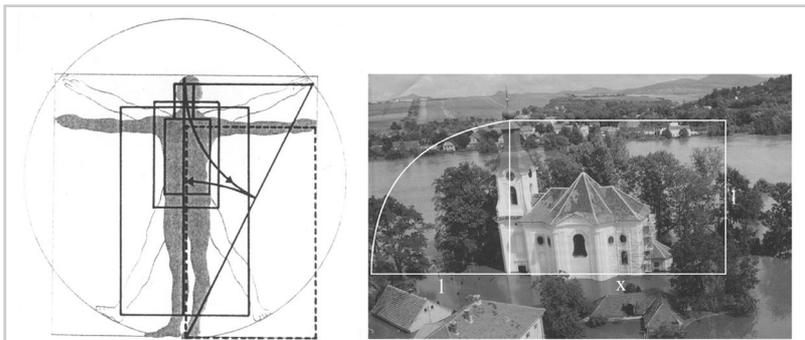


Fig. 13.3. Illustration of the general problem of incommensurability of both the side and diagonal of a rectangle showing that the number $\sqrt{2}$ exists as a special quantity in some mysterious sense. It is related to the simplest possible expansion of continued fractions, $x = 1 + (1/(2 + 1/(2 + 1/(2 + 1 \dots))))$, assuming the equation $(x^2 + 2x - 1 = 0)$. Similarly the golden mean is $x = 1 + (1/(1 + 1/(1 + 1/(1 + 1 \dots))))$, i.e., $\log(x + 1) = 2 \log x$ and equal to $1.62 \cong (1 + \sqrt{5})/2$. The golden mean is also naturally hidden in the ratio of sides and diagonals of an isogonal pentagon, which, as a matter of curiosity, was the caste-mark of Pythagorean School, and often taken as a sign of cryptic wisdom. In general, the golden mean should stand for a most positive graphical sentience. Such an observer's insight ('artistic eye-view') was already introduced by Leonardo da Vinci (left) in his early studying the proportions of figures. Since that, it has been widely used by artists in an opposite dividing the proportions and the literal positioning a major object to be asymmetrical in the frame, a traditional habit in medieval painting. The photo (right) tries to endorse this custom (moreover pointing that floods were sensed as spontaneous human cataclysms analogously as the catastrophes are due to fires).

the associated domain of chaos [9–11]. The limits create and characterize new quantities and new objects and the study of these unknowns was the pacemaker in the early mathematics and consequently has led to the creation of some most beautiful mathematical inventions [11–17]. It involves the analysis of *patterns* and *forms*.

Let us mention the discovery ascribed to *Pythagoras* regarding the theme of *incommensurability* of side and

diagonal of the square, i.e., the ratio of the diagonal and the side of a square is not equal to the ratio of two integers. The computation of square roots is an interrelated problem and has inspired mathematicians to discover marvelous geometrical constructions. A most common construction yields the family of Pythagorean trees when encompassing continuous attachment of a right triangle to one hypotenuse side of the initial square continuing by the attachment of two squares and so on, see Fig. 2. It rosettes broccoli and such a (fractal-like) branching construction is of a help to botany. Even more allied is the construction passing from equilateral triangles to isosceles triangles with angles exceeding the right angles. It is worth noting that all these beautiful constructions are *self-similar*. The computed situation is, however, different to natural image of a broccoli, or better a tree, where the smaller and smaller copies accumulate near the leaves of the tree so that the whole tree is not strictly self-similar but remains just *self-affine*, as seen in Fig. 2.

When *Archimedes* computed π by his approximation of the circle by a sequences of polygons, or when the *Sumerians* approximated $\sqrt{2}$ by an incredible numerical scheme, which was much later rediscovered by *Newton*, they all were well aware of the fact that they are dealing with the *unusual numbers* [18]. As early as in the year 1202, the population growth was evaluated by the number of immature pairs, i.e., $A_{n+1} = A_n + A_{n-1}$ with $A_0 = 0$, $A_1 = 1$, continuing 1,2,3,5,8,13,21,34,55,89,144,... (meaning that the state at time $n+1$ requires information from the both previous states, n and $n-1$, known as two-step loops) called the *Fibonacci* sequence. The ratio of A_{n+1}/A_n is steadily approaching some particular number, i.e., 1,618033988..., which can be equaled to $(1+\sqrt{5})/2$ and which is well-known as the famous golden mean ('*proportio divina*'). In fact it is a first member of a general series $x = 1 + (1/a + (1/a + (1/a + \dots))$, where $a = 1$, while the second member for $a = 2$ represents the limit of $\sqrt{2}$. This golden mean characterizes the side ratio of a rectangle, i.e., $x/1 = (x+1)/x$, cf. Fig. 3, which over several centuries inspired artists, architects and even scientists to wonderful speculations about such a lovely asymmetrical manifestation.

It is almost ironic that physics, at its most advanced level, have recently taught us that some of these conjectures, which even motivated *Kepler* to speculate about the harmony of our cosmos, have an amazing parallel in our modern understanding of nature. It literally describes the breakdown of order and the inquisitive transition to disorder, where the golden mean number is factually characterizing something like the 'last barrier' of order before chaos sets in. Moreover, the *Fibonacci* numbers occur in a most natural way in the

geometric patterns, which can occur along those routes [18].

Instructive case is the geometry of spirals, which is often met and admired in nature as a result of self-organizing processes to take place in the distinctly reiterating steps. One of them allow us to construct \sqrt{n} for integer n , which can be called the *square root spiral*, best exhibiting the so-called *geometric feedback loop*, see Fig. 4. Another, but yet traditional *Archimedes* spiral is related to the arithmetical sequences when for an arbitrary but con-

stant angle, ϕ , and points on the spiral r_1, r_2, r_3, \dots each consequent number r_n is constituted by an arithmetic sequences, i.e., $r_3 - r_2 = r_2 - r_1$ or $r \equiv \phi$. Replacing the arithmetic mean, $(r_1 + r_3)/2$, by the geometric mean, $\sqrt{r_1 r_3}$, the other spiral is attained, which is known as famous *Bernoulli* logarithmic spiral, where $r_1/r_2 = r_2/r_3$ or $\ln r \equiv \phi$. Most amazing property is that a scaling of the spiral with respect to its center has the same effect as simply rotating the spiral by some angle, i.e., it shows a definite aspect of self-resemblance. Analogously we can generate an infinite polygon, which can easily be used to support any smooth spiral construction where the radii and length of the circle segments are a_k and $s_k = (\pi/2)a_k$ respectively. By adjusting a_k we can achieve the total length either finite ($a_k = 1/k$) or infinite ($a_k = q^{k-1}$ if q is a positive number smaller one). If for q we choose the golden mean we acquire a golden spiral which can also be obtained by a series of smaller and smaller reproducing rectangles (cf. Fig. 4).

We can see that any structure can become self-similar if it can be broken down into arbitrarily small pieces, each of which is a small replica of the entire structure. Here it is important that the small pieces can, in fact, be obtained from the entire structure by a *similarity transformation* (like photocopying with a reduction feature). Assuming a trivial cube, the self-similarity of involved line, square or cube is well expressed by the *power law*, i.e., by the relation between the number of pieces, a , and the reduction factor, s , i.e., $a = 1/s^D$, where D can set up integers one, two and three. In other words, the exponent agrees exactly with those numbers which we are familiar with as topological (Euclidean) dimensions. More universally, however, for a given self-similar structure there is a relation between the reduction factor, s , and the number of pieces, a , into which the structure can be divided, so that $d = \log(a)/\log(1/s)$, where d captures general meaning of the self-similarity dimension in a more general sense.

It has a widespread applicability ranging from solid-state chemistry (sintering) to physiology. Already *Galileo* noticed that a tree cannot grow to unlimited height as the weight of a tree is proportional to its volume. Scaling up a tree by a factor, s , means that its weight will level by s^3 but the cross-section of its stem, however, will only be scaled by s^2 . Thus the pressure inside the stem would scale by $s^3/s^2 = p$ not allowing, p , to grow beyond a certain limit given by the strength of wood, cf. previous Fig. 1. From the same reason we cannot

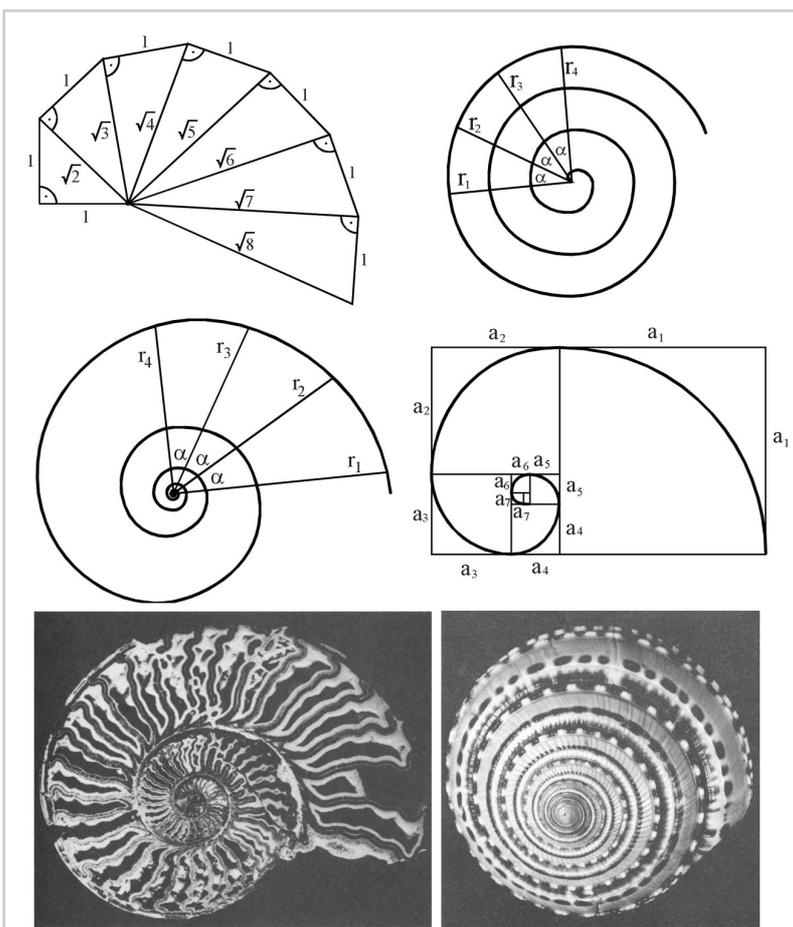


Fig. 13.4. The previously shown structures (Fig. 13.2.), responsible for yielding the family of Pythagorean trees, are very much related to the construction of the square root spiral depicted here. It is much related to the construction of square root, \sqrt{n} , for any integer, n , (maintaining the sides adjacent to the right angle to have the starting length 1 and $\sqrt{2}, \sqrt{3}, \sqrt{4}$ and so on, upper left). This construction belongs to the class of objects, which defies length measurements, the most famous model is the *Archimedes* spiral exhibiting the winding of a rolled carpet, which maintains the distance between its winding invariable (constant angle, α , arithmetic sequences of radii, $r_2 = (r_1+r_3)/2$, see upper right). Stepping along the logarithmic spiral in steps of a constant angle yields the geometric sequence of radii (often known as wonderful spiral holding $r_2 = \sqrt{r_1 r_3}$ where $r_i/r_{n+1} = a$). Yet another case is the golden spiral, which starts from the a rectangle with sides, a_1 and a_1+a_2 , where the ratio, a_2/a_3 , is proportional to the golden mean, $(1 + \sqrt{5})/2$. The rectangles break down into squares and even smaller rectangles and so on. In general, the spiral growing has, in general, a very important consequences in nature, such as life-grown structures of shells (bottom right) or even inorganic objects are attracted to exhibit logarithmic intensification akin to the crystal growth of ammonite (bottom left) safeguarding thus a law of similarity, as shown bottom row.

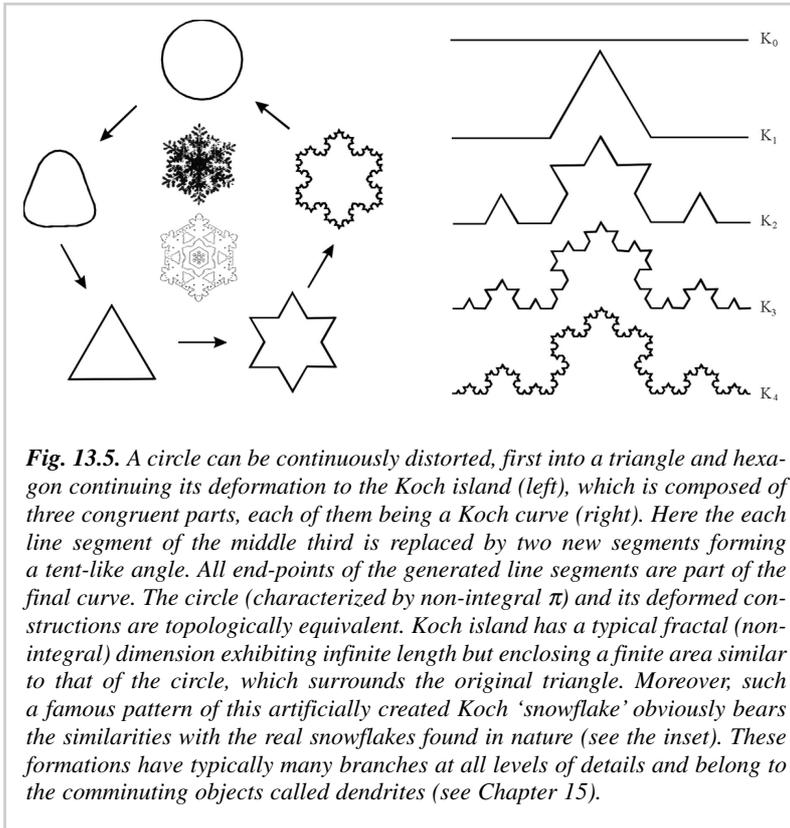


Fig. 13.5. A circle can be continuously distorted, first into a triangle and hexagon continuing its deformation to the Koch island (left), which is composed of three congruent parts, each of them being a Koch curve (right). Here the each line segment of the middle third is replaced by two new segments forming a tent-like angle. All end-points of the generated line segments are part of the final curve. The circle (characterized by non-integral π) and its deformed constructions are topologically equivalent. Koch island has a typical fractal (non-integral) dimension exhibiting infinite length but enclosing a finite area similar to that of the circle, which surrounds the original triangle. Moreover, such a famous pattern of this artificially created Koch 'snowflake' obviously bears the similarities with the real snowflakes found in nature (see the inset). These formations have typically many branches at all levels of details and belong to the comminuting objects called dendrites (see Chapter 15).

straightforwardly enlarge a match-to-sticks model to an authentic construction from real girders because each spill-kin must be allometrically full-grown to the actual building beam. Another case is the body height of beings, which is growing relatively faster than the head size. These features are quite common in nature and are called the *allometric growth*.

One of the most common examples of self-similarity are the space-filling curves, i.e., the derivation of a precise construction process, best known as the *Koch curve* [19], see Fig. 5, often serving to model the natural image of a snowflake upon a derived figure known as *Koch island*. The curves are seen as one-dimensional objects, because they are filling the plane, i.e., the object, which is intuitively perceived as two-dimensional. This view envelops the sphere of *topology*, which deals with the way shapes that can be pulled and distorted in a space that behaves like 'rubber'. Here we can imagine that a straight line can be bent into a curve, colligated to form circles, further pulled out to squares or pinched into triangles and further continuously deformed into sets, and finally crooked into a Koch island, see Fig. 5.

We define the primary object used for such a construction as *initiator*, in our case to be a straight line. We can partition it into three equal parts and replace the middle third by an equilateral triangle taking away its base. As a matter of fact it completes the basic construction step forming the initial figure which is called *generator*. By repeating and taking each of the resulting line segments, further partitioning and so on, calls for the Koch curve in the requested details. A different choice of the generator,

usually a polygonal line composed of a number of connected segments, produces another fractal with self-similarity, such as three equal lines symmetrically pointing toward the central point will provide continual assembly of joined hexagons, which is the routine honeycomb structure common in nature.

For a given patch of the plane, there is another case of the space-filling curve, which now meets every point in the patch and which provides the fundamental building blocks of most living beings⁴. It is called *Peano-Hilbert curve* and can be obtained by another version of the Koch-like construction⁵. In each step, one line segment (initiator) is replaced by nine line segments, which are scaled down by a factor of three. Apparently, the generator has two points of self-intersection, better saying the curve touches itself at two points, and the generator curve fits nicely into a square. Each subsquare can be tiled into nine sub-squares (reduced by 1/9 when compared to the whole one) and the space-filling curve traces out all tiles of a subsquare before it enters the next one. It is worth noting that any finite stage of such construction is rather awkward to draw by hand and is even difficult to manage by a plotter under computer control.

We should bear in mind that the coast of a Koch island has the same character as a circle (calculated circumference is as inaccurate as the implicated constant, π) but its length approaches infinity. In contrast, the area of the Koch island is a finite number. Alternatively, a typical coastline may curiously not exhibit the 'meaningful' length, as it is dependent to the adopted compasses set at a certain distance. By varying the size of our compass setting we can arrive to the above mentioned *log-vs.-log* diagram where horizontal axis comprises the logarithm of the inverse compass setting, t , interpreted as the precision of measurements. The vertical axis is reserved for the logarithm of measured length, h . The plot essentially falls onto a straight line exhibiting the power law again and enabling to read off the exponent, d . It regularly approaches the relation $t = 0.45 h^{0.5}$ which surprisingly is in agreement with the classical *Newtonian Law of motion*, which implies that the distance fallen, h , is proportional to the square of the drop time, t , i.e., $h = g t^2/2$. Inserting the gravitational acceleration of 9.81 m/s^2 it yields the similar power relation, $t = 0.452 h^{0.5}$.

Correspondingly, we can measure the length of the Koch curve with different compass settings to obtain $\log t = D \log (1/h)$ with d approximately equal to 0.2619 which is smaller than the value obtained for the real coast measurement $d \cong 0.36$. This approach becomes important even for some physical measurements such that of porosity, where we employ different scale setting by using different size of molecules, typically from mercury to

nitrogen. For a basal metabolic rate it ensues a power function of body mass with exponent $d = 0.5$. Therefore we may generalize the dimension found in the alternative also to shapes that are not strictly self-similar curves such as seashore, interfaces and the like. The *compass dimension* (sometimes called divider or ruler dimension) is thus defined as $D = 1 + d$, where d is the true slope in the *log-vs.-log* diagram of the measured length versus reciprocal precision. For the measured coast, for example, we can say that the coast has a fractal (compass) dimension of about 1.36. Of course, the fractal dimension of a straight line remains one because $1 = 1 + 0$.

In conclusion, the curves, surfaces and volumes are in nature often so complex that normally ordinary measurements may become meaningless. The way of measuring the degree of complexity by evaluating how fast length (surface or volume) increases, if we measure it with respect to smaller and smaller scales, is rewarding to provide new properties often called dimension in sense of fractal, self-similarity, capacity or information. All are special forms of well-known *Mandelbrot's* fractal dimension [20]⁶. Worth of extra noting is the *box-counting dimension* useful for structures that are not at all self-similar thus appearing wild and disorganized. For example a cloud (of lines, dots or shadows) can be put onto a regular mesh with the mesh size, s , and simply counted regarding the number of grid boxes which contain some trace of the structure involved. Certainly the accounted number, $N(s)$, is dependent on our choice of s , and would change with their progressively smaller sizes. $N(s)$ plotted against $1/s$ gives a line, which exhibits the slope close to 1.45 and which confirms no difference if the boxes are superimposed over a coastline to account the number of intersects. The historical roots of such fractals roots back to *Hausdorff's* work from 1918 [21] although his definition of what became later known as a *Hausdorff dimension* is not practical in the sense that it is difficult to compute even in elementary examples.

c) Sierpinski gaskets and fractal dimensions

One of the most instructive example and much-studied phenomenon is the case of *non-random (geometric) fractals* best represented by the so-called *Sierpinski gasket* [22], cf. Fig. 6. Such a gasket is assembled in the same growth rule as a child brings together the castle from building blocks and is also enlightening the network models convenient in structural chemistry. First, we join three tiles together to create a large triangle, with one

missing tile inside, which produces an object of the mass $M=3$ and the edge $L=2$. The effect of stage one is to produce a unit with the lower density, $\pi(L) = M(L)/L^2$. We can repeat this rule over, and over again, until we run out of tiles (physics) or until the structure is infinite (mathematics). There come two important consequences. Firstly, the density, $\pi(L)$, decreases monotonically with L , without boundaries, so that by iterating sufficiently we can achieve an object with as low density as we wish. Secondly, $\pi(L)$ decreases with L in a predictable fashion following a simple power law with fractal dimension of the inherent allometric plot, i.e., $\log 3 / \log 2 \cong 1.58$. Such a kind of 'multiple-reduction copy machine' is based on a collection of contractions, which uses the transformation providing the reduction by different factors and in different directions. We should note that such a similarity transformation maintains angles unchanged, while a more general transformations may not, which give basis for defining so-called *admissible transformations*, which

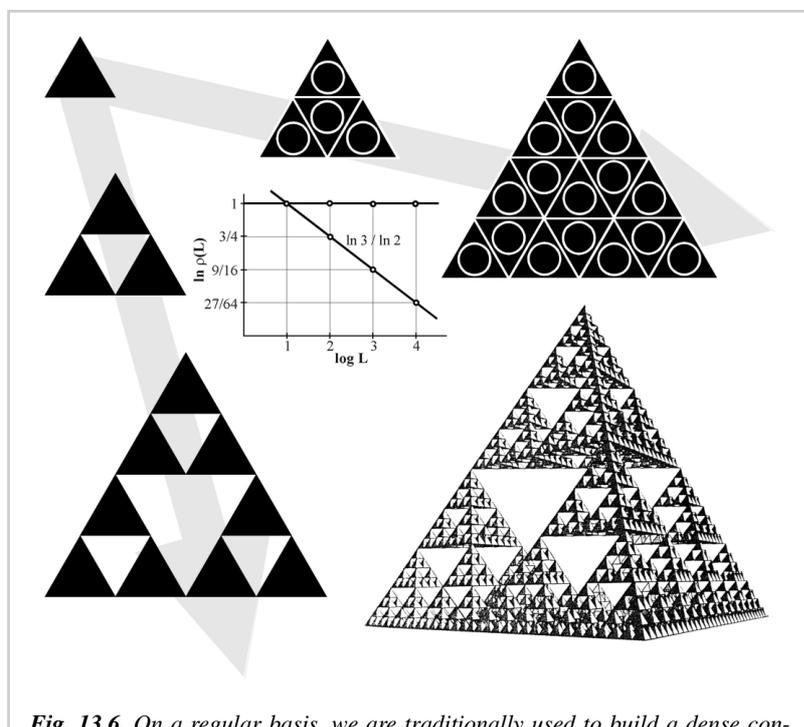


Fig. 13.6. On a regular basis, we are traditionally used to build a dense construction of periodical (isogonal) sequences, of, e.g., triangles with the side, L , and the mass (area), M , which is known to provide, for example, the traditional hexagonal crystal structure with the strict 3-dimensional periodicity (upper). On the other hand, we can build another triangle's aggregation in a different periodic sequence when we purposefully and repeatedly remove the middle part of the remaining triangle creating thus a porous composition. The final set of such a construction is a subset of all preceding stages and can be even assembled in three dimension aggregates (bottom). Though the structure would appear somehow bizarre, its porosity, $\pi(L)$, would monotonically decrease in a predictable fashion such as the following series given for the length, L , and the mass, M :
 $L = 1 (2^0) 2 (2^1) 4 (2^2) 8 (2^3) \dots$
 $M = 1 (3^0) 3 (3^1) 9 (3^2) 27 (3^3) \dots$
 $\pi(L) = M/L^2 = (3/4)^0 (3/4)^1 (3/4)^2 (3/4)^3 \dots$ (see the inset plot).
 It continues without reaching any limits and is obeying the simple power law $y = a x^d$, where a is the slope of plot $\ln \pi(L)$ against L . In particular, it demonstrates the relation, $\pi(L) = a L^{d-2}$, giving in our case the fractal dimension equal to $\log 3 / \log 2$, which is about 1.58 (see the inset plot).

permits scaling, shearing, rotation and translation, as well as reflection (mirroring), all well known in chemical crystallography (*Bravais*).

Configurations illustrated in Fig. 6 can be of help in the elucidation of structures of percolation clusters. We can see that an infinite cluster contains holes of all sizes, similar to the *Sierpinski* chain of gasket island. The fractal dimension, d , describes again how the average mass, M , of the cluster (within a sphere of radii, r) scales, i.e., following the simple power law, $M(r) \sim r^d$. The correlation length gives the mean size of the finite cluster, ξ , existing below the percolation transition, p_c , at which a new phase is to occur exhibiting an infinite cluster (typical, e.g., for a magnetic phase transition). We can interpret $\xi(p)$ as a typical length up to which the cluster is self-similar and can be regarded as a fractal. For the length scales larger than ξ , the structure is not self-similar and can be considered as homogeneous. The crossover from the fractal behavior at small length scales to homogenous behavior at larger scales can again be portrayed on the basis of Fig. 6 again. The fractal dimension of the infinite cluster (at p_c) is not independent, but relies on the critical exponents (such as the order parameter in transformation and the correlation length in magnetism and superconductivity).

On the other hand, our nature exhibits numerous examples of the so-called *natural fractals*, i.e., objects that themselves are not true fractals but that have the remarkable feature, in the statistical average of some of their property, to obey the rules given by the standard allometric plots.

The customary case of a random walker (often treated in terms of the self-styled ritual of a “drunken ant”) is worth noting as a useful illustration [16]. With the advancement of time, t , we may see that the walker progresses its wandering in such a way that the average of the square of his displacement increases monotonically. The explicit form of this increase is contained in the law, which concerns the mean square of displacement, i.e., $\{x^2\}_t = t$, or better, $\{x^2\}_{t+1} = t + 1$. Additional information can be found in the expectation values of higher powers of x and we can assume that $\{x^k\}_t$ equals zero for all odd integers, k , while $\{x^k\}_t$ is nonzero for the other even integers. The displacement can be identified either with certain length, say L_2 , which is given by $\sqrt{\{x^2\}} = \sqrt{t}$ or with another length, $L_4 \equiv \sqrt[4]{\{x^4\}} = \sqrt[4]{3} \sqrt{t} [1 - 2/3t]^{1/4}$. The both distances display the same asymptotic dependence on time regardless of the definition of L 's. We usually call the leading exponents as the scaling exponents, while the non-leading exponents associate with a correction-to-scaling, which is easy to generalize for $k\sqrt{\{x^k\}}$ as $A_k \sqrt{t} [1 + B_k t^{-1} + \dots]^{1/k}$.

We can see that several different definitions of a certain, universally characterisable length, ξ , scale correspondingly to the value of \sqrt{t} , which naturally involves the above-mentioned interrelation between the general behavior of power laws and a symmetry operation. The scaling symmetry [23] is thus a natural root of the wide applicability range of fractal concepts in physics. The

relation, $t \sim \xi^d$, gives the scaling exponent, d , which explicitly reflects the asymptotic dependence of a characteristic mass on a characteristic length. The most important consequence is related to diffusion limited aggregations, which are in the centre of interest of many physical systems such as electrochemical deposition, dendritic solidification and growth (cf. following Chapter 14), viscous fingering, chemical dissolution, rapid crystallization or dielectric and other kinds of electric breakdowns. It covers as many as thousands of recognized fractal systems known today in nature, which even includes diffusion-limited aggregations of aficionados (neuronal outgrowth, augmentation of bacterial colonies, etc.).

We can presuppose that transport properties due to fractal nature of percolation changes physical laws of dynamics. For an enough randomly diluted system, we can even admit that the localized modes occur for larger frequencies, which can be introduced on basis of bizarrely called ‘*fractons*’ [24]. Their density of states then shows an anomalous frequency behavior and, again, the power laws can characterize the dynamic properties. On fractal conductors, the density is proportional to L^d and approaches zero for $L \rightarrow \infty$. If we increase L , we increase the size of the non-conducting holes, at the same time decreasing the conductivity, σ , which, due to self-similarity, decreases on all length scales, leading to the power law dependence, thus defining the critical exponent, μ , as $\sigma \sim L^{-\mu}$. Due to the presence of holes, bottlenecks and dandling end, the diffusion is also slowed down on all length scales. Classical *Fick's Law*, assuming that the ‘random walker’ has also a probability to stay in place (using the standard relation, $x^2(t) = 2dDt$, where D is the diffusion constant and d is the dimension of lattice) loses here its validity. Instead, the mean square displacement is described by a more general power law, $x^2(t) \cong t^{2/d_w}$, where the new exponent, d_w , is always greater than two. Both exponents can be related through the *Einstein* relation, $\sigma = e n D / (k_B T)$, where e and n denote respectively the charge and density of mobile particles. Simple scaling arguments can be used to interrelate, d_w and μ , since n is proportional to the density of the substrate and thus the whole right-hand side can be taken proportional to the term, $L^{d-d} t^{2/d_w-1}$. As a result, $d_w = d' - d + 2 + \mu$, where d' can be substituted by the ratio relation, $\log 3$ -vs- $\log 2$, so that d_w becomes proportional to $\log 5 / \log 2$, which, however, is not so easy to ascertain in general cases.

For auxiliary modeling, we can start with a model of walker again. Let us assume that the walker has four perimeter sites to enter with an equal probability, followed by two walkers with six growth sites and their corresponding (but non-identical) probabilities, and so on. The most that we can say about the walker's forming cluster is to specify the probability distribution of growth sites. If the growth rule of diffusion limited aggregation is simply iterated we obtain a larger cluster characterized by a range of growth probabilities that span several orders of magnitude, possibly stretching out literally from tips to fjords. Aggregation phenomena based on random walkers correspond to the *Laplace* equation, $\nabla^2 \Pi(r, t)$, which stands

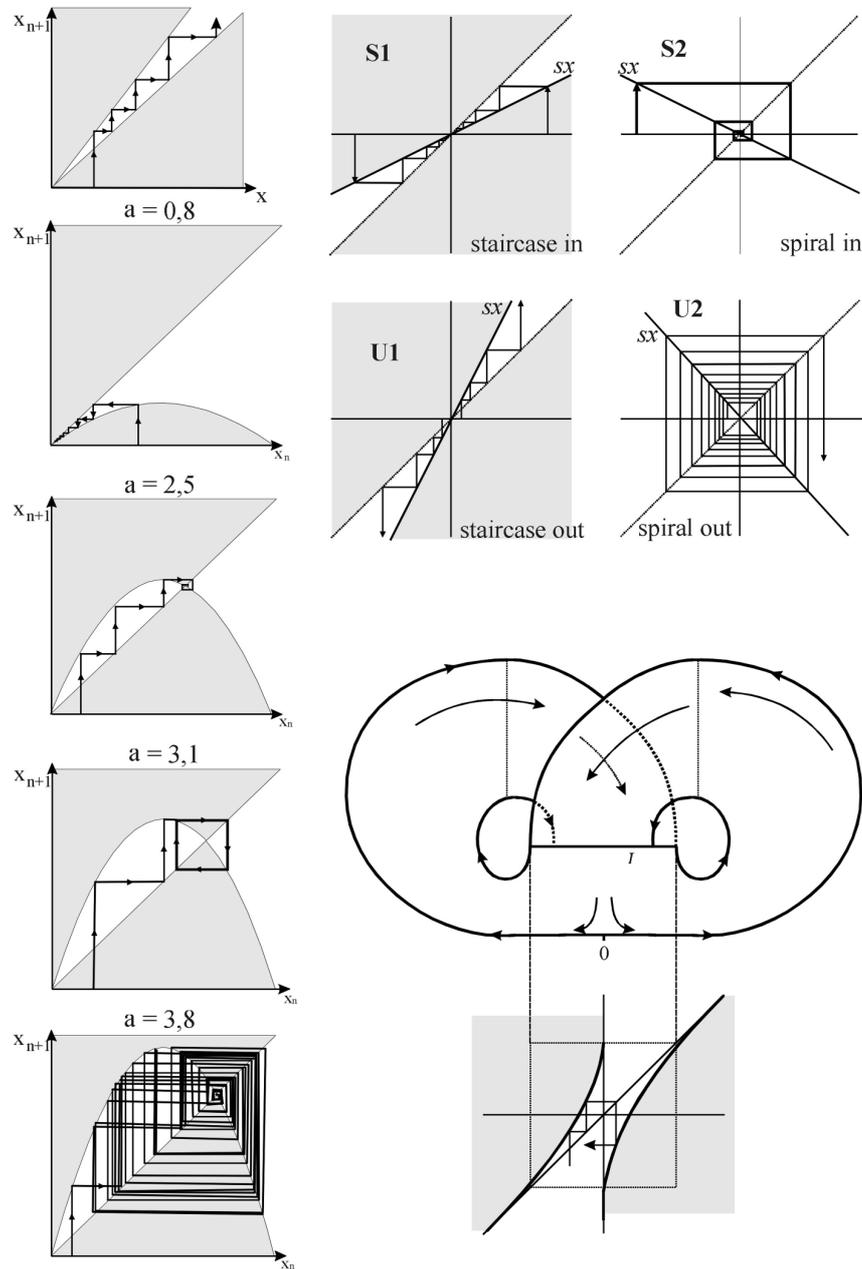


Fig. 13.7. Illustration of a simple feedback process through the quadratic iterator, $ax(1-x)$ (left column), where the number of iterations ('time-like') is on the horizontal axis while the vertical axis displays amplitudes. Sequences of diagrams show the trajectory of repeated iterations of a quadratic equation for different values of the multiplying constant, a , which is called 'logistic map'. The revealed behavior (representing factually the degree of prosperity, x , and crises, $1-x$) is sensitive to the steepness and the degree of applied function non-linearity (upper two). Too shallow profile yields extinctions ($a = 0.8$), growing slope assure certain stability (attraction to a point, $a = 2.5$) while too steep profile falls to the period-doubling regime ($a = 3.1$), which ends by chaotic oscillations called 'ergodic' orbits at the shown instant for $a = 3.8$ (see also Fig. 15.2 in the next Chapter 15). Upper, two figures right, show the four basic types of the local dynamics, i.e., the style of iterations behavior near at a fixed point, which is possible when considering a linear feedback process ($x_{n+1} = s x_n$). Iteration (S1) staircase inwards to the stable fixed zero point ($0 < s < 1$). On contrary the case (U1) spirals inwards the stable fixed zero point ($-1 < s < 0$), (3) staircase outwards from the unstable fixed zero point ($s > 1$) and spiral outwards (U2) from the unstable fixed zero point ($s < -1$). Bottom, right figure exhibits the most complex diagram of the stretch-split-and-merge process in the dynamic (Lorenz) system related to the cylindrical roll-type of fluid motion (in which one of the dimensions can be disregarded pretending that these rolls extend to infinity (cf. also Fig. 16.8). Trajectories around such a 'chaotic attractor' diverge even more, remaining within a bounded area by stretching and folding of the phase space, which thus includes the 'chaos-generating mechanism'. There remains a component of the so-called Bénard-Rayleigh convention theory, which happens in rectangular region whose bottom is heated in such a way that the temperature difference between the bottom and top remains constant (cf. Fig. 16.9 and weather related phenomena discussed in Chapter 16).

for the probability, Π , with which a walker is at the position r and at time t . However, a range of circumstances can turn up that have nothing to do with random walkers, but have a crucial effect, such as that experienced in viscous fingering phenomena.

We can also consider a random walker on the infinite cluster under the influence of a bias field. This can be modeled by giving the random walker a higher probability of moving along the unrestrained direction. In a *Euclidean* bias field, the walker gets a velocity along the direction of the field. In a topological bias field, the walker can get stuck in loops and kept in dangling ends so that both act as random delays on the motion of the walker. The length distribution of the loops and dangling ends in the fractal structure determines the biased diffusion. At the critical concentration, due to self-similarity on all length scales, the length, L , of the teeth is expected to follow a power distribution and the time, τ , spent in a tooth increases exponentially with its length. A random walker has to wait on the average time steps, τ_i , before he can jump from a site i to one of the neighboring site, $(i + 1)$. The singular waiting time changes the asymptotic law of such diffusion drastically, from the power law to the logarithmic form. We often meet a paradoxical situation that on the fractal structure of the percolation cluster the motion of a random walker is slowed down by a bias field.

In general, the experience with a simple random walk provides one familiarity, whenever entropy literally prevails over energy, the resulting structure will be dominated by randomness with disorder rather than by a strict Euclidean order. Therefore, we may well expect to find fractal structures with a scaling geometry analogous to that of the simplest unbiased random walk discussed above. Of course, the real structures such as dendritic growth patterns, which are most familiar in the case of snowflakes, see Fig. 5 again, do not often occur in the acquiescent environment of periodic fluctuations. Rather, their curious shape arises from the local asymmetry of the constituent water molecules and their capability to bias random walk by mutual limiting the inward and outward transport from the growing crystals (latent heat released away and vapor or liquid water moved inside). Such fractal models achieve practical use for the description of roughness of materials' surfaces (even the texture of fabric [25]) as well as in the portrayal of thermal waves (hyperbolic heat conduction) under the application of global space-time modeling [26].

d) Deterministic chaos, periodic points and logistic functions

Mathematical research in the field of *chaos*⁷ can be traced back at least to 1890 when *Poincaré* became curious if planets would continue on indefinitely in roughly their present orbits or might wander off into eternal darkness or crush into the sun. He thus discovered chaotic behavior in the orbital motion of three bodies, which mutually exert gravitational forces on each other. Extended by *Kolmogorov's* view to irregular features of dynamics and within *Smale's* classification of disordered

phenomena, chaos found its place as a natural feature taking shape completely on a par with regular behavior of periodic cycles. While a truly general definition for chaos to most spheres of interest is still lacking, mathematicians agree that for the special case of iteration there are four common characteristics of chaos: sensitive dependence on initial conditions, mixing behavior, dense periodic points and period-doubling (bifurcations). Let us briefly remind some of their bases [9–11,16,17].

It can be shown that many dynamical systems can regularly produce a chaotic behavior. We, however, would like to concentrate to the most obvious case, the quadratic transformation, which comes in different forms, such as $x \rightarrow a x(1 - x)$, the relation that has a wide applicability from the *logistic function*⁸ to self-catalytic models in chemical kinetics (cf. Chapter 12). By defining the iteration as $x_{n+1} = a x_n(1 - x_n)$, we can illustrate the process graphically upon the superimposed parabola (x^2) and straight line (x) in the interval $0 \leq x \leq 1$, see Fig. 7. We can arrive to the two types of iterations by adjusting both the initial point, x_0 , and the multiplying coefficient, a . It can either exhibit a sensitive-irregular pattern or non-sensitively stable behavior. Very important phenomenon is thus sensitivity, which either can magnify even the smallest error or dump the larger errors, if the system is finally localized in the stable state. This behavior is called *sensitive dependence on initial conditions* and is central to the problematic of chaos, though it does not automatically lead to chaos.

Let us remind that the error, E , propagating in the simple linear system as $x \rightarrow a x$, increases by the factor a , i.e., through the power law, $(E_n/E_0) = a^n$. This, however, cannot be expected for the quadratic iterator, $x \rightarrow 4x(1 - x)$, which is often called as a generic parabola (a graph, which precisely fits into a square and which has one of its diagonals on the coordinates bisector). We, nevertheless, can pretend that it is possible so that we can proceed by taking the logarithm to derive that small errors will roughly double in each iteration because k is approximately $e^{0.7} = 2$. This is true when the parabola is rather flat and errors are compressed but, on the contrary, it is enlarged near the end points. Such reasoning leads to the important concept of *Ljapunov exponents*, λ , which well quantifies the average growth of errors within the amplification ($\lambda = 0.42$ and $e^\lambda = 1.52$) or the contraction ($\lambda = -1.62$ and $e^\lambda = 0.197$). This behavior becomes very important for the limited extent of decimal places often ministered by small pocket calculators, but falls beyond our too short and thus somehow effortless explanation.

Another phenomenon, worth mentioning, is the *mixing behavior*, the intuitive interpretation of which lies in the subdivision of the unit interval into subintervals and requires, at the same time, that by iteration we can get away from any starting interval and are capable to reach any other target interval. If such a requirement is fulfilled for all finite subdivisions, then the iteration of an initial value from any launch interval is spread all over the unit interval. Such orbits are often called *ergodic* and their more detailed analysis become significant in the process of

satisfactory smooth command of controlled parameters. Thus, it is of further interest for all those regarding the theory of temperature regulation (cf. Chapter 10).

Yet another appreciable occurrence is the *kneading of dough*, which provides an intuitive access to many mathematical properties of chaos. Curiously, there is almost nothing random about such a *kneading process* itself: just stretch, fold, stretch, fold, and so on, up to the idealized situation when the dough is homogeneously stretched to twice the length. Folding the layers does not change the thickness and we can represent the dough by a line segment of layers while neighborhood relations are destroyed. This process becomes imperative in description of all physical processes of homogenization. Such a stretch-and-fold process is closely related to the discussed quadratic iterator because one application of the transformation, $4x(1-x)$, to the interval $[0,1]$ can be interpreted as a combination of a stretching and folding operation. The joint representation of this quadratic parabola with the *saw-tooth transformation* (cf. also Chapter 11) is also important to mention as it can establish a nonlinear change of coordinates through the function of $h(x) = \sin^2(\pi x/2)$, where, h , transforms the unit interval to itself

called *periodic* with two trajectory states (period of two). The length of branches, l_k , relative to each other decreases according to some law, conceivably following a sequence, which is asymptotically geometric, leads to several consequences. It would constitute a ceiling parameter of a, beyond which the branches of the tree could never occur marking the end of the period-doubling regime. It is a very important threshold called the *Feigenbaum point*, equal to $3.5699\dots$, at which the final-state diagram splits into two very distinct parts of order and disorder, the latter being not simply a region of utter chaos as it hides a variety of beautiful structures. When it attains the value of $(1 + \sqrt{8}) \cong 3.8284\dots$, called the tangent of bifurcation, the stable (laminar) phases alternate with erratic and chaotic behavior showing the interlay between the burst of chaos and order. The more important *universality* threshold, however, is the sequence of magnification called the *Feigenbaum constant*, δ , equal to $4.6692\dots$ [27], which obviously arises from the associated iterations, i.e., from the ratio of measures of two succeeding branches, l_k and l_{k+1} , i.e., $\delta = \lim_{k \rightarrow \infty} (l_k/l_{k+1})$. Its universality is known for a whole class of iterations generated by functions similar to a quadratic function, such as $\sin(\pi x)$, and thus is com-

prehended as a general constant of chaos comparable to the fundamental importance of numbers like π and $\sqrt{2}$. The *Feigenbaum* constant was found verifiable through the real physical experiments, such as sophisticated measurements in electronics (where $\delta = 4.7$) hydrodynamics (4.4), laser feedback (4.3), acoustics (4.8), etc.

Further instructive geometric construction of chaos in continuous system was introduced by *Roessler* in 1976 by solving the system of three differential equations $x' = -(y + z)$, $y' = x + ay$

and $z' = b + xz - cz$, with three adjustable parameters, a , b and c , which was factually hiding the non-linear stretch-and-fold operation. This simple autonomous system has a single non-linear term, the product of x and z in the third equation. Each term in these equations serves its purposes in generating the desired global structure of trajectories. Assuming z to be negligible the two remaining equations can be transformed to the second-order linear oscillator, $x'' - ax' + x = 0$, and with positive parameter a , it exhibits negative damping. It follows that the trajectories of the full system of three first-order equations spiral outwards from the origin. When the orbit has attained some critical distance from the origin, it is first lifted away from the x - y plane and later reinserted into the twisting mode through the feedback of z to x equation and trajectories' fold-back. This procedure of spreading adjacent trajectories is the first sign in the mixing action of chaos

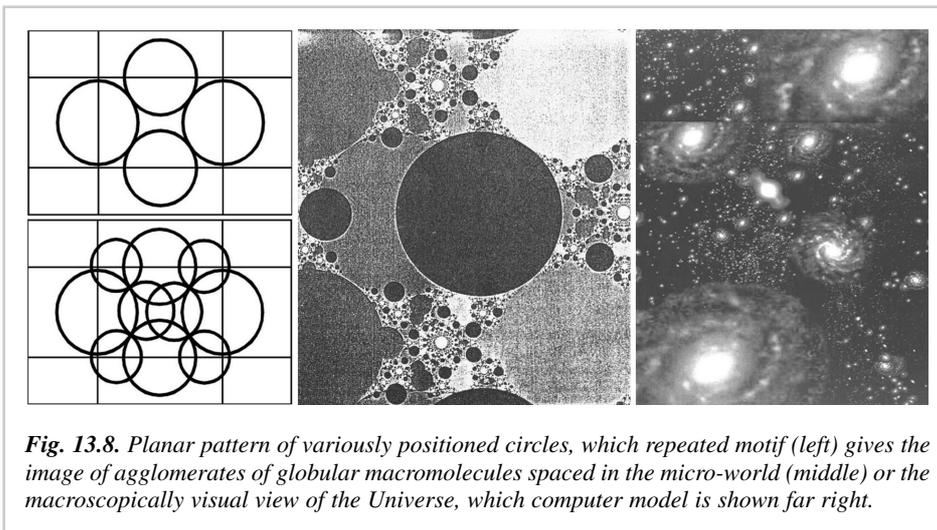


Fig. 13.8. Planar pattern of variously positioned circles, which repeated motif (left) gives the image of agglomerates of globular macromolecules spaced in the micro-world (middle) or the macroscopically visual view of the Universe, which computer model is shown far right.

in a one-to-one fashion. This again is of significance in analysis of various profiles of noise or in mathematical treating the different modes of oscillatory heating.

Let us see the famous *Feigenbaum* diagram that has become the most important icon of chaos theory (illustrated in the following Chapter 15). We start from investigating the behavior of the quadratic iterator again looking for all values of the parameter, a , between 1 and 4, cf. Fig. 7. After a transient phase of a few iterations the orbits settle down to a fixed point for all low values of $a < 3$. For the value of $a > 3$, the final state is not a mere point but a collection of 2, 4, 8 or more points. The resulting fork-tree portrays the qualitative changes in the dynamical behavior of the iterator $x \rightarrow a x(1-x)$ witnessing two branches bifurcating, and out of these branches we see two branches bifurcating again, and so on. This is the so-called *period-doubling regime* and the behavior is

as well as the self-regulation of the system as whole, which is typical for modeling the weather, see Fig. 7. (bottom right).

The differential equations have become the language in which the modern science encodes the laws of nature. Although the topic of differential equations is, at least, three centuries old and the results have filled libraries, nobody would have thought that it is possible that they could behave chaotically, as found by *Lorenz* in his 1963 experiments [28]. So that we cannot avoid a glimpse trace on the previous logistic equation assuming the population change per unit time, i.e., $\{x(t + \Delta t) - x(t)\}/\Delta t$, which can help to compute the population size as $x(t + \Delta t) = x(t) + \Delta t a x(t) \{1 - x(t)\}$. As $\Delta t \rightarrow 0$, the iteration makes a transition into the world of differential equations (famous *Euler's* method) so that $x'(t) = a x(t) \{1 - x(t)\}$, where the right-hand side is non-linear. We can linearize it by substituting $p(t) = 1/x(t)$, which makes possible to obtain solution in the form $x_0 e^{at} / \{x_0 e^{at} - p_0 + 1\}$ showing that the population will eventually go into saturation. On the other hand, if $\Delta t \rightarrow 1$, it coincides with the original logistic formula, or, interpreted differently, the growth law for arbitrary time step Δt reduces to the discrete logistic model replacing the expression $(\Delta t a)$ by mere a . In other words, if we have $a > 3$, then chaotic orbits for $\Delta t = 1$, while we orbit converging to 1 for $0 < \Delta t < 2/3$, see Fig. 7. (bottom left), which provides the so-called stability condition for any numerical approximation, i.e., $(\Delta t a) < 2$. The crucial difference between the discrete logistic system and its continuous derivative-like counterpart is the fact that it is plainly impossible for the dynamics of the differential equation to be chaotic. The reason is that in the one-dimensional system no two trajectories, for the limit $\Delta t \rightarrow 0$, can cross each other, thus typically converging to a point or escaping to infinity, which however is not a general consensus in three dimensional system often displaying chaos.

These types of differential equations are the most important tools for modeling straightforward (vector) processes in physics and chemistry, though, often no analytical solution is known, which could be written in terms of a common formula, cf. Chapter 15, related to some aspects of advanced chemical kinetics. Life in the real science is not simple and almost in any physical system the state cannot be described by a single variable. For example, with a pendulum, which is allowed to swing in a plane, we need, at least, to know the angle and the angular momentum in order to be able to forecast the motion (cf. next Chapter).

e) Order, entropy and information

Along with the preceding Chapter 6, related to the classically seen thermodynamics, we can behold here that any better organization of a system drives it into a less disordered state, less chaos, which does require some definite effort (structured *input*), such as some kind of work. Let us remind that '*work*' is a transient phenomenon, factually it is a process, which cannot be put in storage as such, only its product may be stored as a change

of energy content of the system acted upon (and we can literally define heat on a similar basis as work). Therefore, the application of energy to a system may result in four possible changes: It is

- (i) energy merely absorbed as non-specific heat, thereby increasing the entropy,
- (ii) input of energy causes the system itself to become more highly organized (causing, e.g., the atom to achieve a richer 'more improbable' thermodynamic state),
- (j) system performs a physical (mechanical, electrical) work (mostly on bases of human innovative ideas – transducers) or
- (jj) information work is implemented, creating thus a more organized organism (such as an organic living cell). Accordingly, we need to analyze more closely the meaning of the term 'entropy', which is the earlier accepted measure of an infinitely small increase of heat related to given temperature.

The randomness, probability, organization and/or information, which have been later attributed to greater or lesser entropy of substances [29-33], are somehow a perceptual manifestation of the same basic phenomenon, which is the absorption of thermal energy. Entropy is a mathematical function not having a direct 'physical reality' characteristic of material bodies, but when multiplied by the temperature, for which the entropy has been calculated, the product becomes the quantity of thermal energy that must be absorbed for a substance to exist at the temperature above absolute zero.

Entropy has been related to information following the well-known paper by *Shannon* on a mathematical theory of information [34] without a detailed definition *what really information is*. Consequently, the change in entropy may be brought about not only macroscopically by changing the heat content of the system, but also by altering the micro-organization of system's structure, which, in other words, is actually adding order or information. We may disorganize a system by directly applying heat or alternatively by otherwise disordering its structure upon hypothetical 'withdrawing' information of its ordering.

By identifying entropy with 'missing information' we can even get a deeper way of approaching the central question "why does the second law hold" in the sense "why does missing information increase with time"? Rather than puzzling over why heat flows as it does we are now curious how nature defines questions that can be asked, the number of answers that can be given to those questions, the extent to which the answers are known in some way, and how these things change with time. So, analyzing the situation that may challenge the second law of thermodynamics, we have a new way to look at them, in terms of whether there is some aspect of the system that becomes better defined without a compensating loss of information somewhere else. This opens up new avenues for understanding these systems and for seeing the fundamental restrictions expressed through the second law.

In 1929, *Szilard* presented several ‘gedanken’ experiments from which one can conclude that additional information about a system can lead to decrease its entropy, even for a single molecule imprisoned by a piston-and-cylinder boundary⁹. It may well provide the conclusion that there is a thermodynamic cost for *any* measurement. Eventually, it can be enumerated and seen to be regularly paid when a measuring instrument is reset, turning thus off its standard interaction [35]. In the above-mentioned micro-scale, however, the crucial step is to realize that fluctuations of miniature instrument (e.g., piston) are as important as those of the molecule filler.

Let us take example from the daily physics: on heating the solid structure of ice it first melts, then boils and on further heating (above, e.g., melting point of platinum at 1700 C) it continues to transform to a plasma of ions and electrons. At even higher energy level, the integrity of the atoms themselves becomes compromised and with sufficiently high temperature, matter can be observed to ‘boil’ again to yield plasma of quarks and gluons (so-called ‘quagma’). Entropy is eventually coming to tie in the extreme state of complete randomization. On the other

hand, if we cool ice down to the temperature of absolute zero, where entropy is supposed to eventually become zero, we reach an ideally ordered state of perfect crystal with supposedly no thermal vibrations (which would be factually inaccessible due to inevitable scrunch of charged particles so that any collapse can be avoided only by some residual motion – athermal orbiting innate to vacuum, see Chapter 20). The thermal energy, however, cannot be apparently decreased by merely further withdrawing heat. However, it was experimentally shown that for certain inorganic molecules or states (glasses) there may exist exemptions for a particular crystalline modification, such as N_2O , which can have either $S = 0$ or $S = 5.76$ J/K, both at $T = 0$. It is comprehensible that there remains information about its ultimately perfect structure and its definite occupation of space, so that there is no theoretical reason why one may not additionally cause a further ‘decrease’ of entropy by certain hypothetical ‘incorporation of spatial information’ [33,38].

It seems to be impossible, but we can equally suppose to have a force field which could ‘freeze’ the constituents to total immobility at higher temperatures, as well. In

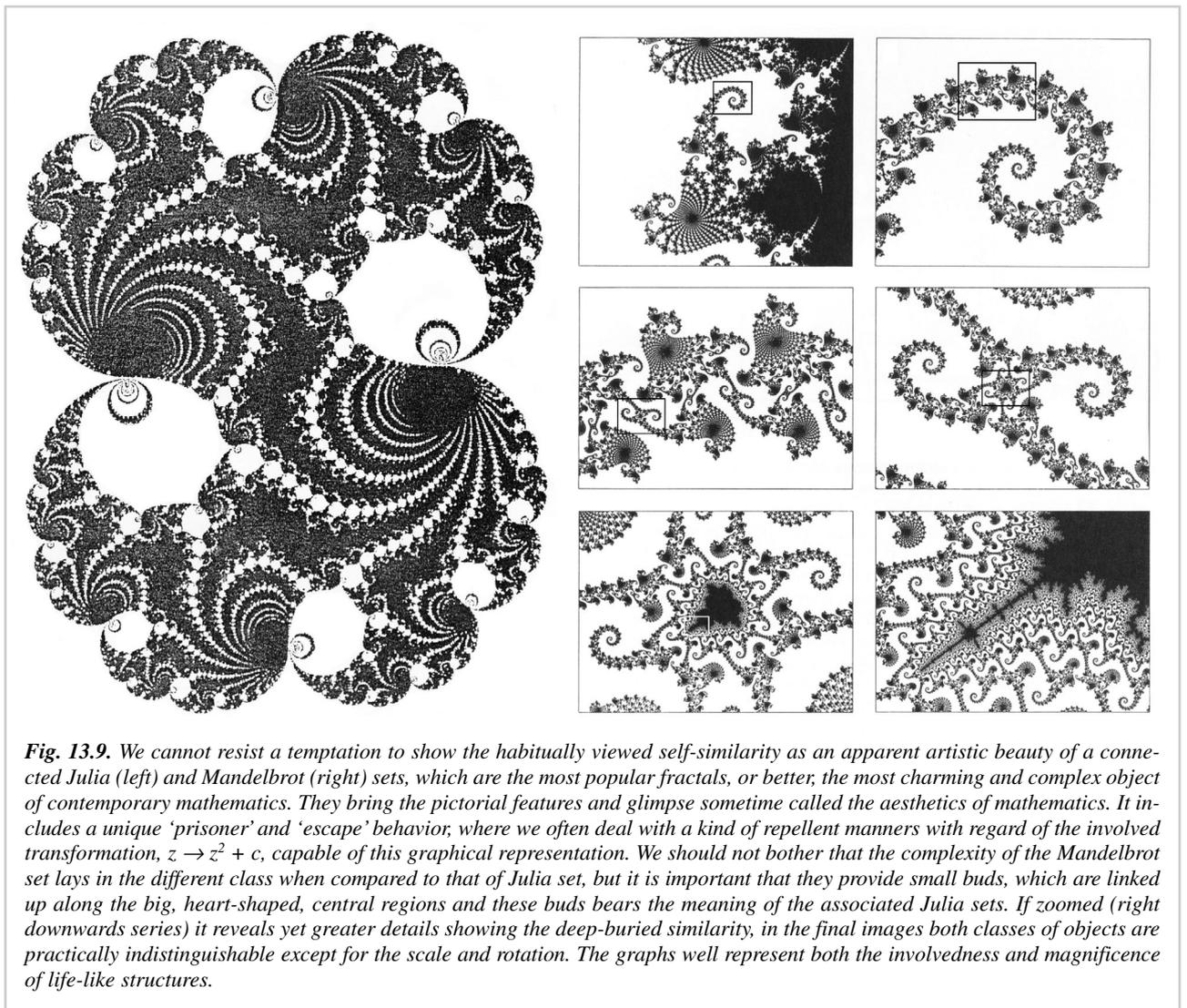


Fig. 13.9. We cannot resist a temptation to show the habitually viewed self-similarity as an apparent artistic beauty of a connected Julia (left) and Mandelbrot (right) sets, which are the most popular fractals, or better, the most charming and complex object of contemporary mathematics. They bring the pictorial features and glimpse sometime called the aesthetics of mathematics. It includes a unique ‘prisoner’ and ‘escape’ behavior; where we often deal with a kind of repellent manners with regard of the involved transformation, $z \rightarrow z^2 + c$, capable of this graphical representation. We should not bother that the complexity of the Mandelbrot set lays in the different class when compared to that of Julia set, but it is important that they provide small buds, which are linked up along the big, heart-shaped, central regions and these buds bears the meaning of the associated Julia sets. If zoomed (right downwards series) it reveals yet greater details showing the deep-buried similarity, in the final images both classes of objects are practically indistinguishable except for the scale and rotation. The graphs well represent both the involvedness and magnificence of life-like structures.

fact, we can actually identify such a phenomenon as we can approximate the supposed force field to hold atoms in a relatively immobile state at elevated temperatures recalling certain organic molecules in which the resonating π – (“pi”) clouds of electrons act as an inter-atomic force stabilizing the positions of atoms. The best example, however, are met in all biological systems that, for example, use the absorbed heat in order to maintain a stable temperature so as to minimize externally induced entropy changes. Whether looking at the DNA molecules and related genetic or metabolic systems, cellular organization, the evolution of organisms or other ecosystems, the process is always the same: there is an entropy limitation by inserting certain ‘information’ as the simple systems become more complex, more differentiated and integrated, both within the internal organization and with the environment outside the system, evolving itself to become *thermodynamically increasingly improbable*.

On the other hand, we have to realize that the absorption of thermal energy has a constant effect on entropy that is a function only of the temperature and therefore seemingly no influence on what we perceive as randomness or organization. We cannot regard qualities to be independent of heat particularly when considering, for example, the triple point of water where the same state functions equal for the three phases that can coexist at equilibrium temperature. The only way that ice can be converted into water is for the environment to have a temperature greater than that of melting point, whereupon heat will pass from the environment into the system. The question is whether the heat exchange can be considered active or passive. It is not entropy that is exchanged, as entropy is a quantity that is acquired or lost, which does not perform a function or does work.

Such an inquisitive concept of adding information into the zero temperature state of an ideal crystal would certainly violate a traditional understanding and would also appear intuitively false as there is no way how to achieve this feat anyhow. We, however, may admit that it would be somewhat possible to add more information to a system that is already perfectly ordered by making it *more complex*. Therefore we cannot fully refuse an idea of the existence of a kind of very hypothetical conversion-like process of energy to *structural information* and hence the possibility to accept the concept of negative entropy (so-called ‘*negentropy*’) [36].

Let us continue to analyze the statistical meaning of entropy, $S = k \log W$, starting with traditional *Boltzmann’s* investigations of W , assumed as ‘*complexion*’, i.e., the number of possible microstates of a system¹⁰. It was modified by *Schrödinger* who suggested in his book that a living organism is „fed upon a negative entropy“, arguing if W is a measure of the *system disorder*, its reciprocal, $1/W$, can be relatively considered as a *measure of order*, O_r . According to *Stonier* [38] organization or structure is factually a reflection of order. Organization and associated information, I , can thus be seen as naturally inter-linked, though information is a more general and also more abstract quantity bearing an conceptual neces-

sity to be freely altered from one form to another (structure of a written text can be different due to various alphabets but the information contained is the same). In the first approximation, we can assume a linear, d , dependence so that $I = d O_r$ or $W = 1/O_r = d/I$. By rearrangement of traditional entropy $S = k \log (d/I)$ and $I = d \exp (-S/k)$ which can define somewhat a more fundamental relationship between information I and entropy S (Fig. 10). In consequence we can assume that the inherent parameter d represents certain information constant of the system at zero entropy. Recalling the ideal crystal of ice at 0 K, $d = I_0$, which is not so imaginary assuming that I_0 is a constant for all values of I and S within the system but may not be a constant *across* the systems. This becomes intuitively apparent when one compares such a single inorganic crystal with an organic crystal of DNA. Surely, at any comparable temperature below melting or dissociation, including 0 K, the molecule of DNA would unquestionably contain more information than that of ice. Returning to the fundamental equation rewritten as $S = k \log (I/I_0)$, we can assume it as another quantitative expression of the system disorder. The ratio between this so-called ‘*information content*’ of the system when its entropy is zero, and the actual information content of the system at any given entropic value, S may remain as a generalized probability function to correspond the *Boltzmann’s* original W , but now known from the information theory, as the *number of possible coding*. We, however, are familiar with the original derivation made for gases in which I would never exceed I_0 and therefore S would never become negative.

Let us turn again to the demonstration case of ice now calculating the change of entropy between a perfect crystal of ice at 0 K ($S=0$), and its vapor state (S_{vap}) at the boiling point (373 K). It yields a value of about 200 J/K per one mole of water. Now we can make use of two possible representations of the proportionality constant, k , in the relation of $S = k \log W$. In physics it has the meaning of

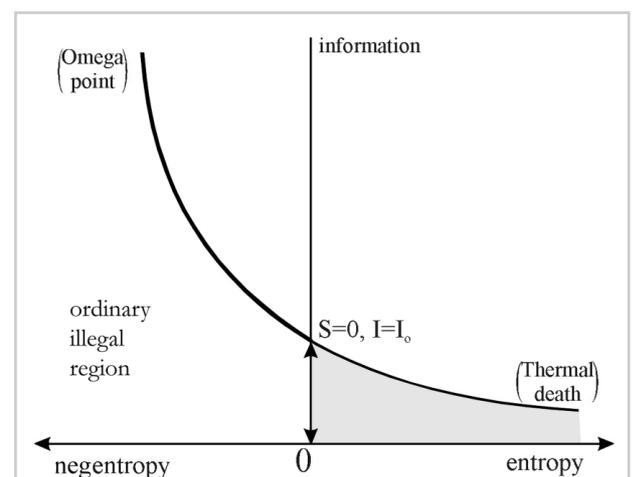


Fig. 13.10. Underlying relationship between the entropy, S , and information, I , related by the formal equation $S \cong \ln (d/I)$ where the constant, d , represents the apparent information content at the zero value of entropy.

the Boltzmann constant, $k_B = 1.38 \times 10^{-23}$ J/K, while in the informatics it can either retain unity (yet nonstandard unit called 'nats') or reach the value of $1/\ln 2$ known as 'bites'. It may provide a 'linkage' between information (coding) and entropy (complexion) so that and we can formally write $I = I_0 \exp(-1.45 \times 10^{25})$ or, on the binary base, $I = I_0 \cdot 2^{-(2.1 \times 10^{25})}$, where the exponent is to the base 2 so that it may be stated in bits. It is worth noting that the increase in information/entropy manifests itself as a negative sign in the exponent indicating a loss of information. Consequently, the information needed to organize a mole of water from the chaotic state of steam into a state of perfect crystal of well-structured ice, which would require an input of about 35 bits per a single molecule. One may even calculate that an entropy change of approximately 6 J/K is required to bring about the required loss, on average, of one bit per molecule, so that we can assume that

$$J/K = 10^{23} \text{ bits.}$$

Certainly, this covers a complicated process of trapping gaseous molecules existing in a cloud state by means of complex arrangement of electric and magnetic fields. The randomly moving molecules become fixed by the force fields into a regular array. This is a general characteristic for the formation of a crystalline state, in general, and there is a spectrum of crystalline states ranging from a powder up to a perfect crystal usually to be classified by customary X-ray diffractions patterns, or so. There are certainly greater angles of the spread of information content. What more, a gas consisting of molecules contains also information residue because the organization intrinsic to molecules affects their behavior as a gas, like ions in plasma. Similarly, we can consider the formation of a single crystal, letting, for example, silicon to grow from the appropriate solution remembering the quest of chip industry, which is based on the insight that it is possible to obtain silicon of define purity and structure. Such a crystal is acting as a template growing according to thermodynamic rules or may be hypothetically viewed in the role of a progression where the growth information is provided by its environment (temperature, solution, tension and inherent gradients).

The development of an organic nucleus is metabolic and interstitial and thus far more complex. For example, the DNA molecule produced as a string of simpler molecules of nucleotides, amino acids (whose sequences represent a series of messages), may be isolated in a test tube as a crystal to contain all the necessary information for reproducing virus or a baby. Here we can envisage that such a structure, thermodynamically as improbable as a perfect crystal at absolute zero, can be created to exist at room temperature in the form of a perfectly organized organic crystal. Restricting our protein to be composed of the 21 essential amino acids only, we arrive at 21^{200} possible primary structures in the binary terms being equivalent approximately to 878 bits per molecule. (In contrast, if language would consist of only ten-letter words, the total vocabulary available would amount to 26^{10} to require mere 47 bits per word). The entropy change can also be measured for denaturation of a molecule of

enzyme from biologically active to inactive states, which involves about 900 J/K. The exponent of the information ratio can be interpreted again to represent an information change of 155 bits per molecule. If these information assumptions prove to be correct, that the bits per molecule lost when a perfect ice crystal is vaporized (35) is much lower than that for the inactivation of an organic trypsin molecule (155) completed, however, within a much narrower temperature interval.

We, however, should be more realistic in our forethought [39]. For example one gram of dried *Saccharomyces cerevisiae* cells has entropy of about 1.3 J/K at room temperature while the same mass of crystalline a-d-glucose, which is a common organic substrate used to grow this yeast, has entropy of just 1.16 J/(K g) [40]. Does it mean that cellular fabric is more random, more probable, and less organized than the substrate from which it is formed? One should be very careful about mechanical comparisons based on mere entropic values, which do not seem to make sense, particularly dealing with variability in solids. The difference between biological purposeful and purposeless information is yet intriguing [41] and the idea whether we may relate biological order and complexity to thermodynamic entropy has not gone uncriticized [42]. Citing Battley: "it is hard to believe that the absorption or loss of entropic thermal energy is anything other than a purely passive phenomenon, and that the driving force behind a spontaneous reaction is not the entropy change, but the chemical and physical event that cause the change in free energy...it may not necessarily contribute to a greater randomness or a lesser organization, depending on how we as observers conceive these terms to mean" [39].

f) Information and organization

The information, which is processed by the solidifying silicon solution when growing a semiconductor single-crystal or by a human cell interacting with a strand of DNA, is the organizational pattern of the carrier of information independent of human minds. Information existed for billion years prior to advent of the human species and for billion years that information has been processed. DNA itself would be useless unless a living cell processes the information. If the information is an independent reality, which means that it exists regardless to the capability of decoding the inherent text. Information is considered to be distinct from the system which interprets (there is dichotomy between the information intrinsically contained by a system and the information which may be conveyed by the system to some acceptor). Information may even organize information, which is a process occurring in our brains or may take place in our computers in not too distant future. It, however, became next to impossible for a single mind to fully command more than a small, specialized portion of information.

In general, we can imagine that *information has similar behavior as energy*; both exist independently and do not need to be perceived to exist neither understood. Energy is defined as the capacity to perform work and it

is the *nature* of energy supplied or withdrawn, which determines the nature of the changes occurring in the system acted upon. Information is defined as the capacity to organize a system or maintain it in an organized state. Similarly to the existence of different forms of energy (mechanical, chemical, electrical, heat) so do there exist different forms of information. Energy is capable of being transferred from one system to another likewise information may be transformed from one form to another. The information contained by a system is a function of the linkage binding simpler units into more complex units. Thus, all organized structures contain information and, on the contrary, no organized structure can exist without containing some form of information. Information is an *implicit component* of virtually every single equation. Therefore, there must exist an information flux being proportional to the question and to the gradient between information fields. From the thermodynamic and causality considerations a general upper bond on the rate at which information can be transferred in terms of the message energy was theoretically inferred (i.e., $< 10^{15}$ operat/sec as to avoid thermal self-destruction) [35].

Information is governing the laws of physics, i.e., in order to measure distance and time properly, an organized frame of references must be available and thus the measurements of space and time establish information about the distribution and organization of matter and energy. An organized system occupies space and time, therefore, the information content of a system is proportional to the space it occupies. *The universe may be seen organized into a hierarchy of information levels* [38]. Energy and information may put on view certain signs of invented inter-convertibility. In contrast to heat, however, all other forms of energy involve organized patterns and may be said to contain information. The application of heat, by itself, constitutes no contribution in terms of information. Structure represents the product of information interacting with matter. All forms of energy other than heat exhibit, or are dependent on, some sort of organization or pattern with respect to space and time (e.g. an immature steam engine versus refined electric alternative motor).

We need a particular service of the so-called *energy transducers*, which define two necessary conditions for the production of useful work: they create a non-equilibrium situation and they provide a mechanism of countervailing forces necessary for the production of useful work. For a real physical system, such as a steam engine, the energy contained in heated gas is not converted into work until it is contained and modulated by an engine that has accumulated, within it a history of invention, certain information content in the form of know-how of produced machinery. A very advanced information system, such as living cells enables to transform an input energy into useful work under circumstances not possible in other physical system. For example, the cell can provide the dissociation of water and/or enables stripping electrons off hydrogen atoms at room temperature, which for another unorganized system would request heating

above 1000 C to destroy water molecules by the violent collisions.

The structural information content of any energy transducers is the same at the end of a process as it was at the beginning neglecting its wear out. The information kinetics created by the steam engine when it has produced an asymmetric distribution of high and low energy molecules of water in the two chambers separated by a piston is associated with potential energy. The apparent loss of 'kinetic' information that is the part of the information, which has been degraded to rest heat, can be associated with the dissipation of entropy. For energy science it is important to measure the process efficiency (η) given by the ratios of the work output to the heat input, $\eta = W/Q$. The maximum possible efficiency is limited by the temperatures of input (T_{in}) and output (surroundings T_{out}), so that $\eta_{max} = 1 - T_{out}/T_{in}$ and we may be interested to find the relation of the actual (η_{act}) and maximum efficiency to follow that $\eta_{act}/\eta_{max} = f(I_{in})$ or $I_{in} = -\log(1 - \eta_{act}/\eta_{max})$. Using the above conversion factor ($1 \text{ J/K} = 10^{23} \text{ bit}$) and by measuring the ratio of the differences it would become possible to ascribe a real value to the above introduced value of *information inputs* (I_{in}).

Accepting that heat is a certain 'antithesis of organization' and by implication certain duality behavior of energy and information we can venture to imagine a speculative possibility that energy and information may interact to provide an 'assortment', which may be viewed as 'energized information' or alternatively 'structured energy'. Consequently, information and energy may not be viewed as the opposites of a bipolar system, rather they can be hypothetically considered as the partners (like matter and energy) on two sides of a triangle, with matter comprising the third. Such a conceptual model could be conceivably used to define hypothetical 'boundaries' of our newly supposed physical but highly forethought universe¹¹ [38].

We can wind up the recent impact of computers, aware that it has changed our perception of information as something purely static because inside computers information may once appear to gradually achieve a dynamics of its own. Already now, we are not sure where and how we pay compensation for the information often lost accounting for waste heat when imprinting or erasing memory contents. Information written to some memory register by a computer program must be discarded to the environment in order to reset the register and complete the cyclic process. We can even suggest that each energy transfer between two separate physical objects is a measurement. We can thus believe that measurement is the transfer of information between the sample – an examined physical object and the apparatus, and that any energy transfer will carry information about the shift in energy state of the objects under observation.

It is almost sure that the domain of information will soon dramatically change similarly to the comprehension of traditional physics, which learned in the past century how to assimilate surprising ideas, such that energy may be converted into matter and *vice versa*. It brought an

important consequence into nuclear physics and possibility to gain new forms of energy. The field of relativistic theory left the problem how to explain motion solely in terms of matter. The *Dirac's* theory implied negative energy states and his mathematical equations anticipated the existence of anti-matter. *Feynman* mathematically demonstrated that a positron might be regarded as an electron moving backward in time. We should assume that even the empty space, when enclosed in any organized structure, may bear a significant piece of information (like a space

dividing words in most languages) so that the absence of structure within a structure may carry information as real as the structure itself. The *Barrow's* made-believe verdict [43] “*if life will engulf the entire universe the so-called Omega Point would be approached and the infinitive amount of information hitherto stored would logically reach its completion*”. Any fantasy was not the aim of this chapter although we cannot dodge completely out this type of query. Anyhow, we cannot pass over the everlasting question “Is there a purpose in the Nature“ [37,43–46].

¹ The development of what came to be called logarithms was in the air at the end of the sixteenth century, and the Scottish mathematician *Napier* was probably not the first to bring such a sophisticated scheme into practical use. Already *Archimedes* gave a recipe for reducing multiplication to addition by making use of a geometrical progression of numbers and relating them to an arithmetic progression. However, the mediaeval need for large numerical data was crucial for the progress of astronomy, trade, navigation, etc., so that the publication of *Napiers's* “*Logarithmorum Canonis Descriptio*” in 1614 [cf. Bruce I., *Am.J.Phys.* 68(2000)148] caused the sensation in Europe at that time. The word of logarithm was coined from the ancient Greek, meaning ratio numbers and the idea was based on a kinematical model used for a better visualization, i.e., the velocity function has the same form as the displacement function. An independent inventor of logarithms was *Burgi*, a Swiss clockmaker and mathematician, who assisted astronomer *Kepler* while he was in Prague. His system, though not published until 1620, may have had even an earlier beginning. While *Napier* constructed numbers in geometric progression, and solved the problem of finding their associated logarithms, the *Burgi's* “*radix*” method started with the set of known logarithms, and found the associated numbers of ‘antilogarithms’. This turned out to be a far easier task, e.g., $0.5 = \log_{10}(\sqrt{10})$, and this concept was refreshed even in the famous *Feynman lectures*. This was extended by *Mercator* and latter *Gunter*, who devised his “*Gunter scale*” a plot of logarithm on a line followed by *Oughtred*, who placed the two logarithmic scales side by side so that one could slide relatively to the other, which resulted to hand-held device – the principle of the *slide rule* which was preceded by the idea of *Napier's* dices. *Laplace* was latter to comment that the invention of logarithms ‘*by shortening the labors doubled the life of the astronomers*’.

² Power law has instituted its value in such diverse areas as are models for the evaluation of syntactic communication [M.A. Nowak, J.B. Plotkin, V.A. Jansen, *Nature* 2000, 494] where it become an agreeable ingredient to facilitate most theories of language evolution. Its particular form is known as *Zipf's* Law, which states that the frequency of a word is a power function of its rank [G.K. Zipf “*Human Behavior and the Principle of Least Effort*” Addison/Wesley, Cambridge 1972]. Another sphere of operation is the partitioning course of commonality property as discussed in the article by M. Levy and S. Solomon “*New Evidence for the Power Law Distribution of Wealth*” [*Physica A* 90 (1997) 242].

³ In order to get the same increase in loudness as we get between one singer and two, we have to double the size of choir, similarly in sensing weight or light. After all it is not yet fully understood fact that most of our sense organs work logarithmically *Fechner* tried single-handedly to invent a science he called ‘*psycho-physics*’; and whose ideas were extensively used by *Helmholtz* in his, rather more successful investigations. Most important consequences we can find in music. For example, since any real tone is accompanied by overtones we can increase its loudness by strengthening either the fundamental or the overtones. In an organ, for example, which is pretty loud anyway, there is not much point in trying to make it even louder by bringing in more pipes to play exactly the same notes. *Weber-Fechner's* Law is one of diminishing returns in this context. But if, instead, we can bring in more pipes to reinforce the harmonics, we are putting our effort where it produces most effect. It is also possible to calculate the degree of overlap from any pair of notes, and to predict how much dissonance they should generate when sounded together. Clearly the traditional musical intervals ratios stand out from those around them as being particularly free of dissonance. These insights were largely developed by *Helmholtz* and published in his book “*On the Sensation of Tones*” where he pointed out that, when two notes sound together, there will be many difference tones at the frequencies separating the various harmonics. These will only be heard faintly, but unless the fundamental frequencies are in simple ratios again, they will be dissonant with the primary tones. It leads to the theory of chords and understanding of the role of the fundamental bass, which gives a certain paradox about *Helmholtz's* place in the history as seen by musician. It had further consequences in physics, for example, we can see the emitted light produced upon heating chemicals elements to be arranged in a particular set of frequencies, rather like a musical scale. Electron waves trapped inside an atom can be recognized as standing waves. So the reason why *Bohr's* orbits existed was essentially the same as the reason the different modes of oscillation exist inside a musical instrument and the radiation of light from an atom must be very like the sounding of a musical note. *Heisenberg* pointed out that a musical note should never be considered in isolation from the ear that hears it, which involves a fundamental uncertainty because of the ear's critical bandwidth; so also an electron should always be thought of in relation to the experiments which measure it, and this will involve a fundamental indeterminacy – famous principle of uncertainty.

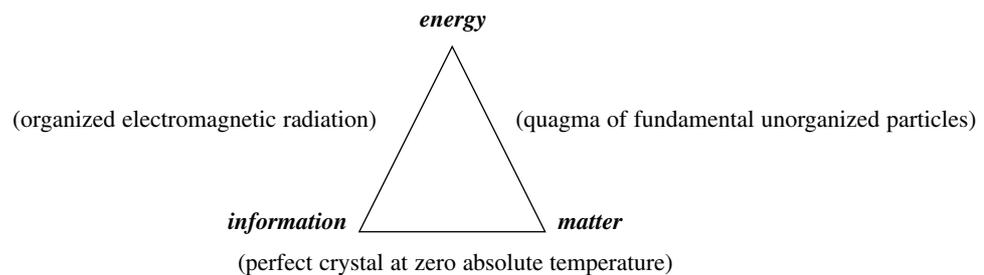
⁴ Any organ must be supplied with the necessary supporting substance such as water and oxygen. In many cases these substrates will be transported through vessel system that must meet every point in the volume of the organ. For example, the kidney houses three interwoven three-like vessel systems, the arterial, the venous and the urinary. Each of them has access to every part of the kidney. The fractal solves the problem of how to organize such a complicated structure in an efficient enough way. The same applies for growing branches of plants and may even be perceived in such a curious areas as the formation of electron patchcord along the interfacial conductive plane, i.e., quantum wire within the low-dimensional system of quantum wells (cf. Chapter 20).

- ⁵ When each step in the construction is performed the length of the curve increases by a factor $4/3$, so the final curve being the result of limitless number of steps is infinitely long. The similarities between this curve and the path of a quantum-mechanical particle become evident when we consider viewing the Koch curve with a finite spatial resolution [L.F. Abbot, M.B. Wise, Amer. J. Phys. 49 (1981) 37]. In this case, the infinitely many wiggles in the curve, which are smaller than some minimum length, say Δx cannot be detected and the measured curve length will be infinite. However, this length will depend on Δx and will increase without limit as $\Delta x \rightarrow 0$. The conventional definition of length gives a quantity, which depends on the resolution with which the curve is examined. It is not very useful when applied to curves like the Koch curve so that *Hausdorff* proposed a modified definition for the length, L , proportional to $L(\Delta x)^{D-1}$, where L is the usual length measured when the resolution is Δx , and D is a number chosen so that L will be dependent of Δx , at least in the limit $\Delta x \rightarrow 0$. This implies that $D (= \ln 4 / \ln 3 \neq 1)$ is the fractal dimension. To define the quantum-mechanical path of a particle we imagine measuring the position of a free particle with a spatial resolution Δx at times separated by an interval Δt . The path is then defined as the curve determined by drawing straight lines between the points where the particle was located at sequential times (at the classical level it will be just a straight line). The localization of a particle within a region of the size Δx results, according to the Heisenberg uncertainty principle, in an uncertainty in the momentum of order $h/(2\pi\Delta x)$. Thus as the particle is more and more precisely located in space, its path will become increasingly erratic. There is another property of the fractal Koch curve to be mentioned in this respect of quantum-mechanical path and which is above-mentioned self-similarity. If we view a Koch curve with a resolution $\Delta x' = (1/3)\Delta x$ then the curve we see is, up to repetitions and translations, just a scaled down version of the curve we saw when the distances being resolved were of the size Δx . The path of quantum-mechanical particle (mass m) will be self-similar if $\Delta L \propto \Delta x$, i.e., to get a self-similar path we must scale the time between position measurements of the particle in proportions to the square of Δx . That is, if $\Delta x \propto 2\pi m(\Delta x)^2/h$, then the resulting path become self-similar. Thus just as the fractal nature of the quantum-mechanical path reflects the Heisenberg uncertainty principle, the conditions of self-similarity is a reflection of the underlying dynamics, i.e., $E = p^2/2m$. When the particle possesses some nonzero average momentum, p (i.e., in the classical limit the particle is moving) since then the translation from the classical result $D = 1$ to the quantum mode $D = 2$ can be seen. It worth noting that the path of a particle undergoing Brownian motion is also fractal with $D = 2$ [E. Nelson, Phys. Rev. 150 (1966) 1079]. Further interrelation between the classical and quantum path will be discussed in Chapter 16.
- ⁶ The term *fractal* was derived from the Latin word '*fractus*' (meaning broken or fragmented) or '*frangere*' (break) and was coined by the Polish-born mathematician *Mandelbrot* on basis of *Hausdorff* dimension analysis. Since its introduction in 1975, it has given rise to a new system of geometry impacting diverse fields of chemistry, biology, physiology or fluid dynamics. The fractals are capable of describing the many irregularly shaped objects or spatially non-uniform phenomena in nature that cannot be accommodated by the components of Euclidean geometry. The reiteration of such irregular details or patterns occur at progressively smaller scales and can, in the case of purely abstract entities, continue indefinitely so that each part of each part will look basically like the object as a whole. The term *fractal dimension* reveals precisely the nuances of the shape and the complexity of given non-Euclidean figure but the idiom dimension bears not exactly the same meaning of the dimension responsive to Euclidean space so that it may be better seen as property.
- ⁷ The word '*chaos*' is familiar in everyday speech. It normally means a lack of order or predictability in mathematics or disordered state of mind or disorganized society. A characteristic feature of chaotic (highly dynamic) systems is the property of pathological sensitivity to initial positions. Let us mention that the hereditary meaning of chaos is an empty space or not yet formed matter (*Theogony*, about 700 BC). It was probably derived from Greek '*chaskó*' – drifting apart, gape, opening and '*chasma*' – abyss, chasm, gap, and was associated with the primeval state of the Universe (also related to '*apeiron*'). In the Chinese tradition, chaos was apprehended as homogeneous space that was preceding the constitution of directions/orientation (i.e., separation of four horizons) in the sense of 'great creation'. In the Egyptian cosmology, chaos ('*nun*') represented not only the state preceding the great creation but also the present state of a coexistence with the world of forms/structure, which serves also as a limitless reservoir of field forces where forms dissolve under infinitesimal time. In alchemy chaos was linked to primeval matter ('*nigreden*') capable to create 'big masterpiece'. Chaos was a symbolic representation of the internal state of alchemists who first needed to overcome their unconsciousness to become ready for transmutation study. In '*Genesis*' chaos is understood as a symbol of paltriness and non-distinctiveness but also as a source of feasibility. The word chaos is sometimes taken to mean the opposite of '*kosmos*' and in that latter term has connotation of order. Arabic meaning of '*chajot*' is also closely regarded with life. For the Epicurean conception chaos was a source of a progressive transformation. Chaos thus became a definite domain of present day science showing by law that disorder can disclose windows of order (order through fluctuations) and that, *vice versa*, order bears inherent minutes of disorder (disorder as information noise). The theory of chaos provided the bases for various progressive specialties of numerous branches of knowledge seemingly important for any further advancement of science and society.
- ⁸ It is often considered in growth terms of a population of organisms for which there is a constant supply of ample food and enough space with no predators (e.g., rabbits, insects). When the population is small it can evolve without hindrance. However, when the population becomes sufficiently large, the new generations are smaller because of food shortage and overcrowding so that the growth slows down or gets oscillating. It well examples the population dynamics and adherent characteristics of chaos.
- ⁹ *Szilard's* model [L. Szilard, Z. Physik 53 (1929) 905] of one-particle gas, executing a work cycle with the aid of an "intelligent demon", has, perhaps, the greatest impact in the development of *Maxwell's* demon known since 1866. Let us imagine that the particle is in a box of length, L , whose walls are maintained at temperature, T . A partition is inserted at the halfway point, dividing the container into two chambers of length $L/2$. The demon determines which chamber holds the particle, and the partition is then replaced by a movable, frictionless piston fitted with appropriate pulleys to enable the particle to do work, W , on the piston, thereby lifting a weight. The piston is then removed and the particle is once again in the container of the length, L . In the process, the energy, $E = W$, goes from a constant-temperature reservoir to the particle, and the net result (ignoring the demon for the moment) is

a decrease of the reservoir's entropy, $\Delta S = k_B \ln 2$. However, the realization that the demon's state has changed by the information added to its memory makes it clear that the memory must be cleared. *Landaer's principle* "erasure of one bit of information sends entropy, $k_B \ln 2$, to the environment" [R. Landauer, IBM J. Res. Dev. 5 (1961) 183] implies that the deletion of the memory content sends, at least, the elementary entropy, ΔS , to the environment, and this is sufficient to save the second law showing that the strong role of entropy is, over again, obvious. Yet an outside observer, who cannot see the particle, does not know which chamber houses the particle. From quantum mechanical perspective, the particle can be considered to be in both chambers, with the probability 1/2 for each, until a measurement is made. Once the measurement is completed, the entropy does not seem to drop, but only for the demon, who alone knows the result of the measurement. Looking for the answer, where is actually produced the entropy that is sent to the environment during erasure, we have taken into account that the phase space consists of the state of the particle (left, right, or both) and that of the demon's memory (left, right, or a standard state) [P.N. Fahn, Found. Phys. 26 (1996) 71]. In a sense, the memory is a redundant copy of the system's state that does not carry extra entropy. In contrast, after the work process, the entropy values of the memory and the systems are independent of one another and just are added together. We can see that any analysis that focuses on information gathering is often done incomplete. (As matter of curiosity, in the extreme quantum state, when the particle and the reservoir are in an entangled-quantum- state we, however, have to assume a special case where the total entropy cannot be written as a sum of the system and reservoir entropies, cf. Chapter 20.) *Bennett* [C.H. Bennett, Int. J. Theor. Phys. 21 (1982) 905 and Sci. Amer. 55 (1987) 106] argued that the measurement itself carries no threshold cost. Instead, it is necessary to consider a complete thermodynamic cycle, in which information is gathered, stored, and eventually erased to restore the initial configuration. *Bennett* also suggested the use of algorithmic information theory making possible to define entropy without using an ensemble. Algorithmic entropy, I_s , is thus defined as the length, in bits, of the shortest computer program that runs on a universal computer and fully specifies a system's state. For a memory state, s , simply a string of $\langle 0 \rangle$ and $\langle 1 \rangle$ so that the algorithmic memory is maximal when a string, s , is random, in which case, I_s , is the length of the string in bits. Perhaps of most importance, algorithmic entropy provides a definition of entropy for a microstate, just as an energy 'eigenvalue' is defined for each microstate.

¹⁰ Certainly we cannot go into deep details when analyzing various meanings of information (schematic, pragmatic, etc.), distinguishing its quantity and quality or even discussing such particularities as its algorithmic complexity or logic depth. Here we can rather demonstrate some fanciful illustration of its phenomenological and statistical manifestations. Totalitarian regimes were always trying to suppress free dissemination of unsafe ideas by traditional burning of books. Let us take a habitual case of burning a bible with its mass about 0.5 kg (having paper heat contents about 10^7 J/kg). The heat produced is roughly five thousand of kJ. Concerning the bible information content possibly evolved in the form of accountable 'heat' we can assume that its text accommodates about million combinations (n) coded via 64 (o) letters that can be used to calculate $W = n! / [(n/o)!]^o \cong n \log o = 10^{10}$ kJ. There is evidently a great incomparability of such obtained values, i.e., $\Delta Q_{\text{book}} \sim 10^6 \text{ J} \gg \Delta Q_{\text{text}} \sim 10^{13} \text{ J}$, the difference approaching as many as 19 orders of magnitude is far below any detectable fluctuations and would become accountable only along with simultaneous burning of unimaginable 10^{12} books. There we ought to ask what about the case of two or more identical books or whether a bible has more valuable information content than a scientific book or a novel, if the same subject matter is written in different languages, etc., etc.. We can similarly proceed to analyze energy conservation curiosity looking upon the source of everlasting fire in Hell. Would it be possible to account for the heat associated with information brought in by souls and estimate how many souls would thus be necessary? First we have to postulate that, if souls really exist, they must have some 'mass' and can possess information content. Then we can account on different religions that often state that 'if you are not a member of that entire religion you would go to Hell'. Since there are more than hundred religions and one does not usually belong to more than one religion we can project that all souls must go to Hell. With birth and death rates we cannot only expect that that number of souls in Hell is to increase almost exponentially but we can also estimate about 1% year contribution from the population of 10^9 , i.e., 10^7 souls. Assuming average brain to bring in memory in Terabites so that the total soul contribution is 10^{19} , which would still be so diminutive donation not exceeding a unit joule production per year, yet significantly deficient for keeping a noteworthy fire. We can proceed still one hypothetical step more to see whether the Hell is exothermic or not. Adhering to the *Boyle's Law* and assuming that the temperature and pressure in Hell is to stay the same, the ratio of mass and volume of souls needs to maintain constant. If the Hell is expanding at a slower rate than the rate at which souls enter the Hell, it will break loose and, on contrary, if the expansion is faster, the temperature and pressure will drop until Hell freezes over. So that there is not only lack of energy for the everlasting fire but also the soul rate must be well controlled, which does not comply with religious teaching and beat out any effort to make a more scientific analysis.

11



Almost sci-fi consequences of such an extreme portrait may be read as follows. If the upper corner would consist of pure energy, E , in an infinite entropy state, and the right bottom corner of unadulterated matter, m , the adjacent right side of the triangle is justifiable within the *Einstein* equation, $m/E \cong \mu_0 \epsilon_0$ (i.e., characterized by the values of μ_0 and ϵ_0 as the permeability and permittivity of vacuum, which may predicate certain structure of our Universe). Associated condition of the absence of information would display

a state of randomly distributed, unlinked 'foundations' (neither imaginably inherent particles nor any form of mass would exhibit no organization whatever) moving aimlessly, with no landmarks, no events or space. It would become impossible to measure either time or space, as such form of information would not exist (- it might be somehow assumed to take place in the center of a black hole). Left triangle side would consist of absolute vacuum traversed by force fields and pulses of energy, possibly capable to measure time, but distances may have no meaning being without landmarks. Bottom triangle side might enable to measure the distances but perhaps no time as in the absence of any motion, or events, time might be frozen. In some way, curious left corner, containing neither matter nor energy, might consist of unspecified information particles. Let us preliminarily label them '*infons*' to be forcibly envisaged as photons, which appear to have stopped oscillations (as fantastic idea as the concept of 'tachyons' with their imaginary mass) propagating through empty space down to absolute zero Kelvin. On the other hand, the above triangle can also represent some philosophical aspects, i.e., mental relations when respectively replacing energy, matter and information by power, property and spirit, which endows with new interrelations linked with the each triangle side being the strife, creativeness and love, cf. Chapter 3.



CHAPTER FOURTEEN

14. Oscillation modes and modern theories of state changes

a) Pendulum and related theory of ordered and chaotic motions

A typical periodic motion can be represented by a pendulum, which was used for long time in pendulum clocks to regulate the mechanism (*Huygens*) that causes the hands to move around the dial or that controls the periodicity of certain manipulation. For small displacement from its equilibrium position pendulum undergoes simple harmonic oscillations [47], best represented by a light object connected to a horizontal spring and moving on a horizontal surface. The net force is due to the spring and dissipative effects of friction are assumed negligible. The acceleration, x'' , of the object is proportional to its displacement, x , but points in opposite direction. The harmonic displacement x (or pendulum displacement, θ) is given by relation, $x = A \cos(\omega t + \phi)$ where A is the amplitude, ω is angular frequency (velocity) and ϕ is the phase constant (shift). Period of motion, $\tau = 2\pi/\omega$, is a time interval during which the object undergoes a complete cycle with the frequency, $\nu = 1/\tau$ with the kinetic energy $E_K = (m/2) \omega^2 A^2 \sin^2(\omega t + \phi)$. The angular coordinate for the simple pendulum displacements (θ) is the same as for harmonic oscillators ($x = \theta$) and $\omega = \sqrt{L/g}$ is the function of its length, L , and gravitation acceleration, g . There is an intimate connection between the simple harmonic motion of an object moving along a line, such as x -axis or displacements, θ , and the motion of a particle at a constant speed along a circle (projection).

If the dissipative effects of friction become effective, the slowing motion becomes characteristic for the damped harmonic oscillator, i.e., $x = A \cos(\omega_D t + \phi) \exp(-\gamma t)$ where γ is the impedance $b/2m$ and ω_D is $\sqrt{[(k/m) - (b/2m)^2]}$ and the oscillator will eventually come to rest. Most of the oscillations that occur in machinery and in electric circuits are, however, forced oscillations, where the driving force oscillates itself under a *sine* or a *cosine* mode. The dramatic increase in the amplitude of the motion is called resonance, which occurs when any oscillating system is driven by or coupled to another oscillating system with similar frequencies. More complicated motions can be compounded from two simple harmonic motions and represented as two-dimensional figures, called *Lissajous figures*, see Fig. 1, remaining still within the domain of so-called linear oscillators. If an oscillator were irregularly enforced, e.g., by magnetic field due to the two fixed magnets placed at the limiting sides of swinging tip, the magnetic pendulum system would act chaotically. The slightest change in its initial position of release can lead to very different swinging states, with tip of the pendulum attracted over either magnet. Such systems become non-linear by nature. Another special case appears when a firm pendulum can swing as much as to arrive at the state of rotation. At the upper position, if reached at equilibrium, the rotation arrests extremely slowly so that it can eventually change its direction, which is often called the moment of bifurcation. If repeated, the boundary between the two possible motions shows the structure called a fractal (mentioned earlier, see Chapter 16) and the non-linear motion is often associated with the state of chaos.

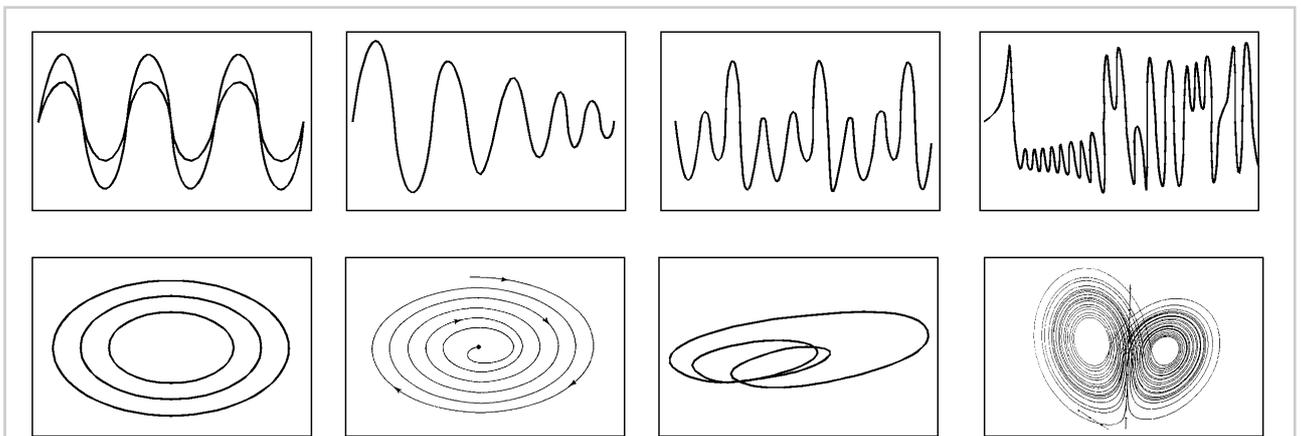


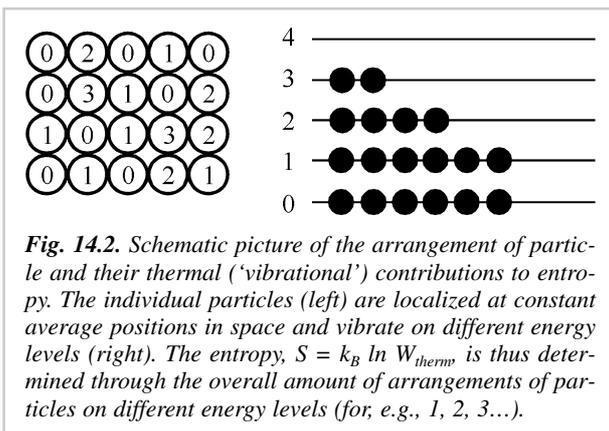
Fig. 14.1. Circular course is equivalent to compound simple harmonic motions along the perpendicular diameters (say on the x and y axes). The two motions must have the same amplitude and angular frequency and must have a phase difference $\pi/2$. Configuration of trajectory in the phase space thus provides valuable information about the long-range behavior. The number of dimensions of phase space is determined by the number of coordinates required to define the complete physical state of the system in question. More complicated motions can also be compounded from simple harmonic motions to form interesting two-dimensional figures, called *Lissajous figures*. One or more of the amplitudes, angular frequencies, or the phase differences must be changed to obtain noncircular figures. Best illustration is offered by the comparison of the traditional time progress (upper row) with the derived trajectories in the phase space (lower row). From left, (a) linear simple harmonic oscillator of an example for archetypal repeating course of action, which is represented in the two-dimensional space of velocity and deviation. Each circle (or generally ellipse) corresponds to a curve of a constant energy and encloses a constant area of the phase space. (b) The energy loss per cycle in a damped oscillator exhibits the reduction of area with each cycle as its trajectory spirals to a point of inertial stability (fixed point attractor at the origin). (c) Repeating process in the 'waltz' rhythm of period three provides a more complex pattern. (d) horseshoe (or 'butterfly-wings') is the characteristic pattern of a chaotic process, cf. Chapter 13.

One typical example of a non-linear oscillator is damped and driven pendulum. For certain combinations of the damping and driving constants, the pendulum exhibits a chaotic motion (see previous Chapter 13), i.e., the motion which is essentially unpredictable. In this way behave numerous actual systems met in the real world, which includes mechanical, electric, fluid and thermal oscillations and which also includes the motion of the Earth's atmosphere and its interactive behavior.

b) Particles and their energies

Any real object can be assumed as the arrangement of many pendulums or, better, oscillating vibrators represented by the behavior of inherent (fundamental) particles [47–49]. Each particle is closely surrounded by similar particles and each particle vibrates in a little volume whose boundaries are determined by the position of the other neighboring particles. In solids this volume may be in order of 10^{-20} cubic millimeters whereas in the case of a gas the available volume may be several cubic millimeters or more. The basic principle of the quantum theory is that when a particle is confined in a certain volume, no matter whether the volume is large or small, the energy of the particle can take only certain discrete values, i.e., the energy of the particle is *quantized*. The state of the smallest allowed energy is called the lowest (*ground*) energy level denoted by ϵ_0 , the next available is, ϵ_1 , and so on, the total energy of all particles being the sum $\sum n_i \epsilon_i = E$. When a group of n particles is sharing a total energy E , it is represented by the total number of their possible states so that if more energy is added to any such a group, additional distribution became possible. The number, W , of possible arrangements of particles is traditionally given by the ratio of factorials, the numerator being given by the number of all particles, $n!$, while the denominator contains a factorial from each quantum state that contains any particle, i.e., $n_0! n_1! \dots n_i!$. When, W , has the maximum value consistent with a certain value of E , small alternations in any or all of the variables, n_0, n_1, \dots, n_i , leave the value of W unchanged, so long as these alternations are chosen so that the total energy and the total number of particles remain constant, see Fig. 2.

Statistical meaning of entropy, S , is literally derived from the number of possible arrangements through a logarithmic relation which is traditionally stylized using



phenomenological thermodynamics as $\ln W = Q/k_B T$. It provides the definition of the absolute temperature, T , and of the constant, k , in such a way that if an amount of heat equal to $k_B T$ is allowed to flow into any body, the increase in $\ln W$ is equal unity. As it is generally identified, the value of W is extremely sensitive to the number of particles, n , in the body and it may seem strange that such a change is independent of the size and composition. For example, a smaller body will have a relatively smaller heat capacity and thus the admission of a given quantity of heat will tend to cause a greater incipient change of temperature. At any rate, it asserts that the addition of an amount of heat equal to $k_B T$ will cause the value of W to be multiplied by the factor 2.718 irrespective of the body size.

For use in many problems, we need an expression that sums up concisely the character of the population of the set of levels at the temperature T . We can consider, for example, a solid that is partially vaporized; we need to know the value of the vapor pressure that will be in equilibrium with the solid. The point of view adopted in statistical mechanics is that in the vapor the particles have a set of energy levels available to them, and in the solid they have another set of available energy levels so that the steady state is reached when the population of one set of levels is in equilibrium with the population of the other set. Every problem of equilibrium is approached in the same way so that we need a simple way of prescribing the conditions for any equilibrium if for each set of levels we could find a compact expression that would describe the way in which the set of levels is populated at a given temperature. In fact, quantities can easily be derived that have the property that any equilibrium can be expressed in terms of a ratio between them. Such quantities are known as *partition functions*. It is clear that the required expression must necessarily contain the energy, ϵ_i , of every occupied level and the temperature, T . For such a set of levels the sum, $\sum \exp(-\epsilon_i/k_B T)$, known as the sum-over-states, bears the desired properties, where the form, $\exp(-\epsilon_i/k_B T)$, is known as the *Boltzmann factor*. Its numerical value depends on the zero of energy from which the values of ϵ_i are measured, i.e., if ϵ_0 is chosen as zero energy, the thermal energy of the particles becomes identical with the total energy, E , so that this forms a natural zero of energy for any group of particles. We can consider the population of any set of levels, which is given by the ratio $n_i/n = \exp(-\epsilon_i/k_B T)/\sum \exp(-\epsilon_i/k_B T)$. A rise of temperature throws particles up from lower to the higher levels, i.e., in each of the higher levels the number of particles increases and *vice versa*. With rise of temperature, both the numerator and the denominator steadily increase, but at different rates, the numerator exhibiting a faster growth. We can see that the ratio $d\{\exp(-\epsilon_i/k_B T)\}/dT$ is positive, providing a useful expression for the total energy $E = nkT^2 d\{\ln \sum \exp(-\epsilon_i/k_B T)\}/dT$.

c) Vibration structures in condensed state and quantitative description of the creation of vacancies

The ensemble particles vibrating at low amplitudes can represent glassy solids as well as crystal-like material. We can presume that the individual vibrating particles of

about a monomer size [50] are localized in the non-linear potential valleys [51], where they perform the oscillations due to the energy of thermal motion $E = f\xi^2/2 - g\xi^3/3 - c\xi^4/4$ [49], where $\xi = r - r_0$ is the deviation from the equilibrium position and r_0 is defined as half the distance separating the bottoms of two potential valleys. Only for the solid state the bottom of r_0 has a constant position while for the liquids it has to be subjected to diffusion movements. It is assumed that many vibrations inside a potential valley take place before the diffusion jump occurs. Parameters f , g , c can be determined from the experiment based upon the values of specific heat C_v or from thermal expansion coefficient α_{exp} . On microscopic level, these parameters f , g , c depend mainly on the distances of closest neighbors of the particles under consideration. It can be found that the parameters f , g , c act selectively on the values of the thermal expansion coefficient and on the value of specific heat [48].

The shape and character of non-linear valley depends on the separation of particles. In close vicinity of vibrating particle [49,51] the laws of solid-state physics keep the positions of particles constant for the majority of cases when no diffusional changes of the mutual position of particles is permitted [52] as the temperature rises. In order to treat the transition of a solid into the liquid state, we place the non-linear potential valley into the equation of motion, which for a single particle reads $m d^2\xi/dt^2 + dE/d\xi = F_{\text{ext}}$, where m is the mass of vibrating particle and F_{ext} represents the interaction force of given particle with its vicinity. It will depend on the level of vibrations, cohesive forces and mutual interactions of particles. The existence of acoustic waves of different wavelengths, in the sense of *Debye's* classical theory [48], will guarantee the real existence of F_{ext} .

In general, F_{ext} can be taken as a functional [49] of integrals over momenta, I_{ph} , and coordinates, I_{cf} , which forms each partition function Z , i.e., $F_{\text{ext}} = \phi(I_{\text{ph}}, I_{\text{cf}})$. Both integrals, I_{ph} and I_{cf} , are defined in relation to the overall partition function, $Z = (2\pi\hbar)^{-3N} (1/N!) I_{\text{ph}} I_{\text{cf}}$, and can be considered mutually interdependent. In particular, I_{ph} stands for the integral over the particle momenta ($p = mv$) within the phase space while I_{cf} represents the cohesive energy of mutual interactions of the particles and their distances [54]. For solids the changes of I_{cf} are usually not considered because the individual vibrating units have constant positions in the body under investigation. In other words, for solids the thermal motion of individual particles is not strong enough to dislodge the individual vibrating units from their average position.

In the following text we perceive glasses below the *Vogel* temperature T_v as solids, similarly as crystals under their melting point T_m . The *Vogel* temperature for polymers is about 52 K below the glass transition temperature, T_g , but even larger difference is often found for inorganic glasses.

The bottom of the potential valley keeps in solids a constant position relative to placements of the particles in closest vicinity and all particles are forced to vibrate only at lower amplitudes, characteristic for the non-linear oscillators. We consider thermal expansion to be usually

connected only to the homogeneous volumetric expansion and to differentially small shifts in frequencies, according to *Grüneisen's* Law of [54].

For solids, the constants of f , g , c will depend on the average positioning of particles that are forming the system. This is not the case for the liquid state, where migration of particles or switching to higher amplitudes (cf. Figs. 3 and 4) are permitted. The positions of the vibrating particles in liquids will eventually change in time, as the migrations of particles occur, due to the process of diffusion. The parameters f , g , c take the complex form as $f = f_1\{x_1(t), y_1(t), z_1(t), \dots, x_n(t), y_n(t), z_n(t)\} \dots F_{\text{ext}}(T, t)$ where f_1 (as well as f_2 and f_3) are symbols of functional dependence and x_1, x_2, \dots, z_n are the average coordinates of vibrating units of particles forming the system in the vicinity of the considered particle [53]. For the solid state, and along the lines of our model perception, we will assume that, for low temperatures, the temperature-dependent mutual interaction force F_{ext} is not large enough to cause a change in average positions of coordinates, x_1, x_2, \dots, z_n and thus also the parameters f , g , c stay constant. This can be assumed for the systems where all forms of diffusion are excluded. The nonexistent diffusion forms also the fundamental idea for C_v assessment established by *Debye* [52] and approved to be valid for crystals, or for amorphous phase according to *Tarasov* [55], *Chvoj*, *Šesták and Tríska* [56] and *Wunderlich* [57], Figs. 2 and 3.

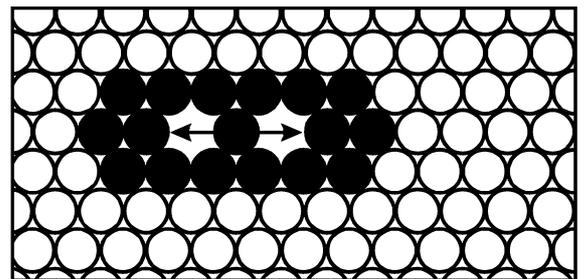


Fig. 14.3. Graphical representation of a vacancy creation in a liquid structure. The central particle is able to spatially displace the particles in its own vicinity and substantially enlarge its vibration amplitude. The agitated spot will give rise to entropy change, $S = k \ln W_{\text{semievap}}$

As the temperature rises, the integral I_{ph} will increase and the average positions of particles in space x_j, y_j, z_j start to be function of time $x_j(t), y_j(t), z_j(t)$ etc., and the diffusion process starts to develop. The diffusion process can act selectively with temperature growth, affecting at low temperature some groups $x_j(t), y_j(t), z_j(t)$ only, whereas at a higher temperature, other groups of particles can be involved as time dependent variables as well. The integral I_{ph} will cause, as the temperature rises, the changes in structural arrangement of the system and can bring time-related changes also into the integral I_{cf} . Through the rise of I_{ph} the system can be brought out of locally 'frozen', highly non-equilibrium configuration and can be thus heading towards other coordinates, characteristic of the situation closer to the

equilibrium [56]. This form of interaction is the physical base for the process of glass or crystal annealing, tempering or other forms of restructuring the materials by heat treatment.

For glasses the ‘liberation’ of individual groups can be made inside of ‘isolated islands’ of mobility (*Johari-Goldstein* beta-maximum [56,57]) and does not have to imply the change of external coordinates, which define the sample external shape. For example, such movements, which can involve the rotational motion of individual groups, will be – only mildly or not at all – connected to the external coordinates defining the laboratory dimensions of sample under study and thus they will not have strong impact on the thermal expansion coefficient. Concerning glasses, when the temperature is raised above the *Vogel* temperature, all particles start to relocate and the diffusion process sets on. Within hours, days or even years the external shape of sample will also change above T_v . The upswing in the C_p value takes place at T_v and at T_g , the expansion coefficient, α_{exp} , undergoes a stepwise change, too.

In our model perception the rise in entropy below T_v is caused mainly by the vibration modes of entropy, as the particles are kept in constant positions considering the solid state model only. The overall arrangement of particles in vibration levels will define the vibration part of entropy W_{th} [47] (cf. Fig. 2). As shown by *Wunderlich* [57], the number of particles associated with the boson peaks, tunneling states, etc., is for many substances very small and thus, the specific heats at the *Vogel* temperature, are almost the same for crystalline as well as glassy bodies. The entropy rise in glassy bodies below T_v is thus connected mainly with the thermal (vibration) entropy increase. For crystals, because of the extra energy connected with melting, a phase change is involved and the thermal entropy part plays a crucial role until the melting temperature T_m is reached. For temperatures $T \leq T_m$ (or $T \leq T_g$) we can write $S \cong k \ln W_{th}$ where W_{th} is the probability connected with the arrangements of particles on different vibration levels of energy.

At the moment when special rearrangements start to play important role (see Fig. 2), the particle positions change in time so that another part of the entropy has to be added, i.e., $S = k \ln W_{th} + k \ln W_{conf}$, where W_{conf} is connected with overall amount of spatial displacements of the particles. In many cases, this conformation term will be active at temperatures where the crystals are annealed and changes of the structural lattice take place, or for glassy/amorphous bodies above T_v and below T_g . In certain cases, however, some exceptions can occur, as for some systems the term W_{conf} can be very active even at very low temperatures 1 K. This is valid for crystals [58], as well as for amorphous bodies [59].

d) Mathematical treatment of strong non-linearity above the T_g transition

As a result of rising local expansions, the system of equations describing the system becomes strongly non-linear in a mathematical sense and the solutions for such systems can be taken from the formative theories of

chaos. According to these hypothesis of determining chaos [17,60], the above-mentioned equation, $m d^2\xi/dt^2 + dE/d\xi = F_{ext}$, will be prone to showing irregular amplitudes of vibrations with time. The substantial changes in vibration amplitudes can only develop, if the fault cracks or structural dislocations in solid matrix start to appear. This was actually confirmed by the experiments of positron annihilation spectroscopy (so called ‘PASCA’ measurements [61]), which have shown that huge voids started to develop in isolated places of amorphous state above T_v . These voids tend to reach the order of magnitude of cubic nanometers when T_g is exceeded. The changes in parameters f , g , c do not have to have even continuous character in local spots. The local, highly expansive spots, which are characterized by hundred time’s larger coefficient of local expansion coefficient, will develop with the onset of liquid state above T_g . The same is valid for the amplitude of vibrations.

The strong non-linearity will mathematically justify the amplitude switch in localized spots (Figs. 3 and 4), where the central particle is able to dislodge pushing

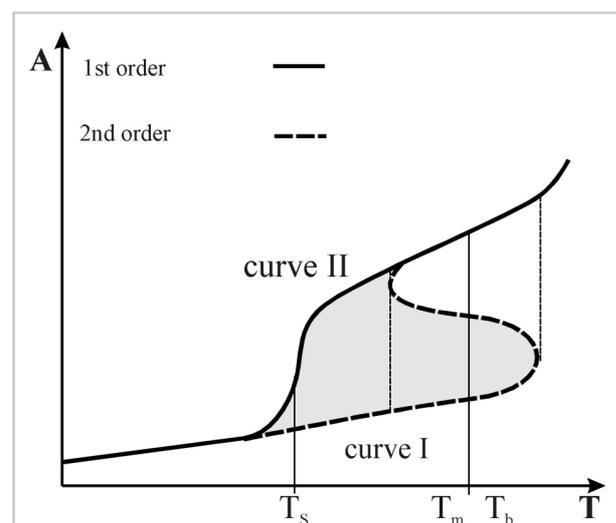
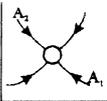
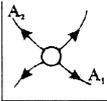
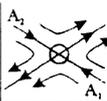
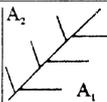
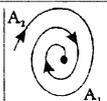
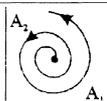
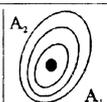


Fig. 14.4. Schematic view of the amplitude rise shown for a strongly damped non-linear oscillator; curve II, as a function of temperature. The second-order-like T_g area is characterized by very high viscosity and the amplitude enlargements proceeds very slowly. Curve I displays the first order transition, such as melting at T_m . The analogical, abrupt amplitude enlargement and creation or annihilation of semi-evaporated spots (in sense of the preceding Fig. 14.2.) will also progress in the liquid state. This portrait is characteristic for ‘hysteresis’ when the value of the bifurcation parameter (here read as T) initially grows and afterward diminishes. In particular, if the system is in the stationary state coupled with the lower branch it stays in it even if T is increased (overheating), but at the moment of $T = T_{melt}$, the system suddenly bounds to upper branch. On the contrary, it jumps down from the upper branch when it is undercooled (which is a more frequent phenomenon bearing a more extensive character due to the associated ‘geometrical’ effects of nucleation, cf. Chapter 6, Fig. 6.5.). We can come across this effect in various remote instances such as lasers, biological membranes, etc..

aside the neighboring particles creating thus in its vicinity a highly expansive spot. Such a cavity can become responsible for the higher expansion coefficients identified for liquids. The entropy contribution connected with such a ‘semi-evaporated’ state (cf. Fig. 3), which is created inside the liquid system in vacant regions, can be eventually contemplated as well, providing a wide-ranging relation, i.e., $S = k \{ \ln W_{th} + \ln W_{conf} + \ln W_{semievap} \}$. Because the vacant regions (thanks to the PASCA observations [61]) have a well-defined size, which is larger than the *Van der Waals* volume, but smaller than the critical volume of the particles involved. We can estimate the change of enthalpy connected with the semi-evaporated state. It can be taken as a fraction of evaporation enthalpy H_{evap} and we can take the $\Delta H_{semievap} = \Delta H_{evap}/n$, where the value of n is about 2–4 (again in agreement with the PASCA experiments as well as with the *Eyring’s* estimate on viscosity [62]).

In order to find a speedy solution of the above non-linear equation and provide illustrative examples, which can be easily visualized, the second-order differential equation is usually transformed into two separate, first-order differential equations. This procedure is usually performed in the determining chaos theories [63] as well as in the studies of self-organized structures considered in non-equilibrium thermodynamics.

Table 14.I: The dominant types of particle interaction for different phenomena in condensed and gas phases, which arises from the solution of differential equation ($md^2\xi/dt^2 + dE/d\xi = F_{ext}$) exhibiting the coefficients $\lambda^2 + a_1\lambda + a_2 = 0$ for $-a_1 = a_{11} + a_{12}$ and $a_2 = a_{11}a_{22}a_{11} + a_{12}a_{21}$. (Courtesy of B. Hlaváček, Pardubice, Czechia).

Shapes of trajectories	Name of singular point	Roots properties	Values of coefficients, a_1, a_2	Phenomenon
	stable node	real $\lambda_1 < 0$ $\lambda_2 < 0$	$a_1^2 - 4a_2 > 0$ $a_2 > 0$ $a_1 > 0$	fast condensation
	unstable node	real $\lambda_1 > 0$ $\lambda_2 > 0$	$a_1^2 - 4a_2 > 0$ $a_2 > 0$ $a_1 < 0$	situation above Boyle temp.
	saddle point	real $\lambda_1 < 0$ $\lambda_2 > 0$	$a_1^2 - 4a_2 > 0$ $a_2 < 0$ $a_1 \neq 0$	the area of critical point
	infinite amount of saddle points	real $\lambda_1 = 0$ $\lambda_2 > 0$ a) $\lambda_1 < 0$ b)	$a_1^2 - 4a_2 > 0$ $a_2 = 0$ $a_1 \neq 0$	the area of critical point
	stable focal point	complex $\text{Re}(\lambda_i) < 0$	$a_1^2 - 4a_2 > 0$ $a_2 > 0$ $a_1 > 0$	condensation
	unsteady focal point	complex $\text{Re}(\lambda_i) > 0$	$a_1^2 - 4a_2 > 0$ $a_2 > 0$ $a_1 < 0$	sublimation
	stable oscillations	complex $\text{Re}(\lambda_i) = 0$	$a_1^2 - 4a_2 > 0$ $a_2 > 0$ $a_1 = 0$	stable vibrations in condensed phase

By choosing the variables $A_1 \equiv \xi$ and $A_2 \equiv d\xi/dt$ we can rewrite the equation, $md^2\xi/dt^2 + dE/d\xi = F_{ext}$, into the forms [64] of $dA_1/dt = a_{11}A_1 + a_{12}A_2$ and $dA_2 = a_{21}A_1 + a_{22}A_2$.

These equations can be analyzed further in the vicinity of the stationary point of vibrations to have a non-zero solution only if the determinant, $\det | a_{11} - \lambda \quad a_{12} \dots |$, vanishes, i.e., only if it holds that $\lambda^2 + a_1\lambda + a_2 = 0$ for $-a_1 = a_{11} + a_{12}$ and $a_2 = a_{11}a_{22}a_{11} + a_{12}a_{21}$, as used in the Table I shown in Fig. 5 [49,53]. The changes from a solid to a liquid state, as well as the other higher-temperature transitions, can be investigated through the change of parameters a_1 and a_2 within a certain range. The overall view of interactions, which are taken as dominant in a given type of transition provides the individual portrayal illustrated in Table I.

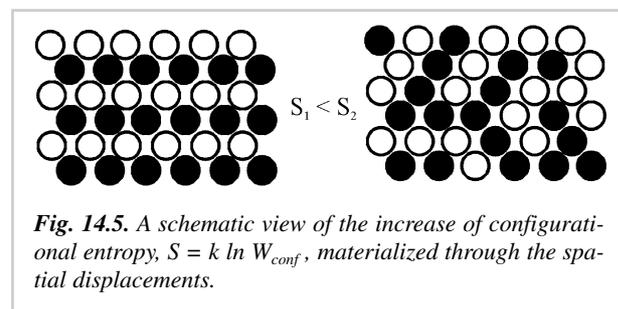


Fig. 14.5. A schematic view of the increase of configurational entropy, $S = k \ln W_{conf}$, materialized through the spatial displacements.

The liquids show us the very interesting phenomena of local high-level expansion in discrete points associated with internal surface enlargement due to the existence of vacancies. The existence of vacancies stems from the considerations of high non-linearity. On the surfaces of vacancies the internal energy is always higher than in the bulk. So the liquid system represents the foam-like structure, which enlarges its surface from inside. The vacancies are not empty voids, but are filled with actively moving particles. In this way, the higher transitions such as the boiling or critical point can also be contemplated (cf. Table I). While only few vacancies exist at lower temperatures, at the critical temperature the amount of vacancies reaches the level at which the condensed phase disintegrates completely [65]. We can remark that according to *Bueche* [66] the ratio of vacancies to vibrating particles is equal to about 1:40 assuming the T_g region and all oscillating particles are able to reach the upper vibration amplitude with the addition of a very small amount of energy.

e) The micro-model of solid – liquid transition: two types of vibration units

The structure containing beads of mass m interconnected with the elastic springs of modulus k_c can be considered as a regular solid-like structure, as shown by *Wannier* [67]. In Fig. 6 we try to show similar structure by only laying more emphasis on the irregular character in separation of masses of individual particles. Fig. 6a illustrates the structure of glassy state just above T_g point, at the moment when one non-linear oscillator changed its vibration amplitude and created “semi-evaporated” spot

connected to a micro-crack [49,65], or to a vacancy, which holds an active vibrating particle inside. The situation above the crossover temperature, T_{cr} , is characteristic by the number of non-linear units, vibrating with high amplitude, which grow whereas the solid structure disintegrates into a structure of smaller mobile blocks, as the sample volume expands. The mechanics of these blocks connected with certain relaxation times forms the central part of this novel approach. For liquids, the isolated non-linear oscillators thus form the cracks, faults or separation interfaces between the solid blocks. Their number increases as the temperature rises [64,65]. This fact provides the basic characteristic of the system showing that the main difference between parameters a and b of Fig. 6 reflect the reality. In Fig. 6a the solid blocks of linear interconnected elements are bridged-over, giving the sample its elastically connected network, characterized by finite level of shear modulus $G(t,T)$. Above T_{cr} we assume the termination of “bridge-over” effect and the level of shear modulus contributed by bridging falls to zero. The isolated blocks remind us in structure of “floating icebergs” (in further comments we will restrict our considerations to glassy system as a Newtonian-like liquid only, trying thus to avoid the rubber-like share of entropy related completely to elasticity).

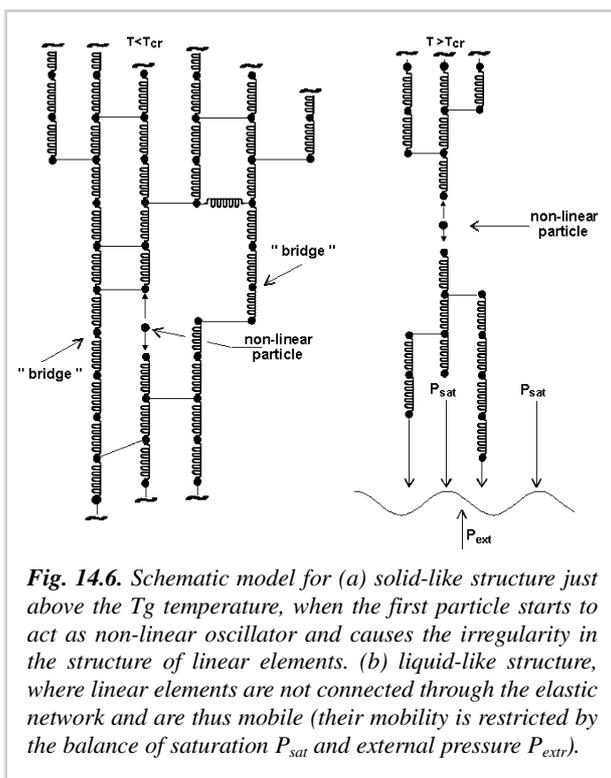


Fig. 14.6. Schematic model for (a) solid-like structure just above the T_g temperature, when the first particle starts to act as non-linear oscillator and causes the irregularity in the structure of linear elements. (b) liquid-like structure, where linear elements are not connected through the elastic network and are thus mobile (their mobility is restricted by the balance of saturation P_{sat} and external pressure P_{ext}).

Such a proposed system contains two mechanically distinct units. One is linear and forms mutually interconnected elements, for which the classic approximate solution is sought. The other consists of non-linear elements that act in isolated spots of the structure, such as structural imperfection points or cracks. For the second type of elements the solutions are challenged through the non-deterministic theories of chaos [17] and Prigogine's type

of thermodynamics [68], or the non-linear dynamics systems [14,69] can also be considered. Beside the approximate solutions, the non-linear oscillators give evidence about the character of T_g and T_{cr} temperatures. The solids in glassy form have to contain irregularly separated structures [49] as the “fossils” of previous existence of highly non-linear oscillators. One important result is coming out from these assumptions already: the process of solidification of liquids into a glassy state contains by its character deterministic as well as non-deterministic elements. As the outcome of existence of non-linear elements the process of T_g transition is time-, history- and process (quenching)- dependent as the high amplitude, the highly non-linear oscillators switch their amplitude size and disappear upon cooling. It was shown in previous studies [49,53,64,69] that the number of linear elements connected together to form a solid blocks, will vary with temperature and will decline as the temperature grows.

f) Source of diffusion movements: non-deterministic elements

Our theory was introduced upon the assumption that the displacements, Δr , are infinitesimally small compared to the sizes of particles denoting thus the shape of potential valley. However, this is not always true when diffusion gets involved, so that the initial positions, r_0 , have to be conjectured as time-dependent. In such a case, the expression for the single potential valley takes on the extended form, $E_{on} \cong f_n \{r_{on}(t)\} \xi^2/2 - g_n \{r_{on}(t)\} \xi^3/3$, which is sometimes capable of instability. To manage such a situation, we can assume the case of boiling point, where the individual particles are escaping out of vibration modes. Here we have to assume that even the individual parameters, E_{on} , f_n and g_n , can traverse the discontinuity. We can adjust again the solution via the set of two first-order differential equations mentioned above, but it should be handled rather through a different technique of the so-called deterministic chaos [17,57,68,69].

The characteristic situations, corresponding to the potential well uplift and the agitated particle life sustenance or termination, are schematically shown in Figs. 7, where the discontinuity in parameter E_{on} is shown schematically. The most common feature of these highly non-linear oscillators is the “S” shaped double-valued amplitude with the bifurcations points where the vibration amplitude changes drastically its values. Consequently, the amplitude jump brings about the particle “push aside” effect, which increases the overall volume of the sample. Such linear particles are subsequently relaxed through the displacements of particles in linear blocks. The way of relaxation into linear blocks has been described mathematically long time ago and leads to exact account of relaxation times. The blocks become the source of continuity of micro-displacements of the particles and also of the predictability of mathematical solutions. Just opposite lies the logic of highly non-linear particles, where the trajectories in phase space depend on starting parameters of the system [70] and two infinitesimally separated points in phase space can lead to completely different trajectories, which are obtainable mostly

through numerical solutions. The most important conclusions, which result from the introduction of non-linear elements and which have an explanatory nature are

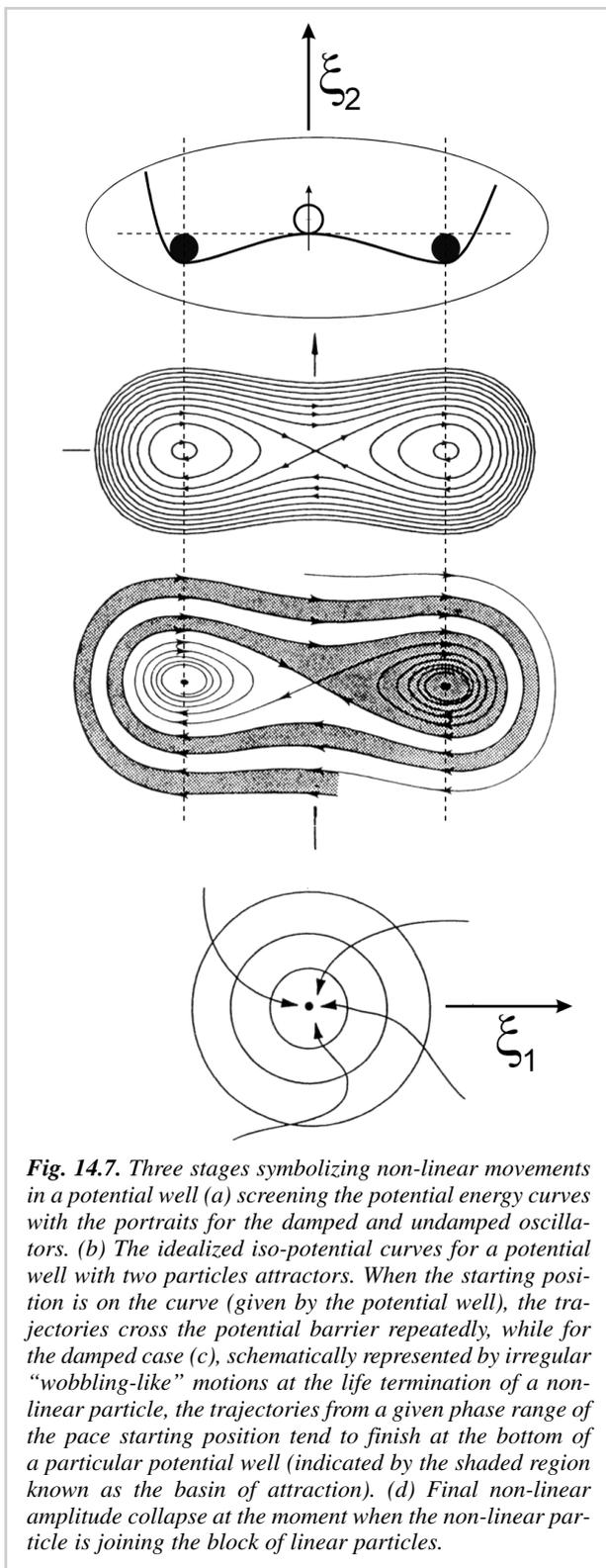
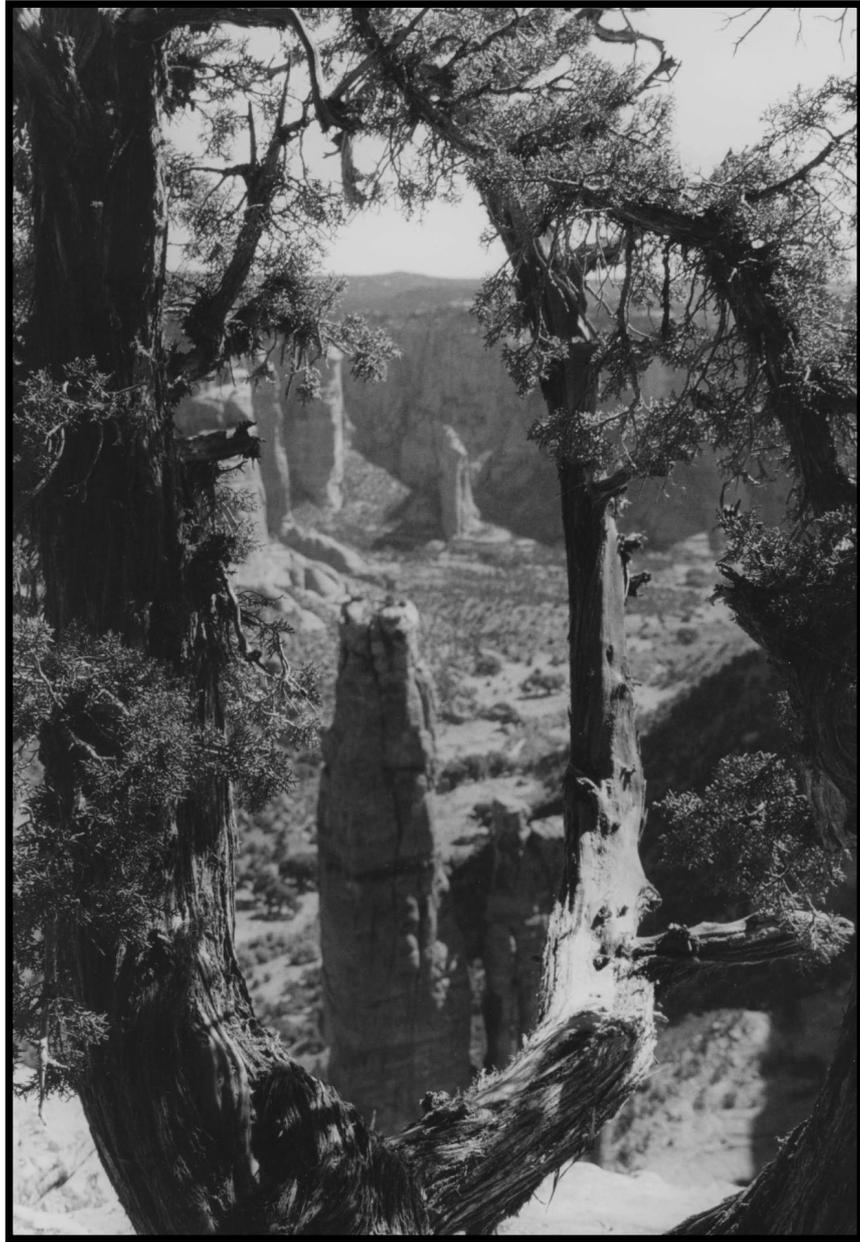


Fig. 14.7. Three stages symbolizing non-linear movements in a potential well (a) screening the potential energy curves with the portraits for the damped and undamped oscillators. (b) The idealized iso-potential curves for a potential well with two particles attractors. When the starting position is on the curve (given by the potential well), the trajectories cross the potential barrier repeatedly, while for the damped case (c), schematically represented by irregular “wobbling-like” motions at the life termination of a non-linear particle, the trajectories from a given phase range of the phase starting position tend to finish at the bottom of a particular potential well (indicated by the shaded region known as the basin of attraction). (d) Final non-linear amplitude collapse at the moment when the non-linear particle is joining the block of linear particles.

shown as follows. There will not be any identical motions of two non-linear oscillators in the sample. The two almost identical starting positions defined by ξ_0 , $(d\xi_0/dt)$ and r_{0n} , will not lead either to identical trajectory in coordinates ξ and $(d\xi/dt)$, or to equal displacements in Δr_{0n} . This feature is a general characteristic of non-deterministic theories of chaos [17,70]. Therefore, the voids, which are created when the particle undergoes the amplitude switch, would not have regular shapes, positions or ordered lifetimes, and would not occupy a regular space volume, either. It is possible to find from various experiments that the average voids above T_g are substantial, reaching the values as large as cubic nanometers. The non-deterministic character of glassy transition stems, therefore, from the presence of non-linear oscillators in liquid system at $T \geq T_{cr}$ all through the non-deterministic character of oscillations that disappear when the system is cooled down below T_g . The volume and thermal state of the sample entirely depends on the experimental processing, i.e., thermal history of investigational procedure performed. The irregular separation of particles in the glassy state is thus a necessity. As the solid material softens and the non-linear vibrating particles come to existence in vacancies, various mathematical views open for discussion. The non-linear particle can perform the vibrations within a certain limiting cycle to be characterized with a certain limiting figure or average values of occupied volume. Considering the non-linear particles, the vacancy volume or the energy associated with vacancy formation can be estimated. To form the vacancy space, the local free volume, which is smaller than critical volume, has to be created. In addition, the energy comparable with the fraction of evaporation enthalpy is needed. The sample is considered to be under an external pressure P_{ext} with a movable responding surface level. For temperatures $T \geq T_{cr}$ the size of the free volume locally created can indicate the validity of approximation, $E_{on} \cong \Delta H_{evap}/n$, where n stands for the ratio of the critical volume and *van der Waals'* volumes ($2 \leq n \leq 4$). Fig. 6 illustrates the ideal creation of vacancy by the action of symmetrical well which is restructuring through a sudden annihilation of high amplitude. For $T \leq T_{cr}$, the effect of elastic bridging has to be considered; for the case of elastic bodies and for spherical-type vacancies, *Frenkel* [71] gave the formula for the elastic energy of vacancy formation as $E_v = 8 \pi G r_0 \Delta r_0^2$, where G is the shear modulus, Δr_0 is the size of the opening and r_0 is the approximate radius of a particle. By combining the action of an elastic force with a viscous force we can get the expression for the energy increase of the well potential bottom uplift in the range of temperatures $T \leq T_{cr}$, i.e., $E_{on} \cong \Delta H_{evap}/n + E_v$. For the temperature range below T_{cr} , where the shear modulus, G , grows from the zero level to the glassy state level, the distance, Δr , characterizing the enlargement of the vacancy volume becomes smaller as E_{on} approaches zero for the pattern of solid blocks.



CHAPTER FIFTEEN

15. Advanced evaluation of processes – disequilibria and dendritic growth

a) Classical kinetics and non-equilibrium thermodynamics

As shown in detail in Chapter 12, reaction dynamics of processes involving solids are extensively studied by methods of thermal analysis and there is a vast amount of data published on such kind of “non-isothermal” kinetics of solid-state processes [72,73], frequently treated on the basis of oversimplified modeling. It became a subject of criticism and discussion, which we do not want to repeat, other than stressing that real solid-state reactions are often too complex to be described in terms of single pairs of Arrhenius parameters and a traditional set of simple reaction orders, discussed in Chapter 8.

In the view of our thermoanalytical practice, the expected results in terms of functions instead of the traditional constants would, however, be quite unfamiliar, but we need to get acquainted with them when facing the new prospects of the 21st century. In fact, it would be a better way to match the real thermal state dynamics than to use the old representation in terms of customary and almost “religious” constants [73], mostly linked with the activation energies that never express the ease of reaction (to be desirably related to the reactivity as a kind of “tolerance” and to the reaction mechanism as a kind of “annexation”). High values of activation energies are often misleading when determining the character of the process investigated, because high values do not mean difficult reactivity (typical for spontaneous and rapid exothermic crystallization) and low values do not imply easy reactivity (e.g. habitual for slow diffusion-controlled processes). The traditional interpretation is exactly the opposite, the best example being the repeatedly studied case of the reversible CaCO_3 decomposition, which is strongly mass- and heat-flow dependent (CO_2 partial pressure and through-diffusion), creating the concentration gradients within the solid samples. Gradient-insensitive (related classically) kinetic evaluation thus can generate the numberless figures of somewhat insignificant values of activation energies strongly dependent on the experimental conditions applied (but often not refined or adjudicated).

However, the modern mathematical tools of thermal physics [48,74] make available powerful theoretical models associated with the true reality of natural processes that are never at equilibrium nor without gradients by appreciating the decisive role of thermal fluxes. In the scientific intent (often directed to generate publications based on non-isothermal kinetics), this approach has not yet been applied, but in the more urgent technological processing, such as industrially significant arc melting or welding, its adoption became a real necessity to overcome manufacturing difficulties. In particular, we can generally assume that at some distance from the reaction zone where the solidification is taking place, the molten material undergoes irregular (turbulent) motion. It creates a mushy zone consisting of cascade of branches and side branches of crystals and interspatial melts, that remains lying between the original reactant (fluid) and the product

(fully solidified region). Some chemical admixtures of the alloy solution are concentrated in the interspatial regions and ultimately segregated in the resulting microtexture pattern. Such a highly irregular microstructure of the final solid can become responsible for alternative properties, e.g., reduced mechanical strength that is a costly factor thus worthy of active search as to resolve the intricacy of the processes involved. It follows that small changes in the surface tension, microscopic temperature fluctuations or non-steady diffusion may determine whether the growing solid looks like a snowflake or like seaweed. The subtle ways in which tiny perturbations at the reacting interface are amplified then become important research topics bringing necessarily into play higher mathematics. The challenge of theorists turns out to be the prediction of spacing of the final crystalline array, which requires computations:

- (i) how the initially stationary flat interface accelerates in response to the moving temperature gradient, how local concentrations (e.g., impurities) adjust to this motion,
- (ii) how the flat interface destabilizes, fluctuates and becomes branched,
- (j) how the resulting crystalline twigs interact with each other and
- (jj) how the branched array coarsens and ultimately finds a steady-state configuration.

In every detail, it is not an easy task at all.

A real solid-state reaction under thermoanalytical investigation, even those most ideal one, is intrinsically more complicated than most of us would like to believe. As emphasized above, we will have to deal with these complications, usually caused by actual localization of generated heat, liquids and gases (or other freely moving products) if we are to achieve new levels of performance. The conceptual underpinnings for much of our more advanced perception of phase transformations have thus to use complicated mathematics that is curiously employed to describe both the pattern formation in crystal growth and the so-called symmetry breaking (the origin and distribution of elementary particles in the early Universe). Therefore, such an intricate approach is not too welcome in the ordinary practice of chemical kinetics and its further application to daily kinetic evaluations has not been assumed yet. We can try to point the direction where the theory should go, but, unfortunately, we are yet unable to show the practical way how to actually bring it in the challenge of incorporation of all fluxes. However, the solution thus represents the imminent task for both the advanced researches to take part during this new century and the newly educated generation of young thermodynamicists to undertake it.

Our theory proposed above in Chapter 6, which is based on near-equilibrium thermodynamics, is applicable to thermal treatment and analysis only if a constant heating is assured, which assumes straightforward heat interaction between the sample and a regulated thermostat. It does not involve the actual effect of heat liberated and/or absorbed by the reacting sample itself. Hence, it is necessary to extend it to areas so far not commonly applied in

the traditional domain of thermal analysis, although it is most pertinent to its feature of “real heating and/or cooling” phenomena (where the second derivatives can often be non-zero). Moreover, classical sphere of thermodynamic definitions of stability is inapplicable to the determination of the morphology of growing interfaces, and current extensions have not yet furnished a fully acceptable alternative. The simplest assumption made is that the morphology that appears is the one, which has the maximum growth rate and/or minimum undercooling (or, less commonly, overheating).

Disregarding the initial process of new phase formation (nucleation) the kinetic models are described in terms of the overall atom attachments to the reaction interface due to either chemical reaction (bond redistribution steps) or interfacial diffusion (reactant supply). A stabilized (steady) state is taken for granted neglecting, however, directional changes (fluctuations). The physico-geometrical models [72,73] also neglect other important factors such as interfacial energy (immediate curvature, capillarity) and particularly internal and/or external transport of heat and mass to and from the localized reaction boundary, which may result in the breakdown of planar

reacting interface, and which anyhow, at the process termination, are responsible for complex product topology. Various activated disturbances are often amplified until a marked difference in the progress of the tips and depressions of the perturbed reacting interface occurs, making the image of resultant structures irregular and indefinable, see Fig. 1. This creates difficulties in correlating traditional morphology observations with anticipated structures that are usually very different from the originally assumed (simple, planar) geometry. Depending on the directional growth conditions, so-called *dendrites* (from the Greek ‘*dendros*’ = tree) develop, their arms being of various orders and trunks of different spacing due to the locally uneven conditions of heat supply. This process is well known in metallurgy (quenching and casting of alloys), water and weather precipitates [75] (snow flakes formation, crystallization of water in plants) but also for less frequent types of other precipitation, crystallization and decomposition processes associated with dissipation of heat, fluids, etc.

It is always interesting to see how far the use of above-mentioned classical methods can be extended into this non-equilibrium situation [76–80]. Growth rates, under-

coolings and supersaturations, are closely related by the functions whose forms depend upon the process controlling growth (the chemical reaction involved in the atomic attachment, heat and electrical conduction or mass and viscous flow). In each case, the growth rate increases with increasing degree of undercooling and the perturbation on the reaction interface can be imagined to experience a driving force for such an accelerated growth that is usually expressed by the negative value of the first derivative of the Gibbs energy change, ΔG , with respect to the distance, r . For small undercooling, we can still adopt the above-mentioned concept of constancy of the first derivatives, so that $d\Delta G$ equals to the product of the entropy change, ΔS , and the temperature gradient, ΔT , which is the difference between the thermodynamic temperature gradient (associated with transformation) and the heat-imposed gradient at the reaction interface as a consequence of external and internal heat fluxes. Because ΔS is often negative, a positive driving force will exist to allow perturbations to grow, only if ΔT is positive. This pseudo-thermodynamic approach gives the same result as that deduced from the concept of zone constitutional undercooling [81] and its analysis is important for the manufacturing of advanced materials such as fine-metals, nano-composed assets, formation of quantum low-dimensional possessions, composite whiskers, tailored textured configurations, growth of oriented biological structures, processes

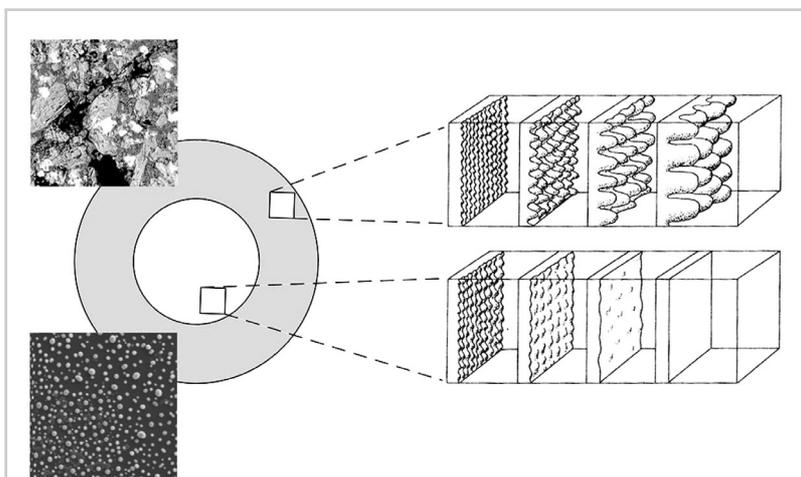


Fig. 15.1. Portrayal of the initial evolution of unstable and stable interfaces when imagining a planar section of a reacting sample interface (middle). During propagation, any such an interface will become a subject to random (spatially regular) disturbances caused by temperature fluctuations, variations of grain boundaries, curvature, insoluble subdivisions, concentration fluctuations, energy irregularities, etc. An unstable interface (upper row) is distinguished from a stable interface (lower row, traditionally assumed in all physical-geometrical modeling) by its response to such disturbances. Projections may find themselves in a more advantageous situation for growth and therefore increase in prominence. Shadow area of the left magpie can represent either the customarily, plainly projected and homogeneously layered product or, in our view, perturbation favored, heterogeneous and thus morphologically vastly structured growth outcome. This is usually best manifested during the casting of alloys, and/or for rapid quenching in general, where a stable interface is only obtained in special cases, such as at the columnar solidification of pure metals or directional solidification during pulling single crystals by the stabilized methods by the Bridgman or Czochralsky technique (cf. Fig. 10. 5.). It seems to operate for all transformations carried out at high rates of cooling/heating, or latent heat extraction/production, where the cooperative outcome of heat, mass (including decomposition products) and viscous (tension) flux initiates local instabilities. We can also meet it in everyday events of snowflakes formation – cf. Fig. 13.5.

involving water freeze-out (in, e.g., cryopreservations) etc. and thus it is worth of more detailed examination.

b) Accounting on multiple fluxes

The local increase of entropy in continuous systems can be defined by using the local production of entropy density, $\sigma(\mathbf{r},t)$. For the total entropy change dS , consisting of internal changes and contributions due to interaction with surroundings, i and e , we can define the local production of entropy as $\sigma(\mathbf{r},t) \equiv d_i S/dt \geq 0$. The irreversible processes obey the *Prigogine* evolution theorem about the minimum of the entropy production [68]. In most real situations, we can assume local equilibrium, where thermodynamic relations remain valid for the thermodynamic variables assigned to an elementary volume ΔV . With each extensive quantity, X , we can associate a density (quantity per unit volume) through the function $x(\mathbf{r},t)$ dependent on position, \mathbf{r} , and time, t , $x(\mathbf{r},t) = \lim_{\Delta V \rightarrow 0} \{X(\mathbf{r},t)/\Delta V\}$.

For the total value of the extensive quality $X(t) = \int_V x(\mathbf{r},t) d\mathbf{r}$, where the space integral, \int_V , extends over the volume, V , occupied by the system under study. By manipulating various factors that influence the rate of change of $X(t)$ in a non-equilibrium system, we can obtain a balance equation for the density $x(\mathbf{r},t)$ by specifying hydrodynamic derivatives (d/dt a total time derivative) thus maintaining the view of continuum mechanics. The general balance of $x(\mathbf{r},t)$ has the form $dx/dt = -\nabla \cdot \mathbf{j}_x + \sigma_x$, where σ_x is density of the source of value x , and \mathbf{j}_x is the non-convective (dissipative) part of the flux of a particular x (e.g. diffusive flux, thermal flux, viscosity flux, etc., namely the fluxes responsible for the actual condition of a given region of the reacting interface) [76,80].

In the case of the mass balance we have: $d\tau/dt = -\nabla \cdot \pi_i \mathbf{u}_i + v_i$. For the energy balance (comprehended as a local form of the first law of thermodynamics) it provides: $\pi dE/dt = -\nabla \cdot \mathbf{j}_E + \pi q$. The involved parameters traditionally read: π is the total mass density and π_i is the

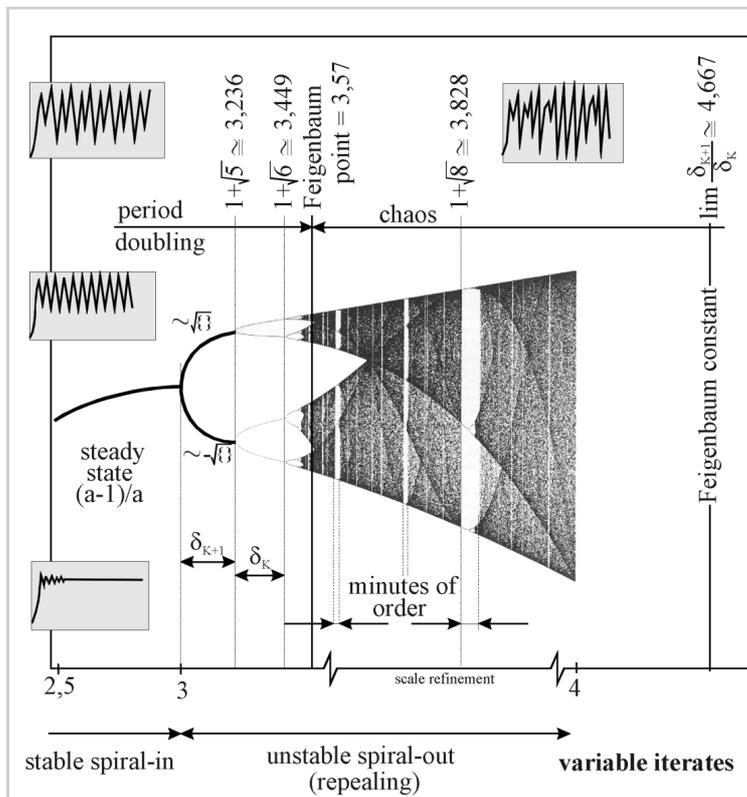


Fig. 15.2. Final-state bifurcation diagram (or the so-called Feigenbaum diagram), which is the one of most important icon of chaos theory. Through the studies of the quadratic iterator, $x_{n+1} = a x_n (1 - x_n)$ (for n gradually amounting to 1, ... 3, ... i), both antagonistic states of order and chaos can be ruled by a single law regarding the effect of multiplying constant, a (compare previous Fig. 13. 7.). The essential structure subsists two branches bifurcating, and out of these branches another two branches bifurcating again, and so on, providing the period-doubling regime. The periods are initially even (2, 4, 8, 16, ...) followed by disordered cycles of chaos exhibiting with its increasing complexity the windows of stable periods of order characterized by odd integers. It is

continued by duplicated even period (6, 12, 24, ...) and so on, with incessant and infinitesimal depth. Factually, shadowed band of chaos is regularly interrupted by white window of order where the final state again collapses to only few points, corresponding to the attractive periodic orbits. Points seem to condense at certain lines which border bands that encapsulate the chaotic dynamics ending at $a = 4$ with a single band spanning the whole unit interval. There are an infinite number of such windows, the one between $3.828 < a < 3.857$ being the most prominent one characterized by 3 (and followed by 5, 7, 9, etc., the period-9 window already hard to find), which can be found in the reversed order (i.e., 3 right of 5, etc.). We can easily discover its inherent self-similarity as we can see smaller and smaller copies of the whole bifurcation diagram finding the complete scenario of period-doubling, chaos, order and band splitting again, however, on a much smaller scale.

Literally, bifurcation moves from the stable state to the period-doubling regime (cf. Fig. 13.7.) where the length of bifurcating branches became relatively shorter and shorter following certain geometric law (i.e., self-similarity of the quadratic iterator, where the vertical values in the first and third magnification are reversed to reflect the inversion of previous diagram). The parameter, a , beyond which the branches of the tree could never grow marks the period-doubling regime. This threshold became known as the Feigenbaum point (the limit of rectangles sequences is reaching the value of 3.5699456...), which factually splits the bifurcation diagram into two distinct parts of (period-doubling) order and utter chaos. There is a rule that quantifies the way the period-doubling tree approaches the Feigenbaum point. Measuring the length of the two succeeding branches in the a -direction the ration turns out to be approximately 4.6692. This number is called Feigenbaum constant and its appearance in many different systems was called universality (to have the same fundamental importance of numbers like π or $\sqrt{2}$).

partial mass density of the i -th subsystem. Some other appropriate fluxes like the momentum density, $\pi_i \mathbf{u}_i$ (for individual velocities \mathbf{u}_i which principally also include diffusion) or the heat flux \mathbf{j}_E , and those expressing the presence of sources or sinks, like rates of chemical reactions v_i or density of supplied heat, q , may also be included. In this generalized thermodynamic view, the notion of irreversibility is of utmost importance and a local field derived from entropy must again obey the *Clausius* inequality. The temporal change of the total entropy S in some subsystem is due to both the interaction of the system with its surroundings (the entropy flux $d_e S$) and the internally produced entropy ($d_i S$). Moreover, $dS - d_e S = d_i S > 0$ and in a like manner as above we may write a local form of the second law of thermodynamics as follows: $\pi dS/dt = -\text{div } \mathbf{j}_S + \sigma$, where \mathbf{j}_S and σ are the entropy flux and the entropy production per unit volume, respectively.

Let us consider the extension into the range of non-linear phenomenological laws where the balance equations hold a general form, $d\Phi_i/dt = f_i(\{\Phi_i\}, \psi)$, where Φ_i and f_i are the shorthand notations for the state variables and rates, respectively. In general, f_i are functionals of $\{\Phi_i\}$ because they contain the effect of space derivatives. The symbol ψ stands for a set of parameters that may enter in the description to define the process. Within the framework of linear non-equilibrium thermodynamics, the mass and entropy balance equations would give certain forms for, f_i , which are summarized in Table I illustrating the various type of fluxes, that can be involved [76,82].

Table 15.I: Fluxes and forces corresponding to irreversible phenomena.

Process	Flow/current	Generalized force	Tensor character
Chemical reaction	Reaction rate, w	A_r/T	Scalar
Heat conduction	Energy flow, \mathbf{J}_E	$(\nabla T/T)$	Vector
Mass transport	Diffusion current \mathbf{J}_M	$-(\nabla \mu_i/T)$	Vector
Electrical conduction	Ion current \mathbf{J}_k	$-\nabla(U/T)$	Vector
Viscous flow	Stress tensor \mathbf{P}	$-(\nabla \mathbf{u}/T)$	Tensor

∇ represents the gradient of the appropriate function, i.e., it means the vector which components are derivatives of the space coordinates x , y and z , μ_i is the chemical potential of the i -th component, A_r is the affinity and U is the potential of the electric field.

The entropy flux $\mathbf{j}_S = \mathbf{j}_E/T - \sum_a \mathbf{j}_i \mu_i/T$ and the entropy production take a remarkable bilinear form $\sigma = \sum_a J_a X_a$, where J_a and X_a are conjugate variables known as generalized fluxes and forces associated with the various irreversible processes (see also Table I). *Generalized forces can be viewed as the driving forces for irreversible phenomena that are manifested through the fluxes (e.g., a temperature gradient is associated with a heat flow).* Such gradients may arise transiently, or be maintained

systematically, by appropriate boundary conditions (constraints) applied on the surface of the system studied.

For the local formulation of irreversible processes, it is necessary to see how the fluxes J_a (which in principle are unknown quantities) are related (if at all) to the forces X_a , which, according to Table I, are known functions of the state variables and their gradients. (We should note that the above-mentioned classical equilibrium is characterized by the absence of both the macroscopic constraints, $X_a^{eq} = 0$ and the traveling fluxes $J_a^{eq} = 0$).

In the linearity range of irreversible processes, the phenomenological *Onsager coefficients*, L_{ab} , are determined by the internal structure of the system, independently of the applied constraints (but dependent on the state variables $X(t) = f(T, P, \dots)$ yielding $\mathbf{j}_a = \sum_b L_{ab} X_b$ where $L_{ab} = (d\mathbf{j}_a/dX_b)_0$, fulfilling $\sigma = \sum_{ab} L_{ab} X_a X_b > 0$. Assuming reversed velocities, the reciprocal relation, $L_{ab} = L_{ba}$, is obeyed, which is useful in studying coupled phenomena like thermodiffusion, thermoelectricity or thermoelectromagnetic effects.

An important issue of dynamic equations is the stationary solution, which describes the state of the system that is independent of time. The answer to the question of how this state remains stable during the action of small fluctuations of physical values (fluctuations are usually damped with time), lies in the criteria of stability. Linearized stability asserts asymptotic stability around its reference state, e.g., $X_i = X_{i,ref} + dX_i$ (for $dX_i/X_i \ll 1$) and, expanding for small dX_b , we obtain, in abstract notation, $d\{\mathbf{dx}\}/dt = \mathbf{L} \mathbf{dx}$, where \mathbf{L} is a linear operator and the problem is solved by determining so-called 'eigenfunctions' and 'eigenvalues' of \mathbf{L} , and the unseen characteristic parameters m . The reference state is asymptotically stable for most m . However, for some m , the solution of such a thermodynamic branch is unstable and, for critical values of ψ_{crit} , *bifurcation* appears; in other words, several quite different evolutions of the system are possible and often realized depending on ψ in a non-analytical fashion as a special domain of non-linear mathematics, discussed in the preceding Chapter 13. The detailed bifurcation graph and characteristic points are shown in Fig. 2.

c) Stereology aspects

In a special case of non-isothermal reaction kinetics, regularly involving solid-state processes, the rate equations are often solved almost naively by analogy with (apparently gradientless) homogeneous reactions [72,73]. Various oversimplified approximations (as mentioned above, where reacting particles are often assumed to be regular bodies – circles or spheres, regardless of their true morphology) are introduced that, however, never match the results of traditional morphology observations, usually obtained by optical or electron microscopy (cf. Fig. 10.11). This is worth of similar attention, being related to the above-discussed case of disregarded gradients of temperature and concentration. This simplification aspect is often neglected, although very important, because we have to keep in mind that all possible images (postulated geometrical models or real structures seen on a screen, or otherwise observed) are only two-dimensional represen-

tations of the real three-dimensional structures. For a more objective evaluation of the numerical characteristics of real geometrical bodies we, therefore, have to employ so called *stereology*, understood here as integral geometry [83].

Invariant measures of the internal configuration of a multiphase body (where individual phases A, B, \dots internally form three-dimensional structures must fulfill three basic criteria: invariance of *motion*, *additivity* and *monotony* which corresponds to a mathematical hypothesis based on the four *Minkowski* functionals [83] (quer-mass-integrals or measures) abbreviated as W^3_i . These measures have, for each i , a definite practical meaning, i.e., volume of A , W^3_0 , mean area (surface), W^3_1 , length, W^3_2 and number of disjunctive features of A (e.g. number of opened against closed structural holes), W^3_3 , needed for a global geometrical characterization M . It follows that $M^3_i(A) = \sum c_i W^3_i(A)$ where each $W^3_i(A)$ is a homogeneous functional of the root $(3 - i)$ and $M^3_i(A)$ is then a monotonous functional ($c_i > 1$). For actual calculations, the two-dimensionally screened images can be used bearing in mind, however, that these evaluations are only statistical. The solution is based on the utilization of so-called symmetrical functions of curvature, $C^3_{i=1,2,3}$, providing the relations for mean curvature ($C^3_0 = 1$), *Gaussian* curvature ($C^3_1 = (k_1 + k_2)/2$) and fundamental curvature ($C^3_2 = 1/(k_1 k_2)$), where $k_1 = 1/\pi_{\min}$ and $k_2 = 1/\pi_{\max}$ are the main curvatures for minimal and maximal

Measure of structure, A	Section by random probe, L^3_i		
	Plane, L^3_2	Line, L^3_1	Point, L^3_0
Volume V_3	A_2	L_1	P_0
Surface S_2	B_1	I_0	
Length D_1			

It is clear that introduction of the actual state of the system, either real body structures or imposed gradients, is not easy. The introduction of legitimate non-equilibrium phenomena in the non-linear range leads to new regimes differing quantitatively from the „reference“ stationary states of regular equilibrium or near-equilibrium descriptions.

d) Dissipative structures

The question that arises is, therefore, whether the move away from a standard configuration can lead to states displaying spatial or temporal order. We call these regimes *dissipative structures* [77,84] to show that they can only exist in conjunction with their environment. It is worth repeating that if influence constraints are relaxed and the system is allowed to approach equilibrium, the entire dissipative organization will collapse. These structures can form only in *open* systems far from equilibrium and dynamic equations have to be non-linear. The best example comes from fluid dynamics when a horizontal fluid layer is heated from below, for details see the next Chapter 16.

Let us analyze the simplest cases of bifurcation, cf. Fig. 2. Upon involving two or even more variables in connection with spatially inhomogeneous systems, the higher-order non-linearity gives rise to more complex phenomena. The best examples are systems controlled by simultaneous chemical reactions and mass diffusion. Their evaluation must be completed by additional assumption that the diffusion flux, \mathbf{j}_i , is approximated by *Fick's Law*, as a special form of the linear phenomenological laws listed in Table I, that is in particular, $\mathbf{j}_i = -D_i \nabla \pi_i$, where ∇ is the above mentioned space derivative and D_i are the

diffusion coefficients, which are in the first approximation assumed constant. The associated reactions rates, w_π , are (generally non-linear) functions of the concentrations (often in a cubic manner). This gives rise to the following evolution equation, $d\pi_i/dt = v_i(\sum \pi_i, \psi) + D_i \nabla^2 \pi_i$, where ψ denotes again a set of parameters descriptive of the system (e.g. initial composition, cooling rate, undercooling, characteristic lengths, etc.).

When $\psi = \psi_{\text{crit}}$, the state of the system may change dramatically causing the symmetry breaking in space and time. From the mathematical point of view, the system becomes localized at the thermodynamic branch and the initially stable solution of the appropriate balance equation bifurcates. New stable solutions suddenly appear and may overlap. One possibility is time-symmetry breaking,

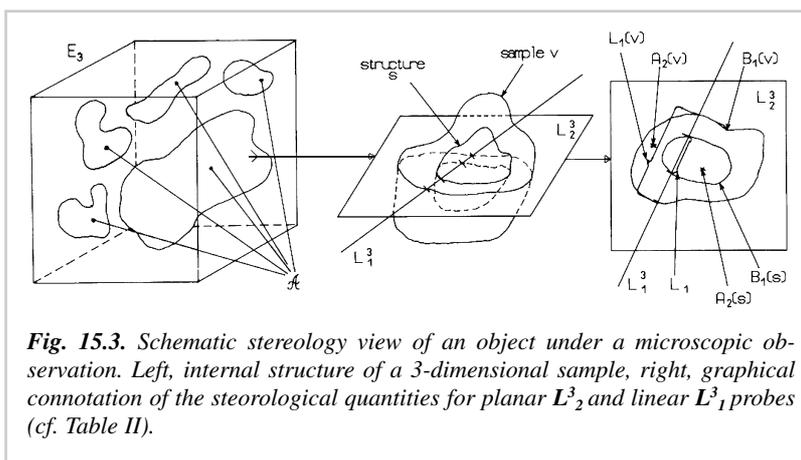


Fig. 15.3. Schematic stereology view of an object under a microscopic observation. Left, internal structure of a 3-dimensional sample, right, graphical connotation of the stereological quantities for planar L^3_2 and linear L^3_1 probes (cf. Table II).

radius of the oscillation circles in a given infinitesimal element of the measured phase surface ∂A . Objective proofs of stereological relations are difficult, but the resultant relations reveal surprising simplicity. A convenient universal relation is based on the so-called *Kubota's* recurrent formula [83] showing that $W^3_0(A) \Rightarrow V(A)$ (i.e., approaches the n -dimensional volume of A in the sample space E), which is the mean value of the W^{n-1}_{i-1} for all projections of the phase A onto the linear subspace with a lower dimension $(n-i)$, providing more generalized values of constants $\sigma_{0,1,2,3} = 2, 2\pi, 4\pi$ and $2\pi^2$. From measurements in a random section (planar or linear probes or random points) of the investigated structure, we can obtain a concrete measure of the induced structure as follows, which is illustrated in Fig. 3.

associated with the merging of time-periodic solutions known as limit cycles whose period and amplitude are stable and independent of the initial conditions, cf. Fig. 2. Their importance lies in the fact that they can constitute models of rhythmic phenomena commonly observed in nature, particularly assuming biological or chemical clocks. Cascading bifurcations are also possible. This opens the way to a gradual increase of complexity by a mechanism of successive transitions, leading either to the loss of stability of a primary branch and the subsequent evolution to a secondary solution displaying asymmetry in space similar to stable rotating waves, as observed in the classical *Belousov-Zhabotinsky* reactions, see next Chapter 16. Such transitions are sometimes accompanied by some remarkable trends, e.g., certain classes of reaction-diffusion systems under zero-flux boundary conditions, may exhibit no net entropy production change when the system switches from the thermodynamic branch to a dissipative structure. On the other hand, there is a systematic decrease in entropy in the vicinity of bifurcation points. Associated fields are the theory of chaos [9–11] and fractals [12–16] even touching some aspects of the prediction of weather [75,85].

One of the most practical applications is the highly non-equilibrium crystallization of largely supersaturated solutions or, as mentioned above, any speedy solidification of rapidly quenched materials (typically alloys). They use to exhibit a free dendritic growth, i.e., unconstrained development of curious shapes of crystals precipitating within changing concentration or temperature gradients (mostly met in the undercooled melts). This phenomenon has long been known in the technology of the crystal growth and melts casting and is exemplified in the formation of the so called ‘cellular structures’ [86]. Explanation of these complex phenomena is usually done in terms of constitutional undercooling, ΔT , and its thermodynamic meaning is associated with the local equilibrium temperature of the melt solidification in an arbitrary point near the solidification front. It corresponds to a local concentration in the melt, which is higher than that for the actual temperature in the same point. Consequently the disturbances (perturbations, fluctuations and/or oscillation) of the solidification front spontaneously increase and the phase interface become unstable and tortuous (cf. subsequent Figs. 5 and 6).

e) Interface stability, perturbations and oscillatory modes

Under the linear theory of stability we understand the stability of equations, which describe the steady-state or equilibrium-like system, i.e., the balance of heat and mass equations with the boundary and with the initial conditions, which are adjusted to be even at the phase front (often solidification interface). The stability is enumerated with respect to arbitrary small perturbations, i.e., the higher powers of amplitudes of this perturbations are neglected. If for the same perturbation the interface growth is preferred and its amplitude increase with time, the phase interface become unstable with respect to this perturbations.

The methods of the perturbation analysis were introduced into crystal growth theory by *Mullins* and *Sekerka* [87]. The stability of a spherical object growing either from the solution or from the melt was thoroughly investigated and the deviation from the spherical form was expressed in terms of a spherical harmonic function $Y_{lm}(\theta, \varphi)$. Cartesian co-ordinates (θ, φ) were parameterised for the given spherical interface, r . Assuming that the principle of the local thermodynamic equilibrium is satisfied and the possible anisotropic property of phase front and the kinetics of phase transformation are not involved the perturbation is possible to calculate using the relationship

$$r = r_0(t) + \varepsilon(t) Y_{lm}(\theta, \varphi) \quad 1$$

where r_0 is the radius of the unperturbed sphere at $t = t_0$, r is the distance of the perturbed surface from sphere centre and $\varepsilon(t)$ is the time-dependent amplitude of the perturbation fulfilling conditions of $\varepsilon(t)/r_0 \ll 1$. The stability of growing sphere is determined by $\partial\varepsilon(t)/\partial t > 0$, which enables perturbations to be amplified inducing thus possible instability in the growth process, i.e., potential departure from the initially spherical shape. The perturbation rate of changes depends on two competitive mechanisms: the destabilising effect of diffusion (which is presented by the normal component of the concentration gradient of e.g. impurities at the unperturbed interface) and the somehow stabilising effect of the surface

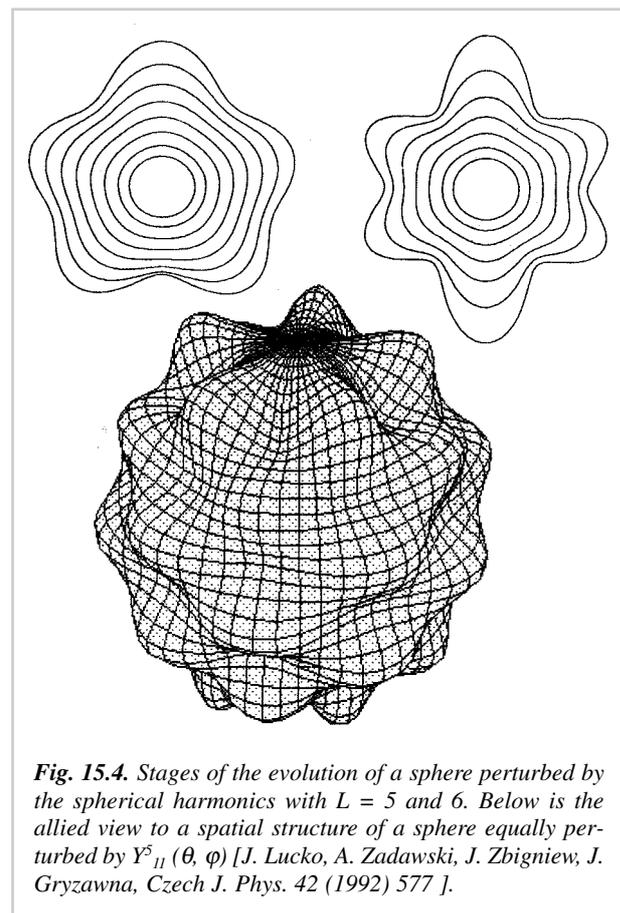


Fig. 15.4. Stages of the evolution of a sphere perturbed by the spherical harmonics with $L = 5$ and 6. Below is the allied view to a spatial structure of a sphere equally perturbed by $Y_{ll}^5(\theta, \varphi)$ [J. Lucko, A. Zadawski, J. Zbigniew, J. Gryzawna, *Czech J. Phys.* 42 (1992) 577].

tension. *Mullins* and *Sekerka* [87] figured the growth conditions upon the expansion with the accuracy to terms of the first order:

$$r_c(L) = \{(L+1)(L+2)/2 + 1\} r_{crit} \quad 2$$

where r_{crit} is the critical radius of the nucleus and $r_c(L)$ is the critical radius of the sphere corresponding to the L -th harmonics of the perturbation, see Fig. 4. This condition implies that such growth is feasible for $r < r_{crit}$, for example, the growth process become unstable when the radius of the solid phase is about seven times larger than the radius of the critical nucleus for the second harmonics (i.e., $L = 2$). For concreteness, the sphere with the radius of 10^{-7} [m] is unstable for a 10% supersaturation and for typical values of the surface tension. This analysis was extended by *Wey*, *Gautesen* and *Estrin* [88] who used the standard model [87] but modified it by the addition of time-dependent diffusion equation. For dilute solutions they obtained a similar criterion of stability but now presented in terms of surface tension, σ_T , density of heat fusion, Q_T , temperature conductivity coefficients, Λ_T , for the melt (M) and solid (S), melting temperature T_M and the undercooling, ΔT , at the solidification front, $T_M - T_\infty$ [56]. When the radius of the sphere reaches the critical value, r_{crit} , the growth of the sphere becomes unstable.

Such case typically happens for metals when the deviation from the spherical form of a radius is about 10^{-7} [m] and relative undercooling exceeds 10%.

The morphological stability near the grain boundaries of the interface [87] of pure and/or binary systems can turn out to be effective, too. It was found that the melting interface is more stable against perturbations than the solidifying one. The measure of the stability of these two processes differs by the reciprocal quantity of the distribution coefficient, $1/K_c$, for given concentration, c , and the growth velocity, v . The critical wavelength, λ_{crit} , corresponds to minimal undercooling at the solidification front in the form of $\lambda_{crit}^2 \cong \Delta c \lambda_s / v$, where λ_s is the capillarity length [89]. It give rise the lamellar eutectics solidification [86] (cf. Fig. 16.4) and involves the existence of a short-wave oscillatory instability for the case of the off-eutectic concentrations of the melt. This unstable behaviour leads to the transition from lamellar to the dendritic growth mechanism.

The associated theories based on the competition of thermal and mass fluxes aim to help the determination of the growth rate of dendrites under given technological conditions¹, specification their orientations and even model their size regarding the radius of dendrite tips, r_m . The balance equations describing the evolution of the appropriate field functions are often scaled in terms of

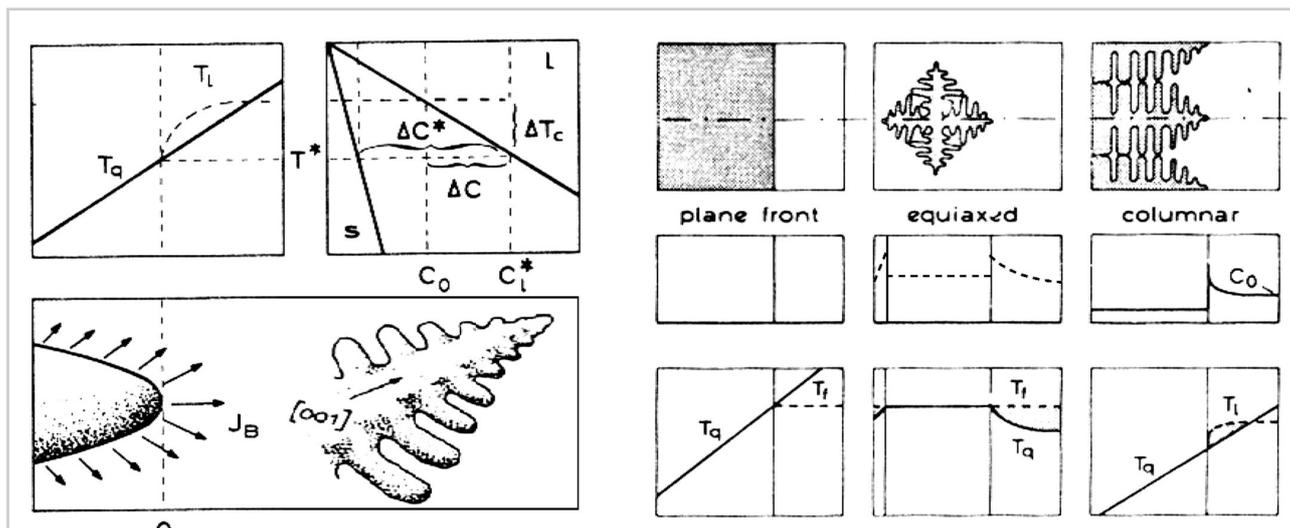


Fig. 15.5. Conditions of dendritic growth where the right diagrams illustrate the reacting front geometry (upper), temperature (bottom) and concentration (middle) fields, resulting in dendrite growth. T_q is the temperature field in the system, T_f is the equilibrium temperature of solidification, T^* is the growth temperature, T_l is the temperature of liquidus, C_0 is the concentration in the liquid phase, ΔC^* is the supersaturation (as a length of the tie-line at the temperature tip), G is the temperature gradient and mG_c is the gradient of liquidus (l). In pure substances with planar ($C_0=0$ and $G>0$) or equiaxial ($C_0=0$ and $G<0$) front, dendrites can grow in an undercooled melt only. The necessary condition of dendritic growth in binary systems is a constitutional undercooling, illustrated for both the columnar (dashed, $C_0>0$ and $mG_c>G>0$) and equiaxial ($C_0>0$ and $G<0$) conditions. When a positive gradient of temperature ($G>0$) is imposed (such as directional columnar solidification) the latent heat is transported together with unidirectional heat flux into the solid (s). When heat is extracted through the solid, the solute diffusion will be the limiting factor only. ΔT_c , see phase diagram left, factually provides the degree of supersaturation, $\Delta C/\Delta C^*$, but its determination is also a function of other parameters and requires its evaluation by a set of differential equations. The simplest solution is obtained when the tip morphology is supposed to be hemispherical; instead, the real form of the dendrite tip is best represented by a paraboloid of revolution. Due to the anisotropy the dendrite will grow in the preferred crystallographic direction which is closest to the heat flow, J_B , whereas cells grow with their axes parallel to the heat flow direction without regard to the crystal orientation (e.g., marked $[001]$). In the opposite case of one component system, the heat is rejected at the interface of a tip into the liquid phase. Consequently the equiaxial dendrites emerge in solid phase.

three independent parameters. They involve the undercooling (or supersaturation) and the critical undercooling wavelength (λ_{crit}) of the melt at solidification front and the so-called *Peclet* number [56,89], which is equal to the ratio between the characteristic length of the system (e.g., tip radius r_{max}) and diffusion length. The latter equals to the ratio of the heat conductivity coefficient and the velocity of solidification front motion. For small *Peclet* numbers, we can approximately say that product of the square root of the tip radius with its growth rate is roughly constant, which means that the slowly growing and broad dendrites tend to split up, whereas the sharp dendrites incline to broaden in consequence of unstable side-branches. The surface tension can be understood to be the selective mechanism: is stabilising the dendrite tip against perturbations and strongly influences the sidebranching instability. The initial sidebranching, r_{in} , is thus related to the growth rate by simple relationship, $r_{in} \sim 1/\sqrt{v}$.

f) Chaotic-like case of dendritic growth

The formation of a dendrite begins with the breakdown of an unstable planar solid/liquid interface (cf. Fig.1). Perturbations are amplified until a marked difference in growth of the tips and depressions occurs. The temperature gradient must be deformed in the liquid at the tip increases, while that in the solid decreases, cf. Fig. 5. Therefore, more heat will flow into the tip and less will flow out of it. Meanwhile the reverse situation occurs in the depressions forcing perturbations to be damped out. Moreover, the equilibrium temperature at the interface, determined mainly by composition, is changed as a consequence of the local interface curvature. Because the tip can also reject the solute in lateral direction, it will tend to grow more rapidly than a depression, which tends to accumulate the excess solute rejected by the tips. Therefore, the form of the perturbation is no longer (initially) sinusoidal but adopts the form of cells which are ellipsoid-like crystals growing anti-parallel to the net flux direction. If the growth conditions continue close to the limit of constitutional undercooling of the corresponding planar interface, tree-like formation occurs and the cells rapidly change to dendrites, which then exhibit secondary arms and crystallographically governed growth directions [90–92]. If the heat extraction is isotropic, dendritic growth is equiaxial. For a single dendrite, a short parabolic tip region can be observed which often constitutes less than 1% of the length of the whole dendrite and perturbation appear on the initially smooth needle as in the case of the breakdown of the originally discussed planar interface. If the primary spacing is sufficiently great, these cell-like secondary branches will develop into dendrite-type branches and thus leads to the formation of tertiary and higher-order arms. When the tips of the branches encounter the diffusion field of the arms of

neighbouring dendrite, they will stop growing and begin to ripen and thicken. Beside the normal temperature gradients discussed above, the radial temperature gradient can also be accounted through convection usually originating by the non-homogeneous distribution of the mass density throughout the fluid (*Rayleigh-Bernard* instability [56,92]) or by variation of the surface tension of free surfaces (*Marangoni* convection [56,92]) for the densities differences between phases or by electromagnetic forces (electrophoresis). Numerical computations provided both a long-wave convective instability and short-wave bifurcations.

These diffusion processes are driven by gradients in the liquid, which are in turn due to temperature on the interface. The interface temperature is related to the interface composition, the surface curvature and the departure of interface from local equilibrium. The last contributions are curvature undercooling, composition and kinetic undercoolings [56,93]. The ratio of the change in concentration at the tip to the equilibrium concentration difference is known as supersaturation and represents the driving force for the diffusion. The form of the tip is affected by the distribution of the rejected heat or solute and interactions makes the development of an exact theory extremely complex, usually involving exponential integrals (known, e.g., from nonisothermal evaluation procedures, cf. Chapter 12.). More complex and complete equations of perturbation balance of the discontinuity interface were derived within the framework of the linear approach, mentioned above. Generalized conditions for the heat transport at a curved interface have the form [56,88,92]:

$$v_N[(\pi c T)_L - (\pi c T)_S] = D_S \partial T_S / \partial n - D_L \partial T_L / \partial n - v_N [Q + C_M (f_S - f)], \quad 3$$

where C_M is twice the mean curvature of the solidification front, v_N is the normal component of the growth rate,

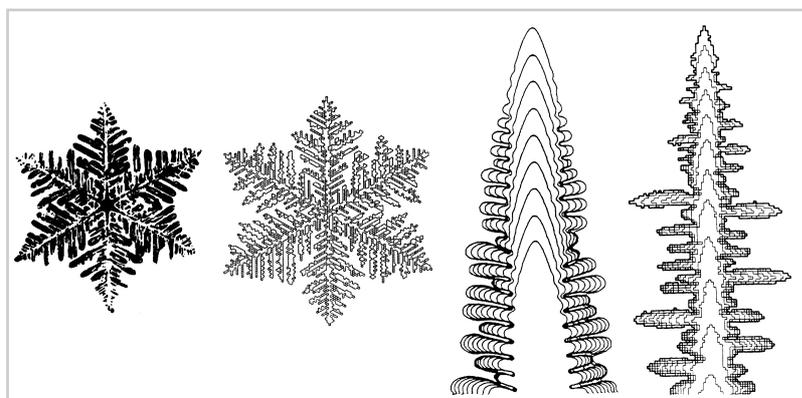


Fig. 15.6. Exemplification of a dendritic growth showing the time-sequential stroboscopic photographs of the dendrite clustering of molecules forming snow flags (left) and/or NH_4Br crystals (right). It shows that the side branches appear non-periodical at any distance from the tip and uncorrelated on opposite sides. The arms side branch amplitude is an exponential function of the distance from the tip. Computer modeling (each case right) is based on diffusion limited aggregation design though the noise reduction program was necessary to speed up the convergence of patterns towards its asymptotic infinite mass limit.

$(f_s - f)$ is the difference between Gibbs and surface energy, $D_{L,S}$ is the diffusion coefficients in the liquid (L) and solid (S) phases, $T_{L,S}$ is appropriate temperatures on interface, π is density and c is heat capacity. All the derivatives are taken with respect to the direction normal to the interface. Since the surface energy can be expressed in terms of interface entropy, the last term on the right hand side of eq. (3) destabilizes the system for negative values of the surface entropy (and *vice versa*).

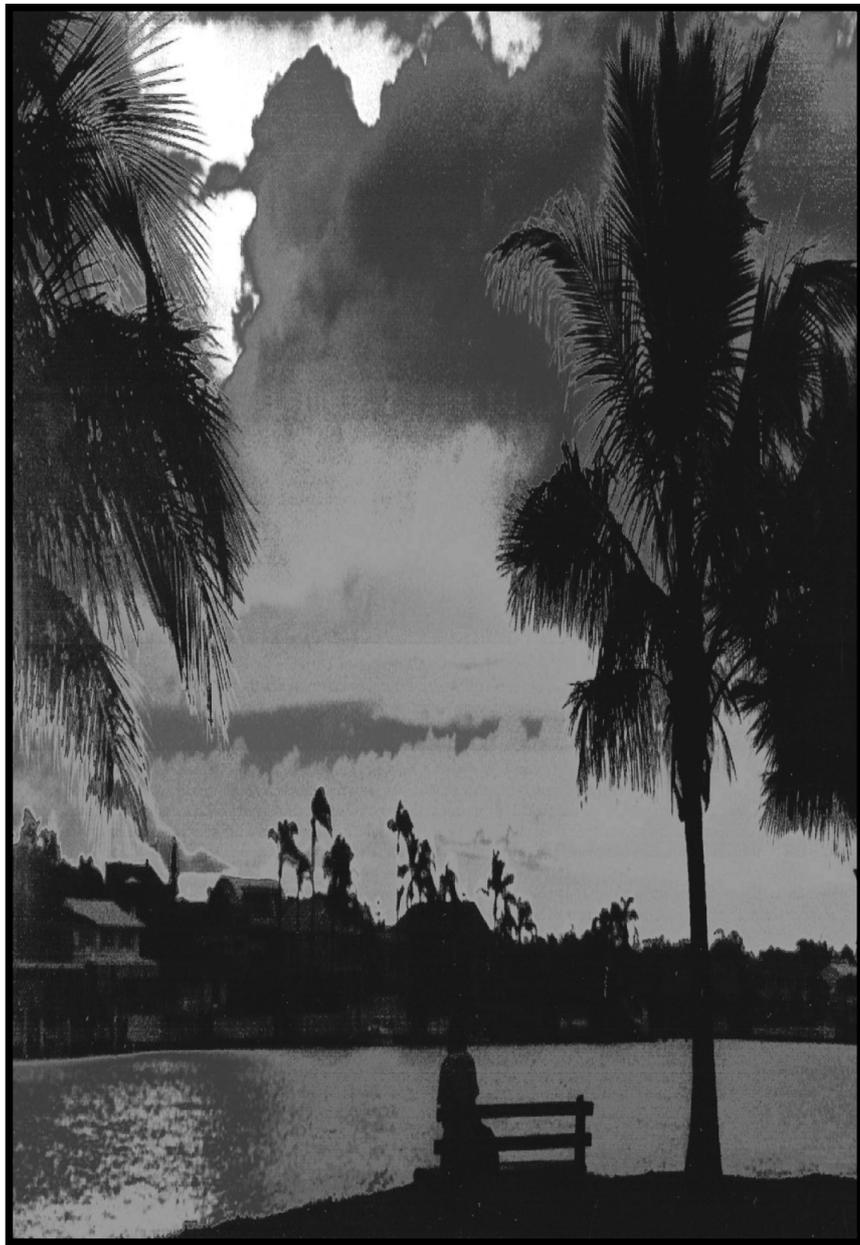
The applications of linear and also non-linear morphological stability theory to diverse areas of crystal growth are developing rapidly. Any steady-state description of dendritic growth ignores the rather obvious fact that dendrites are inherently time-dependent structures. The dendritic side branches also appear to be oscillatory in time and space. These important morphological and dynamical properties of dendrites suggest that a dendrite might be better treated as a dynamical phase transformation displaying time-dependent behavior. So dendritic growth may represent an example of self-organizing for-

mation phenomena (see the following Chapter 16), which is a deeply researched subject within the broader field of nonlinear dynamics and dissipative phase formation, cf. Fig. 6. The effect of temperature flow can affect the degree of ordering of certain directionally solidified eutectics to produce a characteristic growth of well-organized lamellae [83,86] and can be found in directionally grown composites, layered products of decompositions, etc.

In the view of the thermoanalytical practice discussed in Volume 3, the expected results in terms of functions instead of the traditional constants would, however, be quite unfamiliar with respect to the kinetic tradition but we need to get acquainted with them when facing the new prospects of the 21st century. It, in fact, would be better to match the real thermal state dynamics than to use the old representation in terms of customary and habitually 'apparent' kinetic constants². The associated field of 'kinetic phase diagrams' provides more details and is thoroughly described in our previous book [56], which also contains an extended list of references.

¹ Beside the normal temperature gradients, the radial temperature gradients are strongly effective to the interface stability in many technological processes, discussed in Chapter 8. When a binary melt is being withdrawn at a constant velocity, v_o , from the heated batch to laboratory temperature under a constant temperature gradient, the radial heat exchange between the thin sample (e.g. ribbon) and its surroundings becomes decisive to its shape regularity. The planar interface turn out to be strongly sensitive to the perturbations, which can be simply expressed by the relationship, $\Lambda \sim v_o \sqrt{d/h_{ex}}$, where Λ is heat conductivity, v_o is the withdrawing velocity, d is the thickness of the sample and h_{ex} is the heat exchange between the sample and the surroundings (e.g., quenching substrate) [J. Vilnas, R.F. Sekerka, P.P. Debroy, J. Cryst. Growth 89 (1980) 416]. It is clear that both the critical velocity (corresponding to cellular bifurcations) and the critical size of the patterns formed at the solidification front is thickness-dependent. Cellular bifurcations of thin samples (films) occur in this case at a velocity much lower than that for a more massive system. The thickness of insulating layer between the solidifying melt and the cooler is also important – if the layer is diminished that helps to the decrease perturbations. Moreover, when the extent of insulation increases then the radial temperature gradient decreases and, consequently, thermal stresses also decrease within the solid phase created. When the effect of curved solid-liquid interface on lateral solute segregation is small then the difference between the concentration of the solid near the sample surface and at the centre of the solidification front is also small for the unidirectional solidification of a binary melt [S.R.Coriel, R.F. Sekerka, J. Cryst. Growth 46 (1979) 479 and 54 (1981) 167].

² The flux approach discussed above was assumed to be important as early as during the author's 1974 NATAS-Mettler award lecture "Rational approach to the study of processes by thermal analysis" [82] as well as his similarly-aimed plenary lecture at the Scandinavian Conference on Thermal Analysis at the RisØ 1975. This access has naturally expanded upon our invited review article in *Thermochimica Acta* [94] and the 1991 published book on non-equilibrium phase transformations [56] where we introduced a new discipline entitled "kinetic phase diagrams", cf. Chapter 7. The concept of heat allocation has also been recognised as an integrating element in the pathway of ordering not only matter, but also society [95], cf. Chapter 18., thus supporting our better understanding of both our environment and the science of nature in general.



CHAPTER SIXTEEN

16. Principle of least action and self-organization of chemical reactions

a) How to evaluate unusual experiments

It is clear that above-mentioned (see Chapter 8) and previously criticized (Chapter 15) *single-valued characterization* of a process, which takes place under non-equilibrium conditions of temperature changes is not fully agreeable. It thus needs to undergo modifications to match another style of presentation, which would be more adequate to the modern level of scientific treatments. Only for simplified descriptions we can match overall mechanism phenomenology, often accomplished by introducing non-integral exponents accredited in the fractal geometry, as shown previously in Chapters 12 and 13. Therefore, an advanced kinetic portrayal should be brought into concurrence with the more detailed description of fluxes, because the transport properties determine the conditions on the entire phase interface and, *vice versa*, the depletion of interfacial reactants controls the strength of the fluxes. The kinetics of phase transformations is thus influenced by the neighboring values of temperature, stress, concentration and similar distribution gradients across and along the reaction interface as well as by, not yet introduced, phenomenon of certain aspiration to reiteration.

In studying reaction kinetics we should also focus our attention to a specific case often encountered when an experimentalist faces chaotic trends in his resulting data [96,97] while studying chemical reactions in an apparently closed system. Such results are frequently refused reasoning that the experiment was not satisfactorily completed due to ill-defined reaction conditions, unknown disturbing effects from surroundings, etc. This attitude has habitual basis in traditional view common in classical thermodynamics that the associated dissipation of energy should be steadily decelerated to reach its minimum (often close to zero) at a certain stable state (adjacent to equilibrium). In such a case, we are examining the reaction mechanism as a time-continuous development of regularly successive states, as shown above. In many cases, however, the reaction is initiated to start far away from its equilibrium or external contributions are effectual (in a partly open system) or reaction intermediates play a role of doorway agents (i.e., feedback catalysis). In such a case, the seemingly chaotic (oscillatory) behavior is not an artifact but real scientific output worth of a more detailed inspection. In this case the reaction mechanism is understood not only in its traditional terms of time-continuous progress but also as a reflection of reaction time-rejoinder which feedback character yields rather complex structure of self-organization.

In most cases, oscillatory trends are still sensed as a curiosity and the source of apprehension; however, here we see the aim of our contribution. We shall try to look at the reaction mechanism from the point of view different from the previously shown search for the sequential progress, but we shall look at the oscillation regularity and possible links that may join various oscillatory regimes and patterns. We shall try to find a generalized numerical

constant, possibly similarly to the previously mentioned *Feigenbaum* constant [27] (for details see Chapter 13, and Fig. 15.2.) of convergence determined to hold for various geometrical functions. It also well reflects elementary consequences of universal geometry. Let us reiterate the case of a gross organization where we perceive a set of discs, the largest being the main cardioids, one abutting upon the next and rapidly diminishing their radii. How rapidly they diminish their size can be derived from the fact that each one is x -times smaller than its predecessor with the parameter ratio attaining in its limit the universality *Feigenbaum* constant of 4.6692... and thus characterizing the previously mentioned generalization at the transition to chaos.

It can be seen not only within the traditional biological systems [98–100] but also in less known, but by no means less significant systems in physical and chemical world of inorganic substances [101,102] having a fundamental background in the general system theory [103–105]. For example, it is well known that resistors carrying large electrical current can exhibit negative differential resistance, i.e., currents that even decrease with increasing voltage, thus supporting oscillations rather than steady currents. Another example may be shown in studying the instabilities that occur in thin wafers in certain semiconductors (GaAs). If the electrical potential across the semiconductor exceeds a critical value, the steady current that is stable at lower potentials abruptly gives way to periodic changes in the current, often called *Gunn* oscillations [106]. Statistics show that the stability of such a non-equilibrium steady state is reflected in the behavior of the molecular/atomic fluctuations that became larger and larger as the steady state becomes more and more unstable, finally becoming cooperative on a long-range order. In many cases this effect is hidden by our insensitive way of observations. Particularly it becomes apparent for those reactions that we let start far from equilibrium; first, they exhibit non-equilibrium phenomena but later they either decay (disappear) close to their steady state or are abruptly stopped (freeze-in) by quenching (to form the reinforced amorphous state of non-crystallites).

b) Regular patterns provided by living organisms

The unsurpassed example is the basic occurrence of life as a self-replicating, mutable macro-molecular system capable to interact with its surroundings (continuous supply of energy). It involves autocatalysis, which is a process in which the given compound serves as a catalyst of its own synthesis. Certain biopolymers exhibit such an inquisitive property that is basis for self-reproduction, i.e., the feature enabling agglomerates of molecules (possessing similar starting capability – concentration) to develop preferentially for those molecules that grow to become dominant (morphogenesis). It means that a particular linear sequence of nucleotides must code for non-random sequences of amino acids having autocatalytic properties furthering their replication to provide a preferential reproduction. Other coding then provides less effective proteins and their replications proceed more slowly. By mutual co-operative actions of such autocata-

lytic reactions, a larger self-regulating system can be created (gastrulation) to show the cyclic reproduction, exhibiting fixed time of repetition as an important attribute of life. Enzymes that are big protein molecules acting as biological catalysts and accelerating chemical reactions without being consumed by them play a most important role. Their activity is specific for a certain set of chemical substrates and is dependent on various boundary conditions (concentration and acidity-pH of reactants) and interactions with its surroundings (input fluxes of

heat and mass and/or force fields such as gravity or temperature). The system is evidently far from its equilibrium and its fertile behavior cannot be explained by the classically viewed equilibrium thermodynamics that is sufficient to describe the formation of stable static structures (as crystals). Unlike ordinary static equilibrium states, such self-catalyzed states that are created away from equilibrium and are unstable because a small perturbation may lead precipitously to new states rich in their variety.

The field on which studies of such chemical oscillators are likely to have a great effect is better understanding of nerve impulses, which involves the transmission of electric signals from neuron to neuron across gaps called synapses. The mode of transmissions implicates messenger molecules, called neurotransmitters (or mediators, which are biogenic amines such as serotonin) and the change in permeability of the cell membrane to various ions in response to changes both in the neurotransmitter concentration and in the electrical potential across the membrane. This membrane potential undergoes rhythmic fluctuations, often called action potentials. The task of neurobiologists is to specify molecular models, which should account for the membrane periodic oscillations and which are based on the idea arising from the emergence of membrane "voltage-gated" channels. These channels are active for different types of ions, opening and shutting as the membrane potential passes through a threshold value critical for periodicity.

The figure one illustrates the picturesque world of various bayaderes endowed with various seashells. The apparent correlation between a choice of organized structures provided by different living organisms like butterflies, shells or even animals (skin ornamentation – zebra) was elaborated by *Turing* [103]. He formulated the hypothesis that such patterns are, in general, the result of reaction-diffusion processes, which are mostly applied at the early stages of the cell growth. *Mainhard* [107] gave explanation how the incrustation proceeds, starting at the tail of the shell body where the cells are producing calcite-rich matter, which is accreted to the edge of crust-shell. If shell-cells are simultaneously producing pigments, the relevant part of incrustation is stained. The variability of colors depends not only on the character of reaction itself (autocatalytic, cyclic, periodic) but also on the initiation threshold, the state of cells generating and exchanging pigments and diffusion characteristics for activators and inhibitor. If the inhibitor diffuses faster than the activator, the propagation of reaction is soon blocked and the resulting pattern is composed from dyed spots only. On contrary, if the activator diffuses fast enough, it acts as the synchronization factor and the pigmentation proceeds along all edge cells at the same time, which helps to cycle the periods of the growth of dyed and colourless stripes of calcite [108,109]. What more, the calcite micro-crystallites are well organized and with a negligible content of organic matter (aligned as a layered composite) the final incrustation structure achieves extraordinary mechanical strength. The formation of colored stripes perpendicular to the growth rim of a shell is caused by incomplete dye reaction limited to certain areas; it still continuously pro-

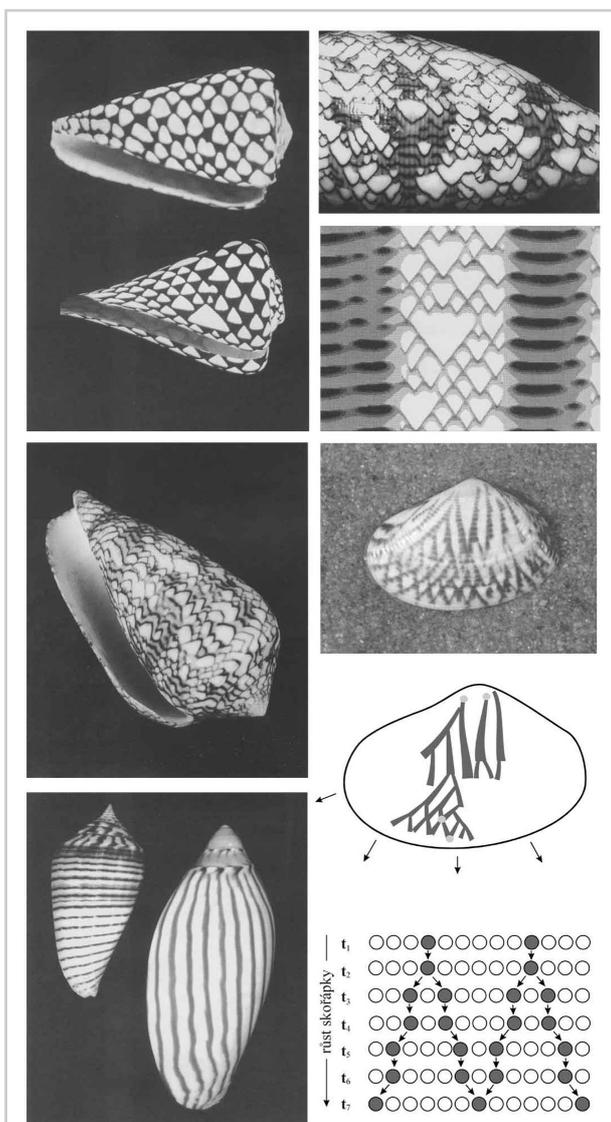
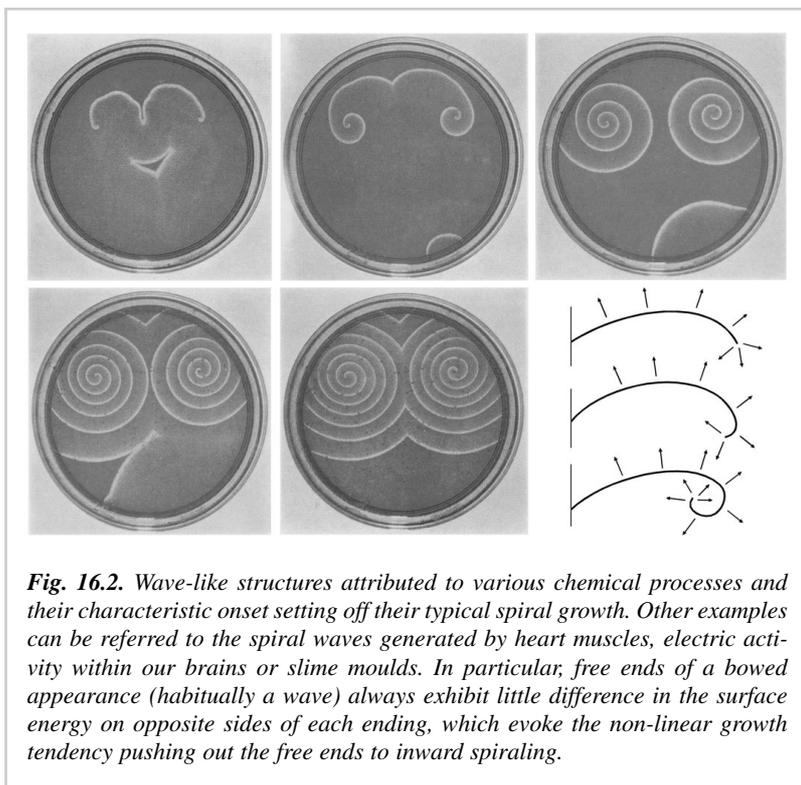


Fig. 16.1. Photo of various shells and the chart of the initiation of dye centers, which are responsible for the continuous pigmentation process. The schematic shell contour (right bottom) envelopes dyed (solid) lines advancing from the initiation centers (shadow spots) down to annihilation sites (white spots), on the whole, characterized by the time development, t_1 down to t_7 , where individual stages distinguish, 1 – peripheral cells, 2 – pigment diffusion to neighboring cells, 3 – initiation of pigmentation in adjacent cell and its termination in the original cells (bifurcation), further incessant diffusion (4 & 6) and coloring initiation (5 & 7), etc. (Courtesy of H. Ševčíková, Praha, Czechia)



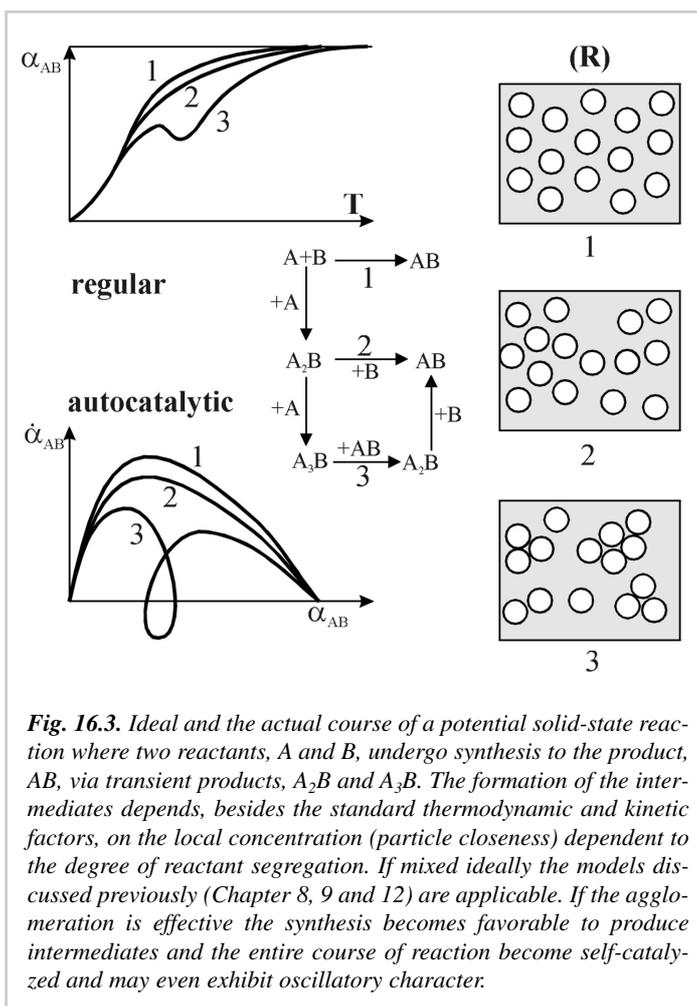
B (SiO_2) undergoing synthesis according to the scheme shown below (left) to yield the final product AB (CaSiO_3) either directly or via transient products A_2B (CaSi_2O_4) and A_3B (CaSi_3O_5). The formation of these intermediate products depends, beside the standard thermodynamic and kinetic factors, on their local concentrations (the degree of mutual admixturing). If A is equally distributed and so covered by the corresponding amount of B, the production of AB follows standard kinetic portrayal (left headed arrow). For a real mixture, however, the component A may not be statistically distributed everywhere so that the places rich in A may affect the reaction mechanism to prefer the formation of A_2B (or even A_3B). The latter decomposition of A_2B is due to the delayed reaction with the deficient B that is becoming responsible for the time prolongation of reaction completion. If the component A tends to agglomerate, the condition of intermediate synthesis becomes more favorable, undertaking thus the role of a rate-controlling process, see

duces pigmentation but is neither shared nor better spread everywhere.

For the periodical propagation of wave-like structures, the concentration gradient of the activator is in its control factually stimulating such an autocatalytic process. At the same time, an inhibitor is co-produced whose certain threshold amount stops the autocatalysis enabling the annihilation of both catalysts (initiator and inhibitor) and re-installation of initial reaction conditions necessary to start once again. If the continuous progress of reaction zone is somehow interrupted, it may generate two free ends of the propagating pulse-wave. While the commencement of a coherent reacting zone proceeds outwards, the propagation of free ends can advance perpendicularly so that it tends to expand. Such a newly proficient propagation outgrows in more directions and is consequential for spiral augmentation, see Fig. 2. The free ends are continuously scrolling enabling the outgrowth of new and new spirals. Such a spiral wave needs just the initiating impulse and then it propagates itself, being self-generated and self-sustained.

c) Repetitive order in some inorganic systems

Inorganic solid-state reactions are often assumed to proceed via branching [72,73,110]. Let us assume a simple case of synthesis known in the production of cement assuming ideal and real reactions hypothetically supposed to follow processes taking place during silicate formation. There are two starting solid reactants A (CaO) and



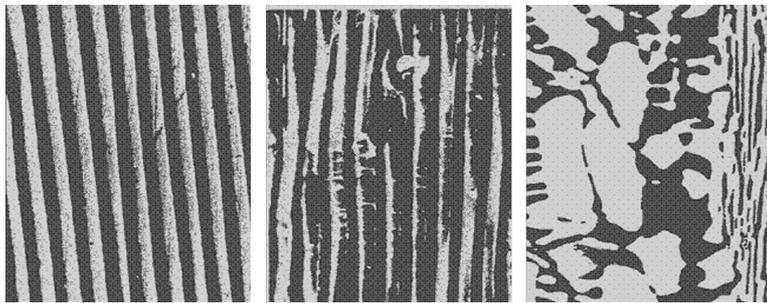
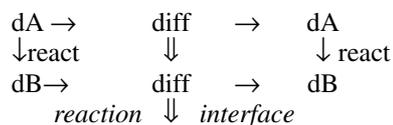


Figure 16.4. Quenched-in morphology of the directionally solidified dielectric eutectic of $\text{PbCl}_2\text{-AgCl}$ processed at a high melt undercooling ($\Delta T=50$ K) and growth rate ($v = 10$ mm/hr) at both the microgravity ($G_0 \rightarrow 0$, left) and terrestrial conditions ($G_0=1$, middle). It reveals the oscillatory growth of PbCl_2 lamellae in the crystallographic direction [100] parallel to the reaction interface (visible at the left-side of right photo). The lamellae that solidified directionally at terrestrial conditions (middle) exhibit, however, characteristic growth defects due to the interference of mass flow with gravitational field that is absent for the space experimentation (left). Time-dependent effect of lamellae coarsening provides thus a common pattern of rough morphology regularly achieved for prolonged equilibration of sinters (not in scale).

Fig. 3. The entire course of reaction can consequently exhibit an oscillation regime due to the temporary consumption of the final product AB, which is limited to small neighboring areas. If the intermediates act as the process catalyst, the oscillation course is pronounced showing a more regular nature. Their localized fluctuation micro-character is, however, difficult to be detected by direct physical macro-observations and can be only believed upon secondary characteristics read from the resulting structure (final morphology). Similarly, some glasses may exhibit a crystallization pendulum: after proceeding very fast in certain direction(s) the growth often stops due to the changes in concentration and converts into dissolution while in the other direction(s), where the growth rate was initially lower, it never becomes negative even if it decelerates effectively. Hence, a competition between several simultaneous processes takes place, typical for such a non-equilibrium system and leading to curious morphology (plate or needle-shaped crystals) [111].

One of the most common phenomena is the self-organization due to the diffusion-controlled processes schematically given as follows.



The local effect of counter-diffusion would become an important factor that may not only create but also accelerate above-

mentioned oscillations, which is often an observable fact coming mostly from the interface reactions. As a result, many of peritectic and eutectic reactions turn out to pass an oscillatory regime providing regularly layered structures. For example, the directional solidification of the $\text{PbCl}_2\text{-AgCl}$ eutectic [83,112] is driven by temperature gradient and provides lamellar structure separated repetitively at almost equal lamella partition (see Fig. 4). Solidification under microgravity starts with higher undercooling compared with that observed in terrestrial condition, obviously due to the lack of convection. Typically, gravity-enhanced mass transfer leads to the effect of coarsening experienced at prolonged time and often at increased temperature [112].

Periodic precipitation patterns appears when two separate solutions, each containing one of a pair of ions, such as silver (Ag^+) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), react to

form a nearly insoluble compound, being placed at the opposite ends of a tube filled with a gel. As the ions diffuse through the gel toward one another, a precipitate of silver chromate does not deposit uniformly, as expected, but in a series of sharp, nearly evenly spaced bands, see Fig. 5 [113]. Recent theories of this phenomenon often

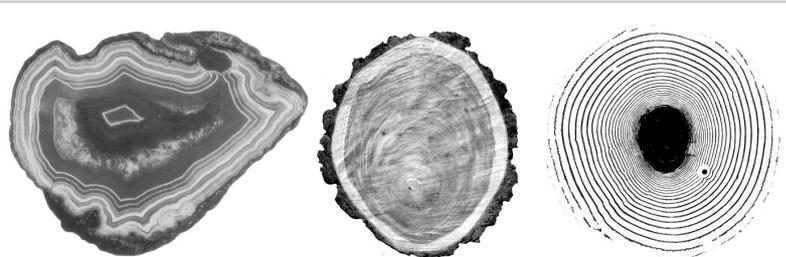


Fig. 16.5. Examples of common, co-centric patterns widely met in nature and believed to arise by way of the same general mechanism. From left, there are shown examples of processes taking place within long-, middle- and short-range interval of reaction time. The cross-section of the natural semiprecious stone agate, shaped by hydrothermal reaction in geological formations, middle, the cross-section of tree trunk of about 100 years old pinewood, indicating the northern direction by more dense tree-rings created due to the less favored growth conditions (lower temperature, etc., typical for the growth-ring separation in general). Right, Liesegang's rings of silver chromate crystallites formed during the diffusion controlled solid-liquid chemical reaction in a Petri plate when placing a crystal of silver nitrate at the center of a glass plate coated with gelatin containing a dilute solution of potassium dichromate. In all such cases the ring-band separation is related to the instant propagation velocity at which the diffusion infiltrates the space available, its geometrical arrangement and the size of propagating species, all constituting the proportionality, which is governed by the value of about 6.6×10^{-34} [J s] that exhibits a striking coincidence with the Planck constant (ordinary acknowledged to control the wave relations in the deep microcosms). For more details see also the early work by W. Schaaps published in, e.g., *Kolloid Zeitschrift* 137(1954)121, which deal with in more details problems associated with the rhythmic crystallization and periodic chemical reactions met in the colloid chemistry and biology, including the puzzle of cooperative involvement of the Planck-like constant within the gradual formation of tree-rings.

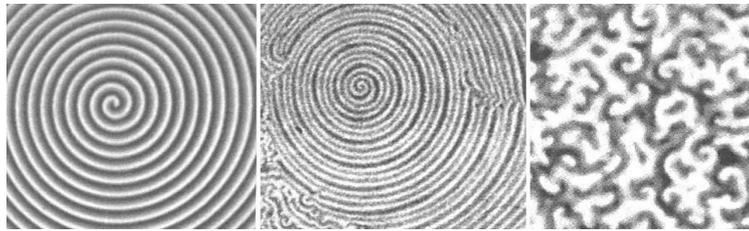
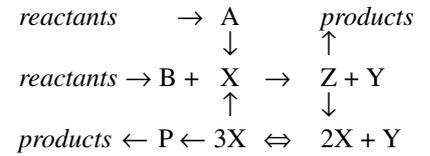


Fig. 16.6. Rotating spiral wave as a simple case of a reaction-diffusion pattern. It is a kind of Belousov – Zhabotinsky 2D-waves experimentally observed for the system $H_2SO_4-NaBrO_3-CH_2(COOH)_2$. This illustrative view shows co-rotating (retrograde) meandering wave shaped in spirals to appear at low malonic acid concentration. Left, the spirals undergo retrograde meandering which for higher concentration turns opposite. At low sulfuric acid concentration the spirals are stable while for higher concentrations the distance between the successive wavefronts starts to vary spatially until a large number of small spirals around the edge of the stable spiral emerge. This process can lead to the turbulent state (middle) beyond the convective instability of the spiral. Enlargement of the turbulent region is called as the ‘Eckhaus’ instability, which is a quite common phase instability of yet periodic pattern (right – but not in scale).

nature of many processes and gave to them the necessary practical dimension when applied to various reality situations:



This scheme has been associated to lie close to the glycolytic energetic cycles where the oscillatory energy-intermediates are adenosintriphosphate (ATP) and adenosindiphosphate (ADP). It is also likely to explain the functioning of periodic flashes of the biogenic (cold) light produced by some microorganisms where the animated transformation is fed by oxygen whose energy conversion to light exhibit efficiency over 90%.

called Liesegang rings [114] explain the pattern formation in the oscillating Belousov-Zhabotinsky system [115]. The banding patterns in agate and many other minerals closely resemble those of Liesegang rings and are believed to arise by way of the same general mechanism. Similar patterns can be found on many other cases, from shell ripening to larger scales of sediments as well as for a variety of biological patterns (some mentioned above). Most evident case is the development of tree rings caused by diffusion, which is specific for each growth year and associated weather conditions, giving rise to a general question why such variously observed separation patterns are so regular and what are their causes.

Equally important is the domain of oscillatory processes common in solution chemistry, particularly known as the Belousov-Zhabotinsky (further abbreviated as BZ) reaction [116,117], cf. Fig. 6. These processes were successfully simulated by the use of computers. Most famous is a simple scheme known as “Brussellator” [101] describing autocatalysis¹ of the type $2X + Y \Leftrightarrow 3X$. A more complex case of so-called cross-catalytic reactions may involve two reactants A and B and two products Z and P. The intermediates are X and Y and the catalytic loop is caused by multiplication of the intermediates X, see scheme below. Fig. 7 illustrates the input effect of reactant concentration within the given reaction mechanism (at the threshold concentration of A the steady sub-critical region changes from the sterile to the fertile course of action capable of oscillations in supercritical region. Although first assumed hypothetically, it enabled to visualize the autocatalytic

d) Bénard convection roles

Oscillatory scheme is very important for all ‘lively’ processes taking place away from equilibrium. The customary case are the Rayleigh-Bénard hydrodynamic instabilities, see Fig. 8, which are responsible for weather. Solar rays heat the air closer to the ground and the air particles rise by air convection when the temperature differential is large enough. In this way, warmer, polluted air escapes from the lower atmospheric layer to the upper layers where it is dispersed. If the temperature difference $\Delta T > 0$ is minimal then the air is driven by steady convection but when the difference becomes sufficiently large, the falling cooler air from the top initiates what is called convection roll, a new fashion of circulating flow. For a specific fluid enclosed in a fixed region with con-

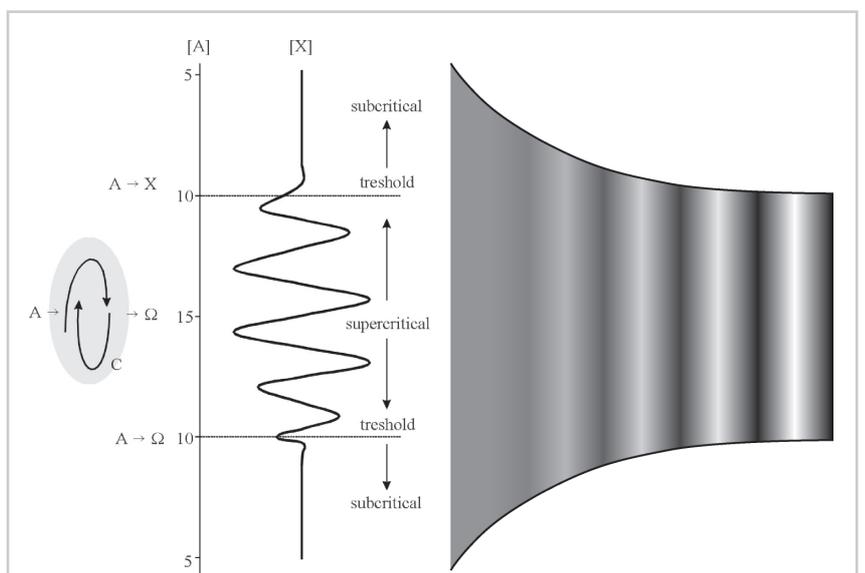


Fig. 16.7. Schematic diagram showing the subcritical and critical oscillatory regimes of a computer scheme (customary called Brusselator)

stant height, the rate of convection flow depends on some characteristic constants, such as the coefficient of thermal expansion, α , kinematic viscosity, ν , and thermal conductivity, λ , forcing frequency, f , and, last but not least, gravitational acceleration, g . It has been first described by *Saltzman* [118] and *Lorenz* [119] using the set of equations ($x' = P_r y - P_r x$ and $y' = R_{a/c} x - y - xz$ and $z' = xy - bz$), where the previously mentioned dimensionless numbers (cf. Chapter 13), called after *Rayleigh*, R , and *Prandtl*, P_r , are utilized together with a constant, b , related to given space dimensionality. Avoiding the details [120] let us just notice that for a fixed number of R three critical points turn out so that it is difficult to conjecture what the orbit of an arbitrary solution might look like. First, the three coordinates grow rapidly when the same signs of x and y indicates the simultaneous process of warmer and colder air to rise and sink respectively. When convection becomes strong enough, there is a reversal, in which warmer air rises above the colder air at the top, allowing the signs of y and x to change. A new mode of outward spiraling capable to continue indefinitely is developed, which is a similar case described mathematically in Chapter 13 (cf. Fig. 13.7)².

Let us see the details as viewed locally. Individual molecules move more or less at random, which is only the statistical average that forms the convection cells. This averaging must have some physical source. In this case it is in the viscosity of the fluid – negligible viscosity makes convection impossible. Cohesion within the system is essential, and in *Bénard* cells this cohesion originates in viscosity. It seems clear that a force must be applied throughout the system. There are two potentials present: downward aiming gravity and upward pointed gradient of temperature. Although the latter has its origin outside of the system, the gradients exists inside the system in

a much stronger sense than the gravitational potential. Unlike the gravitational potential, which is conservative, the temperature gradient induces a non-conservative entropy gradient within the system and convection is an attempt to reduce this gradient. The temperature differential must be large enough to allow the formation of fluctuations sufficiently large necessary to overcome viscosity in a faster rate than the fluctuation are dissipated. This creates instability: a fluid that is not moving microscopically. Buoyancy then drives the convection cells to create a new stable but moving regime. This process is reflected in the delicate balance between the variables involved (particularly R and P_r) and can even be simplified as a series of hypothetical, coupled, reversible and extremely miniature *Carnot's* engines³.

The gravitational force resists macroscopically movement, whereas the temperature difference and lower viscosity encourage it. The exact role of gravity, however, is a bit unclear from the basic hydrodynamic differential equation [120] though it is apparent that R would be zero without it. It seems that there might be an overall vertical pressure gradient due to asymmetrical heating, even without gravity. With sufficient viscosity, this would be able to initiate convection in an adequately strong temperature gradient, too. It follows that three necessary conditions must be simultaneously activated: (i) applied force (gravitation and/or pressure gradient), (ii) sufficient internal cohesion (viscosity) and (iii) formation of large enough fluctuations due to the enforced temperature difference (to overcome viscosity). It is apparent that the system takes the path of least resistance. Instead of certain wasting energy on large random fluctuations, it convects in an orderly manner. The reason that fluid does not convect below the critical *Rayleigh* number ($\cong 1700$) is that the viscous dissipation is too high and the buoyancy of fluc-

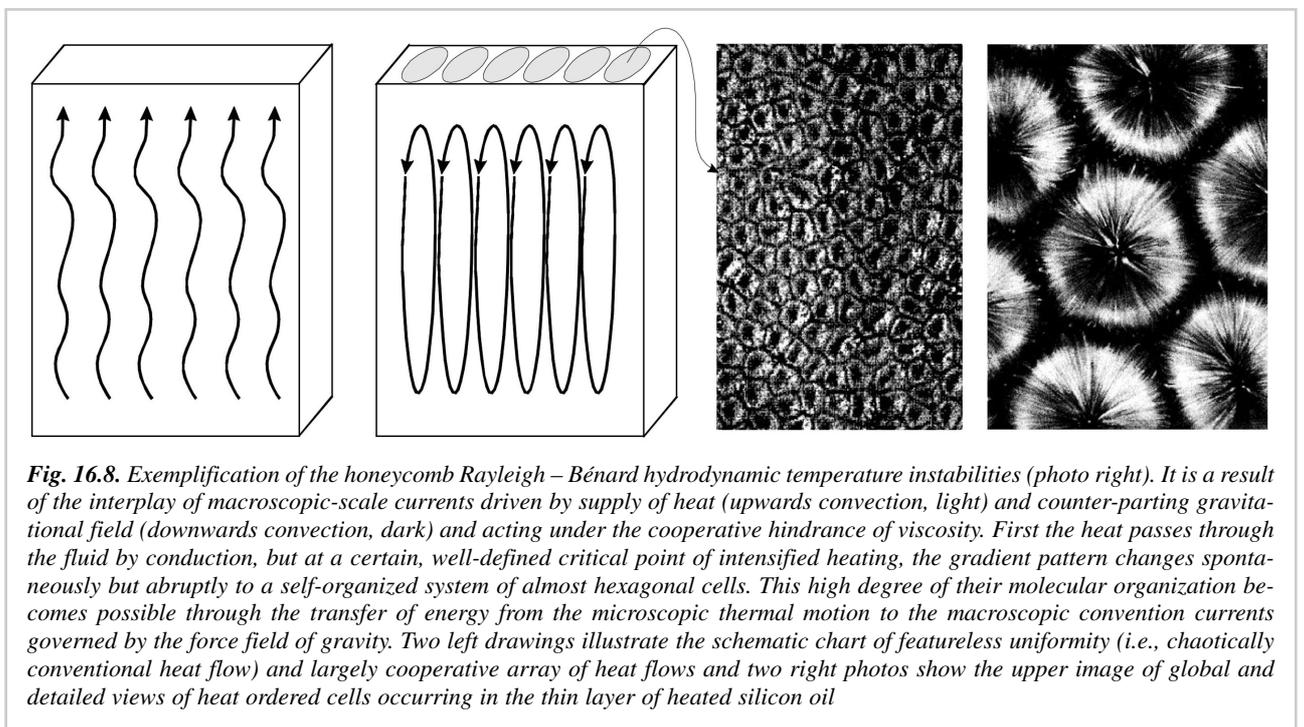


Fig. 16.8. Exemplification of the honeycomb Rayleigh – Bénard hydrodynamic temperature instabilities (photo right). It is a result of the interplay of macroscopic-scale currents driven by supply of heat (upwards convection, light) and counter-parting gravitational field (downwards convection, dark) and acting under the cooperative hindrance of viscosity. First the heat passes through the fluid by conduction, but at a certain, well-defined critical point of intensified heating, the gradient pattern changes spontaneously but abruptly to a self-organized system of almost hexagonal cells. This high degree of their molecular organization becomes possible through the transfer of energy from the microscopic thermal motion to the macroscopic convection currents governed by the force field of gravity. Two left drawings illustrate the schematic chart of featureless uniformity (i.e., chaotically conventional heat flow) and largely cooperative array of heat flows and two right photos show the upper image of global and detailed views of heat ordered cells occurring in the thin layer of heated silicon oil

tuated regions does not overcome the impeding effect of viscosity.

Some of the simpler forms of interesting dissipative processes, like *Bénard* convection, can serve as analogues for the extension of non-equilibrium thinking in biology, cf. Fig. 9. The analogy brings both positive and negative components. We can note that (i) macroscopic structure forms through the promotion of fluctuations to the next level that produce a phase transition, (ii) applied force produces the macroscopic structure (clumping), (j) the incriminated elements must exhibit cohesion (clumping potential) and (jj) the phase transition must be dependent on rates of interactions (optimisation between tendencies to retain and to dissipate fluctuations). Disapproving analogy cannot be excluded because in convection there is (i) no differentiation into kinds, (ii) applied forces acts uniformly, (j) gradients can arise internally in all cases with vertical or horizontal cohesion and (jj) biological state transitions are not restricted to transitions between stationary states (providing thus exceedingly complicated webs).

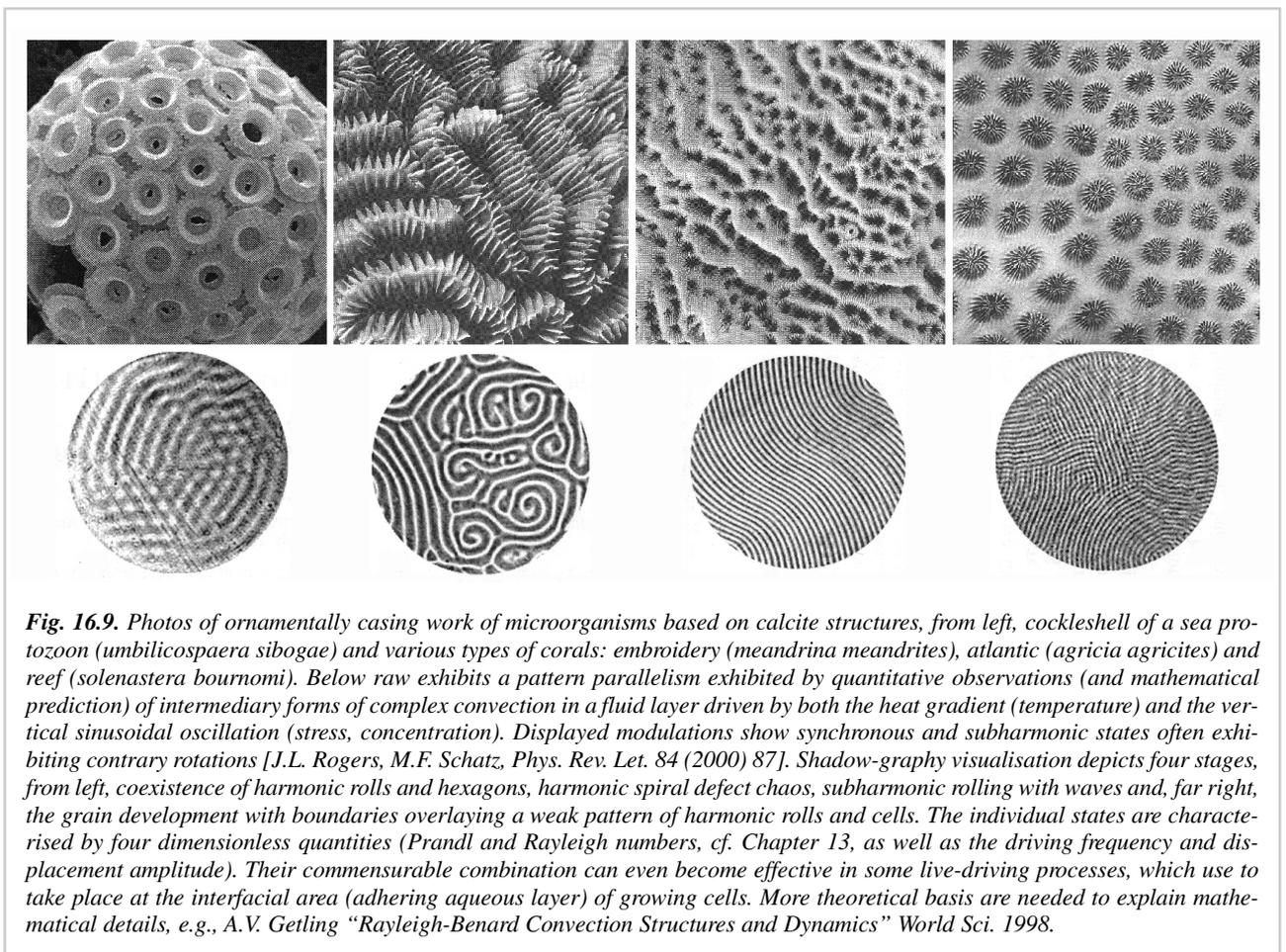
Plant development can be simply perceived as cell elongation and cell division. Growth phenomena, due either development, seem to be mediated largely by energy. As long as the environmental conditions are kept within the limitation of interface tolerance (membrane), and there are no limiting conditions for energy utilisation (nutrient

deficiencies), the rate determinants of growth will be energy imputes in the form of light and heat. The first requisite is that the light is available in appropriate wavelength and intensity (photosynthesis). The second requisite is that there is enough heat available for metabolism to function efficiently (respiration). It is likely that during such a growth process the inherited information expressed to create cells of a similar type is largely identical – they are informationally redundant. Variation within a cell type is largely due to energy fluxes, boundary conditions and any variation introduced by the machinery that reads and interprets configurational information requires for cell division and amplification.

Thus the situation in plants is much more complicated than in the *Bénard* cells because the old structures are retained and constrain future development. This means that correlation will be both temporal and spatial. Thus we see the three necessary components: (i) an internal entropy gradient (lesser to greater informational variability), (ii) cohesion (from two intertwined sources) and (iii) and external potential (provided by the thermodynamic potential difference between solar energy and ambient temperature).

e) Principle of least action

The enormous collection of experimental data on the behavior of BZ waves published throughout the literature



provided for us a very good opportunity for better tuning of the concept. *Stávek* [121] have kept attempting to enlighten the data being aware that any break in the traditional world of physics would be extremely difficult, as the BZ have not been accepted as yet despite several other efforts made during the past decades. We ventured to coin here the term *diffusion action* [96,97,121] that expresses the quantity of action induced by diffusion process of Brownian particles. The experimental values of the diffusion actions of the one dimensional (1D BZ) waves might support the theoretical approach that attempts to interpret the concepts of quantum mechanics based on the behavior of Brownian particles [122]. The variety of its description and search for mutual links was the goal of our long-lasting persuasion [56,96,97,121], while the detailed mathematics of non-equilibrium thermodynamics was discussed elsewhere [77–79].

The non-linear coupling between reaction and diffusion of ions with their concentrations in the range from $\sim 10^{20}$ to $\sim 10^{23}$ ions per dm^{-3} leads under some circumstances to the appearance of chemical waves. When a Russian scientist *Belousov* [116] discovered in the year 1952 such a spontaneous product of self-organization in the form of coaxial rings taking place in some chemically reacting system it took him several years to persuade officials to believe it. He was able to publish his finding in an obscure non-reviewed journal *Radiation Medicine* only and later stopped his further scientific research at all. The reaction was followed and improved by *Zhabotinsky* [117].

We should remind that the basic system consists from one/electron redox catalyst [Ce(III)/Ce(IV)], an organic substrate that can be easily brominated and oxidized (citric acid), and bromate ions in the form of KBrO_3 dissolved in sulfuric or nitric acid. It is worth mentioning that colloid chemists obtained the defined periodic precipitation patterns a long time ago. *Ord* [124] prepared 1D precipitation patterns in 1879, *Pringsheim* [125] introduced the concept of osmotic pressure to this field in 1895, *Liesegang* [114] prepared 2 D patterns in 1896, *Leduc* [126] developed the concept of osmotic pressure waves. Already in 1931, *Nikiforov* [127] proposed the characterization of the spatial and temporal development of chemical waves by the ‘*Principle of the least action*’, which was expressed by *Maupertuis* [128] as early as in 1744, citing: „*when some change takes place in nature, the quantity of action necessary for the change is the smallest possible. The quantity of action is the product obtained by multiplying the mass of the bodies by their velocity and the distance traveled*“. So far more than hundred different combinations of cations and anions were employed to approve so called *Liesegang*’s ring formation [129,130] in the liquid phase all of them matching the quantities of action in the order of $\sim 10^{-34}$ J s. Accounting for the experimental difficulties in the estimation of mass of diffusing units (irreversible formation of clusters) the coincidence with the Planck quantum constant is striking but assumed accidental as yet. It was not discussed properly enough as the *Planck constant* is firmly associated with microcosms of fundamental par-

ticles making thus difficult to believe that its soundness can be extended to the macrocosms of diffusing molecules and even further on the formation of shell ripening or even sea deposits.

Latter such a self-organization attracted deserved attention in a wider analysis of time-symmetry breaking associated with the emergence of time-periodic solutions known as limit cycles whose period and amplitude are stable and independent of the initial conditions. The importance of self-organization was recognized, as it can constitute models of rhythmic phenomena observed in nature; beside such chemical clocks [102] there are more important biological or other evolution processes [98, 100,108]. It became a model focused on the generalized theory of chaos expressing its minute ordering. Curiously even the attempt to imagine a self-organizing ether (primeval matter) became also a source of a related “reaction-diffusion model of space-time creation” [105,131]. It is based on the 1887 *Cu-t’ung* subatomic wave theory (bipolar ether of mutually transmuting states of opposites) and recently even competes with the traditional idea of “Big Bang” hypothesis [131] (i.e., modified theory of ‘self-reproducing inflationary universe’, cf. Chapter 2.).

Such stable rotating waves observed in this classical (ZB) reaction results from the possibility of cascade splitting (identified with bifurcation), which opens the way to gradual increase of complexity by a mechanism of successive transitions. It leads either to the loss of stability of a primary branch and the subsequent evolution to a secondary solution displaying asymmetry in space and/or in time. It is worth mentioning that such transitions are sometimes accompanied by some remarkable trends, e.g., certain classes of reaction-diffusion systems under zero-flux boundary conditions may exhibit no net entropy production change when the system switches from the thermodynamic branch to a dissipative structure. On the other hand, there is a systematic decrease in entropy in the vicinity of bifurcation points known in the associated fields’ chaos touching even the traditional domain of predicting weather. It is clear that a lot of research was devoted to the detailed observation of properties of these chemical waves and a great number of theories were proposed in order to characterize the behavior of these structures. From the mathematical point of view such systems becomes localized at the thermodynamic branch, the initially stable solution of the appropriate balance equation bifurcates and the new stable solution(s) suddenly appear (likely to overlap) [115,135].

f) Diffusion action of Brownian particles

There were many attempts to interpret the concepts of quantum mechanics based on the behavior of Brownian particles [132]. Several groups of colloidal chemists started to evaluate the formation of *Liesegang* rings by the Principle of the least action after 1931. *Liesegang* rings precipitate from collections of cations and anions in liquid phase in the presence of some gel forming agents in order to stabilize patterns in the reaction space. *Liesegang* patterns could be formed from vapor and solid phases, and ordered layered and lamellar microstructures

can be obtained during the eutectic and peritectic solidifications [56] (cf. Fig. 4).

Fig. 10 depicts the penetration of cations of mass m into the surroundings containing anions. The concentration of cations increases along the diffusion path λ until the local osmotic pressure of these waves overcomes the pressure opposed by the surroundings. Thus, the symbol λ describes a path necessary for the accumulation of Brownian particles in order to overcome the pressure of the surroundings. The symbol λ was interpreted as a wavelength of individual Brownian particles in earlier interpretations in the period 1931–1939. In this contribution the symbol λ describes the collective properties of Brownian particles penetrating into their surroundings from their source. The value λ depends not only on the penetrating Brownian particles, but it can be influenced by the osmotic pressure of the surroundings (composed from both ions involved in the reaction and other active particles, temperature, pH, gravity, etc.) and geometrical arrangement of the diffusion process.

When the concentrations of cations and anions have been properly selected, then the local osmotic pressure (supersaturation) creates stable nuclei and starts their growth. The velocity, with which the diffusion field penetrates into the surroundings, is described as the propagation velocity u . The action of diffusing ions depends also on the geometrical arrangement of the experiment – on the dimension of the diffusion experiment K and this diffusivity factor describes the random Brownian motion in the space available for the chemical wave. For one-dimensional space (thin glass tubes) $K = 1$, for two-dimensional space (thin layer in a Petri dish) $K = 2$, in case of three-dimensional diffusion experiment the value of K depends on the solid angle available for diffusion of Brownian particles from their source. If the whole space is available for the propagation of the chemical waves, then $K = 4\pi$. The Principle of the least action for collections of Brownian particles penetrating into their surroundings is expressed as the product:

$$K m \lambda u = h. \quad 1$$

Field and Noyes [133] published a detailed study of the chemical mechanism behind the BZ reaction. This contribution revealed a complicated interplay among the individual components of the recipe. In 1974, they also measured the propagation velocities of bands in the BZ reaction in two-dimensional diffusion experiments. These rates were nearly proportional to the product $[H^+]^{1/2} [BrO_3^-]^{1/2}$ and were almost independent of the concentrations of other species in the system. *Agreda et al* [134] measured the stepwise changes of associated enthalpy.

For the description of chemical waves by the Principle of the least action the mass of diffusing units m , responsible for the appearance of the concentration waves, have to be exactly determined. The ion H^+ shows the highest mobility among the cations and anions of the BZ recipe and may create the osmotic wave in the direction from the center of the propagation of the observed bands and to start the wave propagation into the surroundings. *Tockstein and Treindl* [135] reviewed many variations of the original BZ recipe and concluded that the presence of the H^+ cation was necessary for the appearance of these oscillations. This idea can be easily experimentally confirmed or disproved because all quantities: K – diffusivity factor, m – mass of H^+ cations responsible for the osmotic wave, λ – distance between bands, u – propagation velocity of bands are for the BZ waves available with a reasonable experimental error.

g) Oscillatory regime of the Belousov-Zhabotinsky reactions

In excitable media periodic waves are known to travel at a propagation speed u that represents the product of the distance between patterns λ and their frequency ν (or its reciprocal value period T). The relation between propagation speed and period (wavelength, frequency) of successive BZ waves, known as the dispersion relation, is important for a better understanding of wave properties. The dispersion relation in the form of the dependence of the propagation speed u on the wavelength λ of that wave gives the best idea about the diffusion action of penetrating wave into the surroundings.

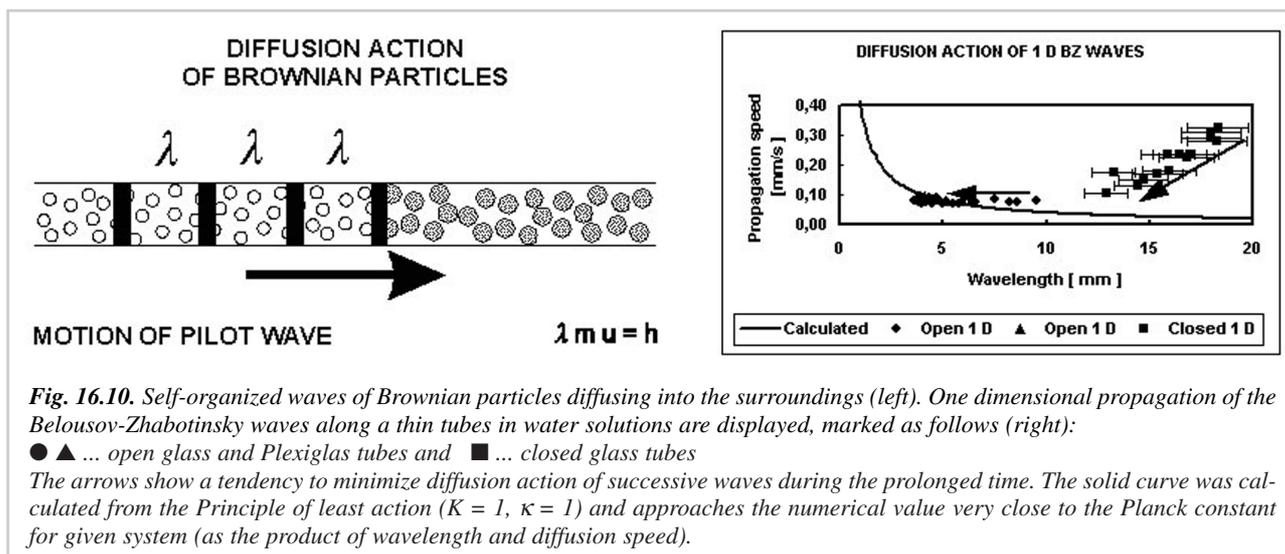


Fig. 16.10. Self-organized waves of Brownian particles diffusing into the surroundings (left). One dimensional propagation of the Belousov-Zhabotinsky waves along a thin tubes in water solutions are displayed, marked as follows (right):

● ▲ ... open glass and Plexiglas tubes and ■ ... closed glass tubes

The arrows show a tendency to minimize diffusion action of successive waves during the prolonged time. The solid curve was calculated from the Principle of least action ($K = 1$, $\kappa = 1$) and approaches the numerical value very close to the Planck constant for given system (as the product of wavelength and diffusion speed).

Tatterson and *Hudson* [136] substantially improved both the recipe of BZ reaction and the technique for a well-documented observation of the dispersion relation in one-dimensional reaction space. They used a stirred tank as an oscillating source whose frequency could be controlled by the intensity of stirring. The waves, emitted from this tank, penetrated into the attached glass or Plexiglas tubes and 1D propagation of waves were observed and measured potentiometrically. Their experimental arrangement served as a reproducible and controllable source for the waves from outside into the diffusion tube. *Winfrey* [137] filled a capillary tube with BZ reagent and stimulated a random sequence of waves in the closed tube and measured the dispersion relation of the successive waves. The experimental results from both open and closed diffusion systems are summarized in Fig. 10 together with a theoretical curve calculated from the previous Eq. 1. The data obtained by *Tatterson* and *Hudson* in their open 1D diffusion experiment give a surprising agreement with the value of the quantum of action. There is an observable departure of quantities of action of waves with longer wavelength from the curve because the detector was placed only 12 mm from the entrance and the diffusion field could not self-organize itself to reach the value of the least quantity of action. This type of observation of BZ waves appears to be very useful for an estimation of the concept of the diffusion action of chemical waves because all four parameters, which have to be determined experimentally, can be easily evaluated: $K = 1$, $m_{H^+} = 1.674 \cdot 10^{-27}$ kg, λ and u are determined with an error of a few percents. On the other hand, the spatial propagation of BZ waves in a close tube is different because the diffusion field of H^+ (self-organization of randomly moved Brownian particles) is not the same in closed and open systems. Moreover, the data set on the propagation of waves created in *Winfrey's* 1D experiment [137] in closed glass tubes are available only from a secondary source and the details of experiments are not known. Nevertheless, the quantities of action of successive 1D waves in their sequence tend to reach the attractor (quantum of action), as it was found for two-dimensional BZ propagation in closed systems, too. The future experiments may bring more accurate data describing the quantities of action of successive 1D trigger BZ waves. The analysis of two and three-dimensional cases verified the validity of the above concept and are the subject of our simultaneous communication elsewhere [97,121].

The 1D (thin tube, $K = 1$, $\kappa = 1$) arrangement of BZ wave propagation in water (non-restricted) media enables to tune the value of the quantum of action of BZ waves to the range $6.63 \pm 0.06 \cdot 10^{-34}$ J s. The experimental error of parameters of BZ waves obtained by recent techniques is about 1. Dispersion relations of BZ waves show a strong tendency of successive waves to reach a minimal quantity of their diffusion action. The dimension of space, characterized by the *diffusivity* factor K , has to be taken into account in non-restricted media to characterize the space available for emanation of wave from its source. The path of Brownian particles becomes more winding in restricted media, so that the so called *tortuosity* factor, κ , of

those media should be used together with the diffusivity factor to express this more complicated geometry of space available for the penetration of BZ wave. The successive waves in restrictive media tend to reach to a minimal quantity of diffusion action, too. The Principle of the least action may be helpful in interpreting the behavior of perturbed BZ waves that return reversibly to the original value of their quantity of action, when the perturbation source is switched off. The observed shape transformation of BZ spiral wave into the target wave and the transformation of trigger target wave into the phase wave seems to be related to the least quantum of action in non-restricted media. It is somehow related to the long lasting discussion on intramolecular diffusion and calculation of unimolecular velocity constants factually analyzing quantum mechanics as a classical diffusion process [138] (cf. Chapter 5.).

We should notice, however, that in this case where the said "speed of diffusion" cannot be observed directly (e.g. as a speed of chemical wave); it is as a rule identified with the ratio λ/t where t means the duration of precipitation. Better quantitative agreement with the experiment (up to 1% accuracy) can be achieved by completing the left-hand side of eq. 1. by a geometric factor (4π for three dimensional case) and by another factor, which characterizes the limiting influence of medium where diffusion takes place and which is of the order of unity. As shown above, the relationship (1) was found by various scholars to be either accidental (without any deeper physical meaning) or enigmatic (with something very important behind). Such diversity in opinions is very likely due to the traditional, rather subjective distinguishing between macroscopic and microscopic phenomena. The quantities v and λ on the left-hand side of the eq. 1 are, namely, essentially macroscopic. They are accessible to the observation by unaided eye, while the *Planck* quantum of action, on the right-hand side of eq. 1, is regarded to be the characteristic for tiny quantum processes on atomic scale.

There are several attempts to explain this discrepancy theoretically. For example, there is a very straightforward interpretation of the above relationship [139] using a concept of *de Broglie* wave known from elementary quantum mechanics as a wave controlling the probability amplitude of a particle ('*onde pilot*' [140]). Accordingly, we have to do with the *de Broglie* probability pilot-wave of an abstract particle of mass equal to the mass of end-product molecule moving with the "speed of diffusion" v . It is further assumed *ad hoc* that the period of precipitation coincides with some integer fraction of *de Broglie* wavelength η/Mv , what is just that meets the want. Such a simplistic and quite formal approach to this problem (tolerable in pioneering works), together with the obscure concepts involved is, as we believe, a nice illustration of the reasons that have led to the scepticism aimed against the quantum theoretical interpretation of eq. 1 and for years effectively damped the activities in this interesting field.

It is clear that for physicists, it is a rather unwelcome idea that the *Planck* constant, so far strictly governing the

world of waves in quantum-mechanics, could stretch up becoming a more general function that can influence the larger scale of our macroscopically comprehended world. Some general mechanism might be found responsible for all the above-mentioned cases, from the shell striation to tree-rings separation, possibly touching the macroscopic layout of deposited layers of geological scale. Before the acceptance of this scenario within the frame quantum mechanics [141,142], however, some other systems should be evaluated by this Principle of least action. The next candidates of self-organized Brownian particles may be electrons forming stripes in Crookes tubes filled by inert gases and atomic waves prepared recently from atoms of alkali metals diffusing through tubes filled with inert gases. Last but not least, the authors, who are convinced that the numerous observations are satisfactorily confirming the validity of eq. 1 under different experimental situations, cannot be ignored

h) Quantum criterion and speed of diffusion

The first step to better understanding somehow empirical formula of the eq. 1 is the opportunity to clarify the physical meaning of the quantities involved. There is a very useful criterion enabling us to decide whether a particular physical problem belongs to the domain of classical or quantum physics. It can be formulated as follow [142]. In every case where the quantity of type of action (Λ) relevant to a given physical problem, is comparable with the Planck's quantum of action h the problem can be solved consistently only within the frame of the quantum theory. Remember that there is no further requirement put on the absolute scale of the system. If, according to this criterion, any particular system is a quantum system, it can be of both the microscopic or macroscopic nature. At the first glance, we can see that this criterion implies immediately the quantum nature of the periodical precipitation and of chemical waves experimentally described by eq. 1 if only one admits that its left-hand side represents "relevant quantity of type action".

The product of quantities Mv and λ has, of course, the physical dimension of action, but the adequacy of its construction as a product of just these three quantities remains uncertain. The physical meaning of λ may be regarded to be more-or-less clear: it is, e.g., the distance between subsequent Liesegang's rings representing the minimal path, which has to be passed by all particles consisting the precipitate. On the other hand, M is the mass of a single molecule of the end product, which as such is not possibly taking part in the diffusion. It, however, is evidently of questionable relevance. Even more difficult is the justification of use of the quantity v , computed, as already mentioned above, as the ratio λ/t . It is not the "speed of diffusion" as introduced here, but it is factually the time t , which characterizes the duration of the precipitation process as a whole. The quantity λ enters for the second time tacitly in the left-hand side term of eq. 1 and the meaning of the quantity v thus remains unclear. Interestingly, as was pointed out by Mach [143], the confusions of every similar type invalidated the original formulation of Maupertuis's principle [128] "de la

moindre quantité d'action" where the quantity of action was for the first time defined. The necessary revision of this concept for a purely mechanical case due to Euler [144] showed that the properly defined quantity of action Λ has to contain the instant velocity v in the explicit form such as $\Lambda = \int Mv dx$, where the integration is taken over the whole path considered. Even this short rendezvous shows that the quantities from the left-hand side of eq. 1 are not fully apt to represent the physical system properly enough. In order to answer the question "why the strange mix of incompatible quantities Mv and λ gives the well-defined universal constant h " it is necessary to reconstruct the action Λ from another quantities, which are more transparently related to the system under investigation. Let us clarify the relation of these new quantities to the previous quantities of M , v and λ and then apply them to the quantum criterion.

Assuming that the decisive process controlling the periodic precipitation or oscillating reactions is the diffusion of reactants, we need for the construction of corresponding "relevant quantity of type action" the definition of something like as the instant "velocity of diffusion". If we, for the sake of simplicity, confine ourselves only to one dimension, the diffusion can be described by the following differential equation, $\partial n/\partial t = D (\partial^2 n/\partial x^2)$, where $n(x,t)$ means the concentration and D the diffusion constant. For continuous $n(x,t)$ the "velocity of diffusion" is not well-defined and has to be assumed to be infinite. This statement can be elucidated by the following argument [145]. If the concentration, n , of a substance at time $t = 0$ is finite only in a certain bounded region (e.g., when n is constant) and which is identically zero in all out-regions, the relation implies that after arbitrary small time interval, dt , the concentration in any point of the whole space is non-zero. Therefore the transport of matter to any distant point would become instantaneous and its velocity is infinite. On the other hand, when taking into account the discrete molecular structure of ordinary matter, the concentration in a given point should remain zero until the point is reached by the first diffusing particle (molecule), i.e., the velocity should be finite in any case. In spite of this disagreeable discordance between molecular and molar approach to the diffusion, there is a possibility of meaningful definition of its velocity even within the continuous approximation of $n(x,t)$. Let us suppose that there are N particles concentrated at time $t = 0$ in the plane $x = 0$ (so called δ - source). The solution of the diffusion equation then reads: $n(x,t) = N/(2\sqrt{\pi Dt}) \exp(x^2/4Dt)$. Since the times of Fourier, a well-known property of its solution is that the time record of concentration, taken in the neighborhood of a certain fixed point x , has a local maximum⁴. The mathematical condition for this maximum reads as $\partial n/\partial t = 0$. This condition is, however, obviously equivalent to the condition $d^2n/dx^2 = 0$ (if D is constant). Second space derivative of the principal solution gives the complex expression, $\partial^2 n/\partial x^2 = \{N/4\sqrt{\pi(Dt)^3}\} \exp(x^2/4Dt) \{(x^2/2Dt) - 1\}$. Using now the above-mentioned condition we can immediately obtain that $x^2 = 2Dt$ and that the time derivative of this formula provides the basic relationship, $xu = D$, where $u = (\partial x/\partial t)$

has a physical meaning of the instant velocity of concentration maximum.

Because the quantity u represents, in fact, the movement of the most numerous swarm of diffusing molecules, it is quite reasonable just to call u the “instant velocity of diffusion”. It has remarkable consequences, as the equation $x^2 = 2Dt$ is practically the same as the equation describing random walk of a single Brownian particle [146,147]. The only difference is that x is here no longer the position of concentration maximum but the mean position of a particular Brownian particle at time t . Naturally, the diffusion constant D must be the same for both, the microscopic as well as macroscopic case, because the diffusion equation describes the identical physical process of diffusion. We can thus say that the typical

“average” Brownian particle follows the position of concentration maximum or, in other words, that the most significant packet of diffusing molecules consists of the “average” Brownian particles. As we believe [149], it is just how the *Planck* universal constant can be introduced into the essentially macroscopic relation $x u = D$. Namely, it would be the movement of a Brownian particle of mass M controlled by a purely quantum process for which the diffusion constant in three-dimension should have the *Fürth's* value of $D = D_Q$ [148], i.e., $D_Q = h/4\pi M$. The equation $x u = D$ formally acquires the same form as the empirical eq. 1, written as $4\pi M u x = h$, provided that the parameters v and λ are respectively identified with u as the velocity of diffusion and x as the distance spanned by diffusion [149].

¹ Assuming concentrations $[X]$ and $[Y]$, perturbation δX , rates $\rightarrow r_{\text{for}}$ and $r_{\text{rev}} \leftarrow$ with the associated rate constants k_{for} and k_{rev} we can express the time derivative of the second variation in entropy (cf. Chapter 6.), $d/dt(\delta^2 S)$, to be proportional to $(dA/T)d\nu$ where $A = RT \ln(r_{\text{for}}/r_{\text{rev}})$ and $\nu = (r_{\text{for}} - r_{\text{rev}})$. Then we can write that $d/dt(\delta^2 S) = -r(2k_{\text{for}}[X][Y] - 3k_{\text{rev}}[X^2]) (\delta X^2)/[X]$. The system can be illustrated in Fig. 7 (see also previous Chapter 15, Fig. 15. 2), where each value $[X]$ represents a state of the system and the parameter Δ displays the distance from equilibrium. When Δ is small we deal with a near-equilibrium state, which is an extrapolation of the equilibrium state and is often called thermodynamic branch. In certain systems, such as those with autocatalysis, the states belonging to the thermodynamic branch become unstable when Δ reaches Δ_{crit} . When this happens, the system makes a transition to a near branch, which may correspond to an organized state.

² The role irreversibility, which plays the role of a destroyer of order near equilibrium and as a creator of order far from equilibrium, is remarkable. Away from equilibrium there are no “extremes” principles that uniquely predict the state to which a non-equilibrium system will evolve. As a result of random factors (inhomogeneities, imperfections, perturbations, etc.) the system evolves to one of many possible states that often possess spatio-temporal organization (i.e., order through fluctuations). We can assume another simple model case of a process, $d\alpha/dt = -\alpha^3 + a\alpha$, which has a stationary state at $\alpha=0$ or $\alpha(\sqrt{a})$. Because of the disparity of reverse conversion degree, $\alpha \neq -\alpha$, the situation has a broken symmetry. The value of a , at which new solution doubles, is known as the bifurcation point, see Fig. 15.2. For a fluctuation, $\alpha = \alpha_{\text{eq}} + \delta(t)$, we can see if α_{eq} is stable or not by making its derivative, $d\delta(t)/dt = -3\alpha_{\text{eq}}^2 \delta(t) + k\delta(t)$. At the stationary state $\alpha_{\text{eq}} = 0$ and the stable solution requires $k < 0$ because $\delta(t)$ decays exponentially. On the other hand if $k > 0$ the solution is locally unstable because $\delta(t)$ grows exponentially. Time dependent perturbation, $\delta(t)$, moves from a value less than zero to that greater than zero, hence the solution $\alpha_{\text{eq}} = 0$ becomes unstable and the system makes a transition to one of the new available solutions (that bifurcate at $a > 0$). The process is not deterministic as it depends on the random fluctuations.

³ According to *Feistel* and *Ebeling* [R. Feistel, W. Ebeling “Self-organization, Entropy and Development” Kluwer, Dordrecht 1989] we can admit that dissipative structure can be considered from a thermodynamic point of view as energy transforming system. In comparison with the *Bénard* convection a classical heat engine has to include certain presumptions. First of all we have to recognise that in both, such as *Carnot's* as well as *Rayleigh-Bénard's* machine-like cases, we can find a fraction of the incoming heat transformed into an upgraded form of energy. That is mechanical work as the ordered motion in the former and the structural and orderly form of rolling in the latter case. Notwithstanding this similitude, an essential difference can be pointed out between these two kinds of this higher quality of energy. *Carnot's* engine produces mechanical work effecting its surroundings through the outcome of the directionally lifting of a weight while the *Rayleigh-Bénard's* motion manifests itself in the generation and subsequent conservation of the ordered arrangement (represented by geometrical structures). This structure is continuously appearing and disintegrating, in other words, a fraction of heat is repetitiously upgraded into structure and degraded back to heat (that ends up in the colder reservoir). This operational characteristic of *Bénard's* convection rolls corresponds with that of those systems, which are termed ‘*autopoietic*’, i.e., with such procedures that are not concerned with the production of any output, but only with its own self-renewal (in the same process structure). Of a special concern is thus a supra-Carnot efficiency of these systems, which cannot be traced to the efficiencies of individual coupled heat engines but to the way in which their operations are coupled to each other (self-organisation). In this intent we can mention the previous objective of *Clausius* second law analysis, whose result was by him expressed in terms of what he called “*the principle of the equivalence of transformation*”. According to *Iñigues* all the possible operations of a simple cyclical process can be subsumed in the relation describing ΔS_u , which represents an entropy change of zero for the universe and is the central equation of the negentropic reformulation of the second law of thermodynamics [J.C. Iñigues “Revision of Clausius Work” Entropy (1999) 111, 118 and 126; Acta Negentropica 1 (2000) 28]. ΔS_u consists of three terms, $-Q_h/T_h + Q'/T_c - w/T_h$. The last one is seen to give the limiting reversible execution as a negentropy operation with an associated entropy change equal to $(-w/T_h)$. The second term corresponds to the limiting irreversible operation in which all of the heat coming out of the hot reservoir (h) finds its irreversible way into the cold reservoir (c). In this situation no work is produced ($w=0$) and we can equal the heat given off by the hot reservoir Q_h with that reversibly transferred to cold reservoir, Q' . The irreversible transfer of an amount of heat from the hot to the cold reservoir, corresponds to an entropy change, $Q_h/(T_h - T_c/T_h)$, which is an entropic operation. It follows that the univer-

se's entropy change for a simple cyclic process transit from a positive to a negative value as we move from the entropic (zero efficient operation represented by the irreversible limit) to the efficient, negentropic reversible limit. Between these limits there exists an operation with an efficiency η' , i.e., $0 < \eta' < \eta_{\text{rev}}$, which can be identified with solving the efficiency of Q/Q_h that is found as $\eta' (= Q/Q_h) = (T_h - T_c)/(T_h + T_c)$. Thus, all the operations with efficiencies smaller than η' will be entropic, while those with efficiencies greater than η' will be negentropic. The particular operation for which $\eta = \eta'$, occurs with $\Delta S_u = 0$. The fact that the entropic and negentropic efficiency regions respectively arises due to the preponderance of unordered over ordered energy (and *vice versa*), allows us to speculate. The emergence, the coming into being of self-organising phenomena, might obey a similar mechanics, i.e., the emergence can be seen concomitant to the universe's transition from entropic to negentropic, with the onset of organisation taking place at that 'umbral' point at which $\Delta S_u = 0$.

- ⁴ When studying the transport situation in a layer ($x + dx$) and when the maximum of concentration passes across then we have to assume that the associated change $\partial n/\partial t$ is equal zero. Because of $\partial^2 n/\partial x^2 = 0$ we can obtain $x^2 = 2Dt$, which shows that the maximum of concentration wave moves in accordance with the same law as the projection path of whole arbitrary motions of a single Brownian particle. Let us derive $\partial/\partial t$, which yields $2x (\partial x/\partial t) = 2D$ so that $x = u = D$, i.e., the concentration maximum at place x moves with the instant speed of u . On the other hand, the same equation should also be valid for a single particle, so that D has a physical meaning of molecular microscopic diffusion constant given by an elementary molecular event, $D_M = \eta/\kappa M$, where M is an absolute molecular weight, κ is a geometric (symmetry) factor and η is the Planck's constant ($\approx 1.05 \times 10^{-34}$ Js). In the case of a central symmetry in 3-D systems where $\kappa = 4\pi$ one obtains the well-known diffusion constant of the *Schrödinger* equation $D_Q = \eta/2M$. In fact, the above-introduced *Maupertuis* principle of least action is put here in the consensus with the *Fermat* principle of least time, citing "*The Nature acts via the easiest and the most accessible way reached within the shortest time*" [P. Fermat "*Synthesis ad reflexiones*" (a letter to de la Chambre 1662) in "*Oeuvres de P. Fermat*", Tom 1, Paris 1891, p. 173]. It is necessary to find conditions under which the diffusion coefficient is a limiting value. It seems very probable that the best candidate for this validity is the H^+ ion (proton), which is likely the most active and intermediary particle in all-aqueous solutions. It is a matter of remarkable interest that the estimate for the classically defined diffusion coefficient of proton in water reads as $kT/(6\pi\eta R) \cong 2.2 \times 10^{-8}$ [m²/s], which well coincides with the quantum *Fürth's* limit of $h/(4\pi m) \cong 3.1 \times 10^{-8}$. It may furnish some further contemplation when assuming that proton provides the means for oscillatory processes in the aqueous media similarly to the oscillatory modes provided by electron in solids, which may even attract speculations about the decisive role of proton in all processes enabling living organisms to be animated (such as the progress of nerve signals).

Literature to Volume four

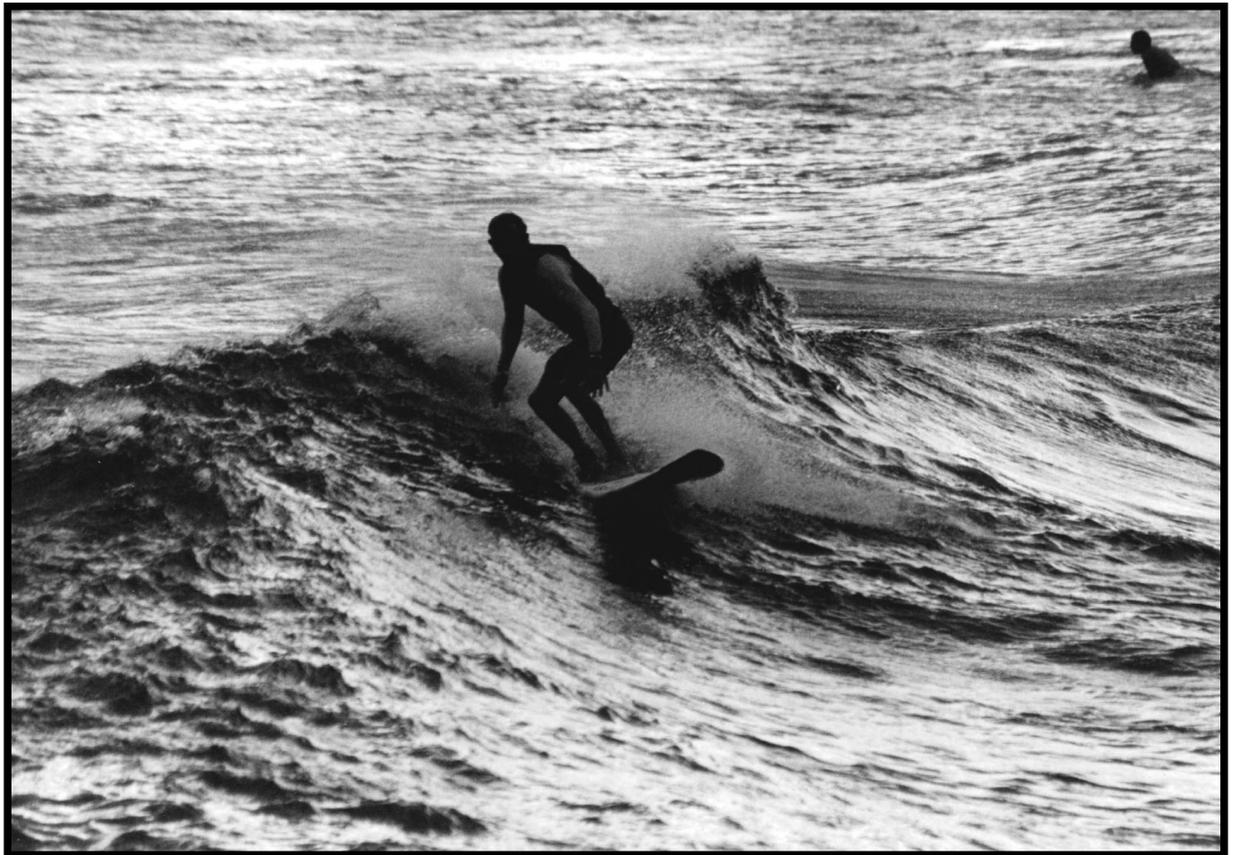


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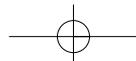
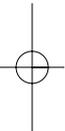
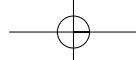
Volume five
**SOCIETY, SCIENCE AND ECOLOGY – PROGRESS AGAINST
SURVIVAL**

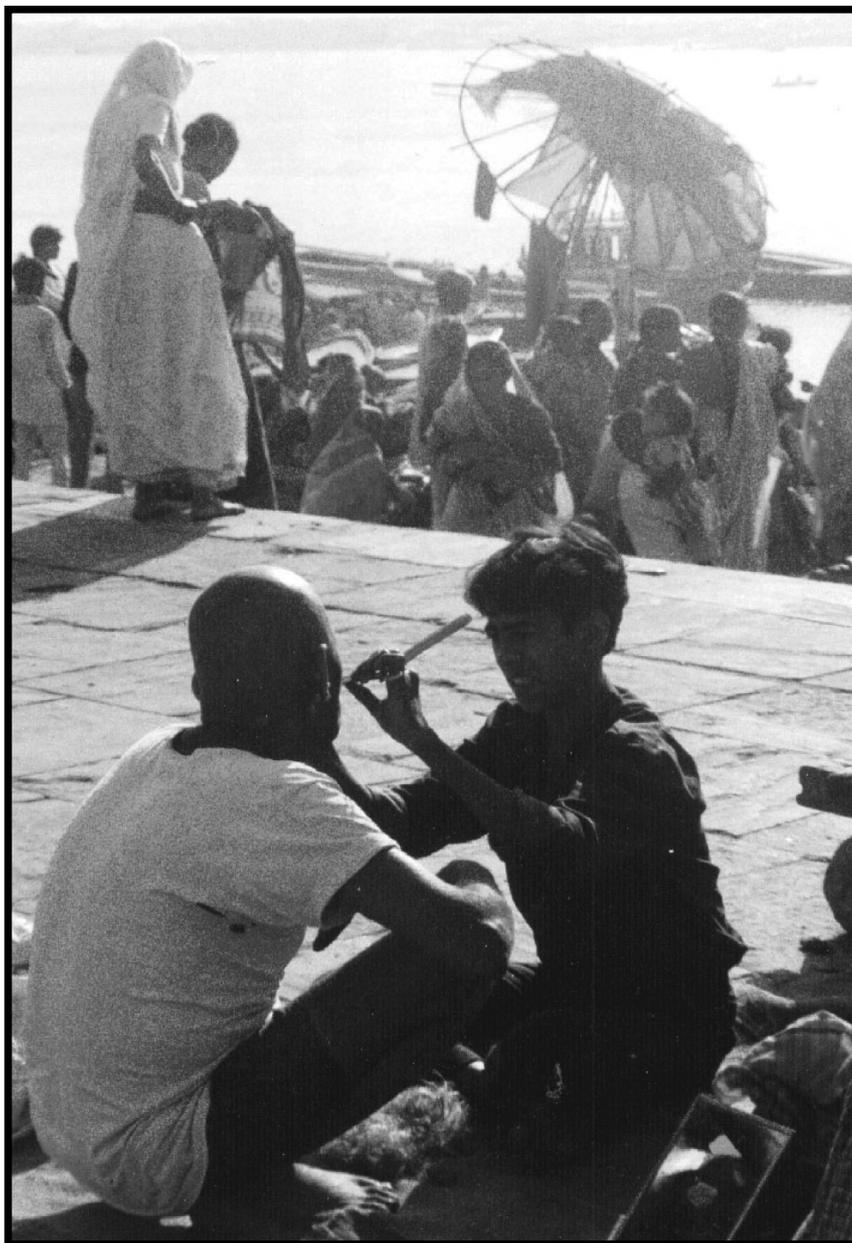
Energy science and society – environmental dilemma

Thermodynamics and society – laws versus feelings

Modern materials and society

Advanced trends in understanding our Universe





CHAPTER SEVENTEEN

17. Energy science and society – environmental dilemma

a) Heat sources of a motive power – engines

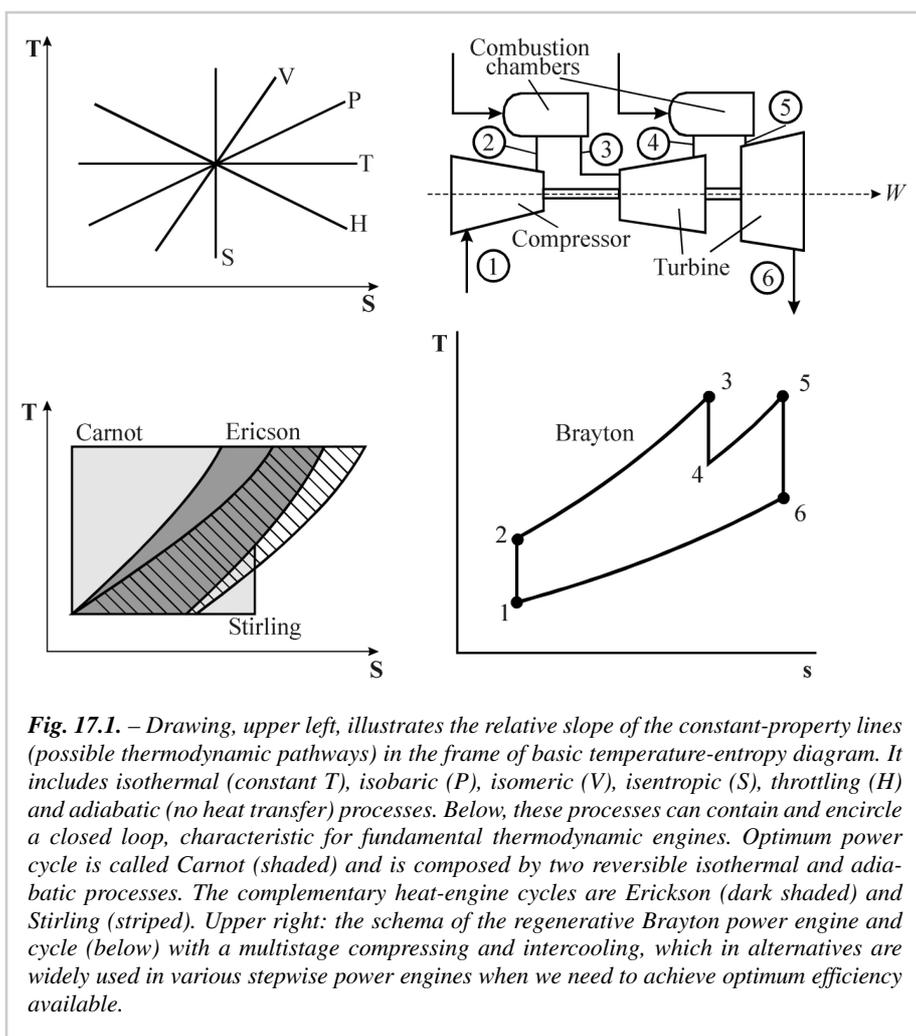
Almost all the mechanical energy produced today is created by conversion of thermal energy in some sort of a heat engine [1–3] (only little is gained directly, e.g., from the energy of water and wind, as exemplified in the next paragraph). As shown above, man-made engines are literally *energy transducers* designed to transform chemical energy, held within the electron configuration and stored in the form of fuel and oxygen, into mechanical work – including the realm of thermodynamics, which is the necessary transformation via the intermediate step of heat. It necessarily needs a gear, an additional energy transducer to transform a reciprocating motion of a piston into continuous directional motion using an eccentric crank-and-shaft mechanism (alternatively using the piston directly as a magnetic core in the impedance coil-cylinder). The efficiency of the overall system cannot exceed the thermodynamic efficiency of the *Carnot* cycle including the energetic efficiency of such a reversible ‘holonomic’ gear, which is ideally equal unity¹.

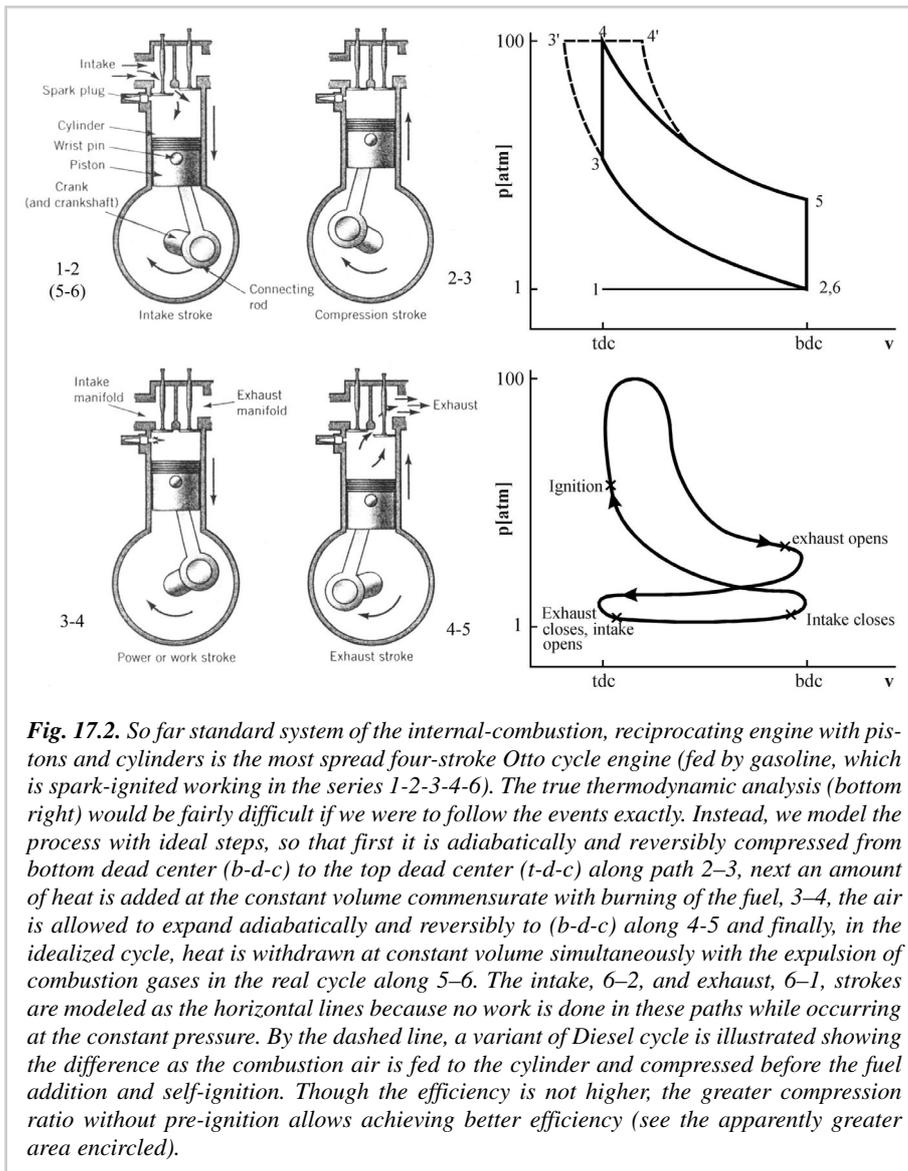
As already said, the engine’s thermal operation can usually be approximated by an ideal thermodynamic power cycle of some kind [1].

Any thermodynamic cycle is made up of a series of processes that must return the working substance, often fluid, to its initial state. Its better perception can often show the power engineer how to improve the operation and performance of the system. During almost all of the processes involved, one property (T, P, etc.) is commonly held constant, see Fig. 1. All reversible adiabatic processes are naturally isentropic ones. It is common practice to plot the processes composing the cycle on a graph of property coordinates, such as T-S or P-V or so, and for such an illustration the cyclic integral of work is equal to the cyclic integral of heat. The figure of merit is defined as the ratio of the desired energy gain to the energy that is input, i.e., the thermal efficiency η equals the ratio of the net work output to the heat added at high temperature. Repeating in short that $\eta = 1 - T_{\text{out}}/T_{\text{in}}$, which means that it is impossible to build a device whose sole effect is to produce work while exchanging heat with a single

thermal reservoir (in) only, without having a low-temperature sink (out). Already *Carnot* and *Kelvin* acknowledged that no real engine can turn the given amount of heat completely to the mechanical work and any real engine working between the temperatures T_i and T_{i+1} must have the thermal efficiency smaller than the ideal Carnot cycle, i.e., $\eta > \eta_{\text{real}}$. It can be easily envisaged upon the separation of a real cyclic process to a set of many consequent infinitesimal processes, so that $\sum_i \Delta Q_i/T_i \leq 0$ and any real thermodynamic process follows the flux inequality $Q'/T < S'$.

In practice, there are four phenomena that render any real thermodynamic process: friction, unrestrained expansion, mixing of different substances and heat transfer across a finite temperature difference, the last being most important. Only three ideal power cycles can be assumed reversible, often called *externally reversible power cycles*, to include the *Carnot* (power optimum), *Stirling* and *Ericsson* cycles (cf. Fig. 1.). However, the Carnot cycle is not a practical power cycle (because it has so little specific work that any friction would almost eat up the net work output) and *Stirling* engine is a rather complicated to run (although its renaissance is on progress reconsidering its worth for economical exploitation of low value waste-heats and sun-heated air). Beside two isothermal





processes, *Ericsson* cycle replaces two originally reversible isentropic (adiabatic) processes by two reversible isobaric processes and the heat transfer is than taking place in all four processes, which requests an internal component called a *regenerator*. The engine is practically composed of a compressor, turbine and counter-flow heat exchanger serving as the mentioned regenerator.

More important are the *internal (combustion) engines* known as *Otto* (gasoline, spark ignition), see Fig. 2, and non-compression *Lenoir* engines (the latter not so known but practically operated in the pulse-jet engine used by the German V-I bombs during the 2nd war). Although enormous sophistication has been added in the last hundred years, the cycle is still the same including the four distinct strokes: intake, compression, power and exhaust. The exact thermodynamic description of this cycle would be too complicated so that, instead, we idealize the process and express the efficiency by substituting for each of the heat terms the corresponding values of $C_v \Delta T$. This yields a simple expression with only the *com-*

pression ratio, r_v , as the important Otto-engine parameter, which is the ratio of maximum to minimum volumes. When cold air is used as the working fluid, the thermal efficiency can be shown to be equal to $\eta = \{1 - (r_v)^{1-c}\}$, where c is the ratio of specific heats fixed at a value close to that of a diatomic gas ($c=1.4$). Comparing the *Otto* cycle efficiency (0.6) with that of a *Carnot* engine (0.9), when operating between the same peak temperatures, it yields 66% because there is a technical limit to increase the thermal efficiency by increasing the compression ratio (standard $6 < r < 12$). It is caused by the premature ignition of the fuel-air mixture before the flame front, initiated by the spark plug (too early detonation).

In contrast to the *Otto* engine, which consists of two adiabatic and two isomeric processes, the *Diesel* engine replaces one isomeric process by isobaric one as the oil-fuel is injected into the hot compressed air to burst immediately without help of spark ignition. Beside the above-mentioned compression ratio the thermal efficiency of the *Diesel* engine includes another ratio which is the *cutoff ratio*, cc , given by volume at the end of fuel addition to minimum

volume related in the thermal efficiency by the relation, $\eta = 1 - (cc^k - 1) / \{k r^{(k-1)}(cc - 1)\}$. Compression ratio can be increased ($18 < r < 25$) and the cutoff ratio (greater than unity but as low as possible) is optimized by the engine design.

External combustion systems have several advantages over the internal ones primarily the lower pollution due to burning fuel with excess of air and at lower temperatures thus utilizing less expensive fuels. In practice, the most important is the *Brayton power cycle* (see Fig. 1) used in gas turbine or turbojet engines. This also is the only major power cycle that can operate as both the internal or external combustion engine. The working fluid is compressed adiabatically in a compressor, heat is added in an isobaric process in combustion chamber (or heat exchanger) and the hot gas expands adiabatically in the turbine and then the heat is rejected in a isobaric process into the atmosphere (or heat exchanger). In the *open cycle*, the working fluid is atmospheric air and the heat rejection process occurs in the atmosphere as the turbine exhaust is dis-

charged. In the *closed cycle*, any working fluid can be employed in continuous cycling and the heat rejection process is accomplished in a heat exchanger.

The most important parameter is the compressor pressure ratio, r , of maximum-to-minimum system pressures and the thermal efficiency relates to $\{1 - r^{(1-k)/k}\}$. This gives a preference to (non-corrosive) noble gases (helium, argon) that possess the highest value of specific heats ratios (5/3), while for diatomic gas (such as air, N_2 , CO) and triatomic gas (water, CO_2) it is mere 7/5 and 4/3, respectively. There are several ways how to improve the efficiency usually by introducing a regenerator as a heat-recovery device. If the regenerator efficiency is full 100%, the thermal efficiency reads as $\eta = 1 - (T_{\min}/T_{\max}) r^{(k-1)/k}$ and thus the efficiency of such a regenerative *Brayton* cycle can be increased by increasing maximum and/or decreasing minimum temperatures, or by decreasing the compression ratio, r , or using a gas with low value of k , having thus an opposite effect as that in the simple *Brayton* cycle.

Further improvement can be achieved by using multi-stage compression with inter-cooling particularly improving the compressor efficiency over a small pressure range. Practical combination of hot-gas turbine placed right after the burning site with subsequent use of a classical heat engine succeeded recently to hit higher efficiencies. Another option uses reheating where the additional heat can be simply added to gas by burning more fuel in the turbine gas before it expands to the atmospheric pressure. The efficiency can be further improved with the application of a regenerator as the higher turbine-exit temperatures make the generator more effective.

Vapor power cycles are generally classified as external combustion systems and they must employ a heat exchanger (here called *boiler/condenser*) for the heat addition/rejection process. The basic ideal vapor-power system is the *Rankine cycle* and the thermodynamic processes are identical to those in *Brayton* cycle. The difference arises from using a two-phase (liquid-vapor) working fluid whereas the *Brayton* cycle is a gas-power cycle. Although the most common fluid is water, there is a variety of options from organics (aromatic hydrocarbons and fluorocarbons) to mercury (making amalgamates and being toxic) and sodium or water-potassium binary. The four components are accounted for each carrying out a thermodynamic process: the adiabatic compression and the isobaric heat-addition process. The latter occurs in a boiler, followed again by adiabatic expansion in the turbine or reciprocating steam engine; and, process isobaric heat rejection in a condenser. Efficiency can be increased by vapor superheating, increasing the condenser vacuum or maximum pressure. Practically there are limits of about 600 C and 1 mm Hg. Another modification is the *reheat Rankine* cycle where the steam is removed from the turbine after partial expansion and returned to the boiler for adding heat at constant pressure. This permits to use a very high steam pressures without excessive moisture at the condenser inlet (forming droplets being dangerous for the blade material erosion). The *regenerative cycle* is again a modification of the basic *Rankine*

cycle improving its efficiency. Before reaching the condenser some steam is separated from the turbine and then used to heat a liquid boiler feed before it is entered by the steam from generator.

For practical applications, we seek maximum energy release per a weight unit of fuel that is fulfilled by external-combustion power systems. They have several advantages over the internal ones, in general, providing less pollution even when taking advantage of less expensive fuels. Most useful is the *Brayton* power cycle utilized in the gas-turbines (a closed system where working fluid can be re-employed) and turbojets (an open system where the heat-rejection process occurs in atmosphere). Water is the most common working fluid used in the advanced vapor-power cycles (*Rankin*) but a number of other fluids have also been employed (NH_3 , aromatic hydrocarbons or liquid Hg, Na, K, Rb). The maximum steam temperature is normally limited by the materials (particularly in the super-heater section and the inlet of high-pressure turbine) and the thermal efficiency is strongly affected by the compression and expansion efficiencies of the pump and turbine.

Beside the standard thermal efficiency, η , we may assume the availability transfer, a , accompanying heat (Q) to move across the source (T_s) boundary. This is evaluated relative to the environment (T_o) to be equal $(1 - T_o/T_s)Q$. Energy carried in by the speed of heat transfer, (dQ/dt) , is either used (u) or lost to the surroundings. That can be described by a second-order efficiency (η'), now in terms of energy rates in the form of product/input ratio $(dQ_u/dt)/(dQ_s/dt)$. In principle, this value of η' can be improved by applying sufficient insulation to reduce loss, rationally to fall between limiting values of 0 and 1. It can be seen that the availability accompanying the heat transfer, dQ_u/dt , is either transferred from the system accompanying both transfers or destroyed by irreversibility within the system itself. Therefore it can be derived by the ratio of $(1 - T_o/T_s) \cdot (dQ_u/dt)$ to obtain the same formula written for Q_s . Consequently $\varepsilon = \eta' [(1 - T_o/T_u)/(1 - T_o/T_s)]$. Note that η' and ε , each gauge how effectively the input is converted to the product – η' does this on an energy basis whereas ε does this on an availability bases so that the parameter ε can be called a second law of efficiency. It shows that the heat game is practically more complicated than normally seen in the textbook thermodynamics.

b) Perspective of alternative energy sources to replace intermediate heat production.

Part of the energy delivered to the Earth's atmosphere by Sun is responsible for the creation of temperature and pressure gradients [4-6], one of the most typical results being the reality of atmosphere flows – wind, see Fig. 3. For a long time it was a source of easily available mechanical motion (sailing ships, windmills), which is recently encountered among alternative energy sources because we do not need to install any 'intermediate' step of the heat conversion to mechanical work as it is factually outfitted by nature itself. However, genuine alternative energy,

which avoids any transitional kind of a 'heat engine' and for which we can employ another philosophy of the chemical energy exploitation, is a direct use of the inherent transfer of electrons as a straightforward source for electric current [7–10]. Let us discuss the two mentioned examples in more detail.

Energy from wind

Most easily accessible motive power is inherited within the force, which is automatically available as a result of the natural conversion of the energy of Sun [4–9]. Neglecting reevaluation of traditional and almost saturated hydropower sources let us concentrate on *wind* and its motive converters – *turbines* or more traditional *windmills* as they transform the kinetic energy of the wind into mechanical rotary work, see Fig. 4. The total wind energy available is estimated to about 10^6 GW, but it is mostly concentrated in higher altitudes so that the readily available part is mere 1 % and because it is widely distributed only about 10^3 GW has a practical use. The estimate for the year 2004 is about several thousand windmills of the total energy production of about 20 000 MW and they can, at best, cover as much as about 3 % of energy demand. There are exceptions: for example, Denmark's output of wind-powered energy would meet 21% of the country's total electricity production in the year 2003 – the highest in the world. It is estimated that the three years' average growth rate would exceed 50%, with top spots of Spain, USA, Italy and Greece, Germany being without doubts the titan of the wind turbine utilization. Today's windmills stand 100 m off the ground, have blades that span 75 m and are capable of producing 3 MW.

Technological improvements have lowered their production cost to about one-fifth of what it was 20 years ago. Because of its yet-high initial investment cost, wind power is, however, still not economical without some form of subsidy.

For the most conventional production of alternating current (ac) electricity, the windmill system must be designed to operate at a constant angular velocity over a wide range of wind speeds to assure a constant frequency. There are many different kinds of windmills, including propellers and other axial-flow turbines. The total power that is available to a given wind source is equal to the product of the mass flow rate of the wind and its kinetic energy and varies as the cube of the wind velocity. The power of windmill is thus proportional to the third power of the wind velocity and the second power of the length of the propeller blades. The total wind energy cannot be recovered because the outlet wind velocity cannot be reduced down to zero and the large assemblage of windmills can even change the established wind environment. The maximum (theoretical) power that can be realized from a wind system is 59.3% of the total wind power. Practically the revolution rate is from 20 to 120 rev/min using the wind velocity within 3–30 m/s with a mechanical efficiency of the propeller between 40–48 % to provide the maximum power output as high as 4 MW. The output is strictly related to the length of blades, which cannot be increased beyond certain limits because angular velocity of the tips must not approach the speed of sound (material strength, loud shouting).

Utilitarian constructions, unfortunately, cannot be practically solved without release of severely offensive sound,

which can seriously disquiet nature. Intensive noise can enforce animals to vacate nearby areas and even desert fishes if installed in the shallow sea waterfront. Low vibration sound, often difficult to observe, can become a source of severe health problems. Because of high loudness, the windmills must be situated in public-isolated areas and their location should not disturb the landscape. Appropriate orientation against wind is again an inevitable technical problem difficult to be solved optimally. Unfortunately, the wind velocity is also not constant in magnitude or direction from the top to bottom of large rotors, which imposes cyclic loads and increases noise problems. All that can well illustrate how many often unseen or even neglected problems can get involved.

One of the unusual wind systems worth of special note is the

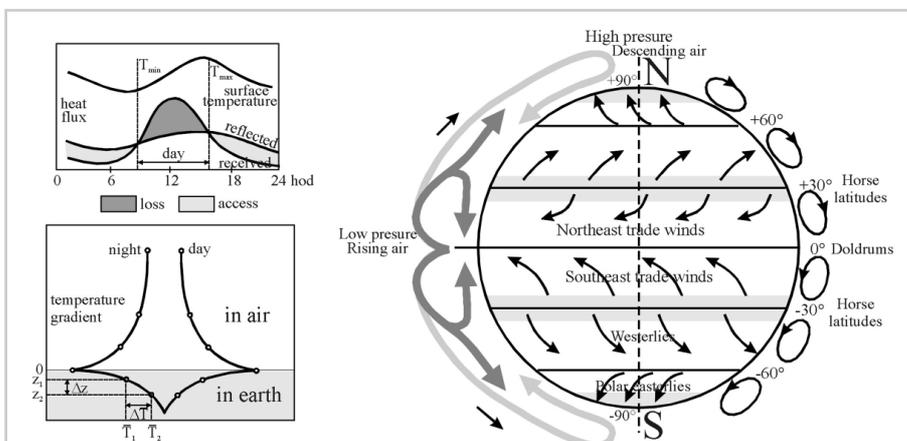


Fig. 17.3. The atmospheric convection on the rotating Earth showing vast rivers of air that cover the globe from the equator to the poles. In the equator the Sun's rays have the large angles of incidence so that the surface and the air is warmed most extensively and, therefore, the air starts to rise. On the contrary, the area of poles are least warmed so that the hot air masses tend to move from the equator towards the poles at higher altitudes of atmosphere while the cold air from the poles moves in opposite direction. The rotation effect, however, breaks both the Northern and the Southern Hemisphere's convection cell into three-to-three parts causing, in addition, circulation of air so that winds in each cell get skewed. The winds between the equator and the thirty-degree parallel are called 'trade winds' while the winds between the thirty and the sixty-degree parallels are called 'westerlies'. On the left is shown a more detailed view on flux and temperature gradients because of diurnal changes in the heat delivery conditions.

Flettner rotor. As the rotating cylinder spins it establishes a high-pressure region on its front part producing so a net force acting on the cylinder, which can thus be used for transport (sailing boats) or production of energy (mounted on movable car on superconducting rail system).

Certainly, this is just an illustration of the aspiration of using straightforwardly available energy income from the Sun. It is not the purpose of this book to review all possible alternatives and their technical, thermal and ecological features – the above-mentioned cases are just a few examples of wide variety of options. We should make clear, however, that the capital source of energy

the quest for ways to *bypass the habitual conversion to heat* and to obtain electric energy directly from the chemical energy inherent in the fuel, the principle of which is the separation of a chemical reaction into two parts. Instead of allowing the reactants to come into direct contact with each other, as in the combustion of fuel in air, they are mutually isolated by a material that transfers ions but not electrons. The electrons involved are then transferred through an external circuit, where electrical work is extracted from them. In fuel cells, the reactants are supplied from external sources, while in batteries they are contained within the device. In addition to high efficiency and low emissions, fuel cells are attractive for their modular and distributed nature, zero noise pollution and their plausible potentiality in any future economy based on hydrogen fuel.

Without going to unnecessary details let us show the standard burning in the case of simplest fuel, hydrogen, which has some advantages: unlimited resources, convenient physical properties (high specific heat and low viscosity), and relatively high heat production while burning. Among its disadvantages, there is high explosiveness when mixed with air in a wide range of composition, high velocity of flame propagation, high diffusivity (causing the ageing of materials) and difficulty to seal and even notices the leakages. Although the latent heat is about one third of

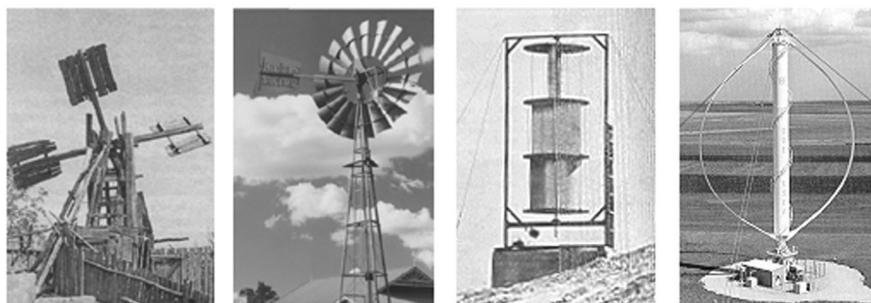


Fig. 17.4. Examples of the long-running attempt of people to enfeather wind in order to capture its capability to provide mechanical energy. From left we would like to exemplify the beauty of some time-honored windmills. For example, an old, simple wooden Mid-European windmill or a traditional standby of the early American and Australian farmers used for lifting water from deep wells. Contrary to the traditional construction of horizontal-axis windmills, the drag-based, vertically alignment turbines can also be operated (typically the stacked 'Savonian' rotor), which can be made in many different ways with buckets, paddles, sails or oil drums. The rotor is s-shaped (when viewed from above) and apparently originated in the olden Finland. Right, the modern, currently operated, 500 kW variable speed machine (early patented by Darrieus in 1927). It is the lift-type vertical-axis machine, which is interesting as each blade sees maximum lift only twice per revolution, making for huge torque sinusoidal output but advantageous in being capable to accept the lower and more turbulent winds.

will, sooner or later, become exhausted so that the world inhabitants will be required to undergo drastic changes: downward shift in their life comfort or radical reduction of human population. Unavoidably, it will happen due to the uncompromising revolution of the energy lifestyle unless a radically new system of energy conversion will be revealed, or at least the existing considerably improved, in order to span our traditional business governed by low-efficient thermal engine. Even within our sophisticated state of comprehension a sudden scientific discovery of new ways in production and accumulation of energy can be anticipated², which the only long-term solution is for the upcoming generations.

Fuel cells and batteries

Because of the inherent second-law limitations for the above-mentioned heat-feed power cycles, as well as the potentiality to reduce environmental impacts and geopolitical consequences of the use of fossil fuels, the sphere of fuel-cells and batteries have emerged as tantalizing alternatives to combustion engines becoming thus a thrilling topic of interest in automotive industry [7–11]. It is

that produced by natural gas, hydrogen can be transported in pipes much faster due its lower viscosity, almost to match in total the energy transport using natural gas. It can be stored similarly to natural gas and also liquefied. The burners and engines must adapt to hydrogen but there is no technical objection against using it. The tanks can store hydrogen as a liquid or chemically bound to metals (metallic hydrides with yet unsatisfactory capacity for cycled refilling).

Hydrogen reacts with oxygen according to the reaction: $2 \text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. What happens at the molecular level is the transfer of two electrons from hydrogen into a molecular bond with oxygen. The energy of electron in this molecular bond is lower by 243 kJ/mol than in the hydrogen molecule. In the transfer, this energy is released as heat.

In the case of a fuel cell, the transfer splits so that the electrons are removed from hydrogen at a site remote from oxygen. These electrons, stripped from hydrogen at a higher energy level, equivalent to being about 1.2 V more negative than in the molecule, can perform electrical work on their path to the oxygen. The reaction is com-

pleted through the ionic transport via a wetted mat. The theoretical voltage is found from standard thermodynamics: because the reaction occurs at constant T and P , the Gibbs energy of formation of water equals -228.6 kJ/mol (assuming that for elements are zero), so that $W_{\max} = -\Delta G_{\text{H}_2\text{O}} = 2 \times -228.6 = 457.2$ kJ yielding the theoretical voltage of 1.184 V and maximum power of 228.5 kW. Important is the dissipated work due to the entropy production, showing up as an addition to the heat loss Q_c , i.e., $T_c \Delta S + (E - E_{\max}) n F$, where T_c is the working temperature of the cell, n is the number of moles of electrons in the reaction per one mole of the reactant, and F is the Faraday's constant of $96\,500$ C/mol of electrons. The difference between the actual and maximum cell voltage ($E - E_{\max}$) is always negative, which is caused by the irreversibility at electrodes and resistive losses throughout. The actual voltage is, therefore, only about 0.8 V at a flux 0.2 A/cm². More practically it is used in connection with the so-called 'reformed' natural gas, $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO} + 4\text{H}_2$, which acts as the source of hydrogen. Due to the extreme sensitivity of alkali hydroxides to CO the service of an acid-based electrolyte is necessary, which is further complicated by CO-poisoning effect on precious electrocatalysts. For the low-temperature operation (< 110 C) the polymer electrolyte membrane composite (Nafion + silica + silicotungstic acid) or blends (sulfonated polyaromatic polymers + benzimidazols) are typically applied upon necessary fueling by $\text{H}_2 + \text{CH}_3\text{OH}$ to achieve quicker reaction kinetics comparing with hydrocarbons and assure crucially high humidification.

Two types of perspective high-temperature variants of fuel cells are in development, i.e.,:

- (i) *molten-carbonate fuel cells* as electrolyte, operable within the temperatures of 700 - 900 C, using the mixture of carbonates (Li_2CO_3 - $(\text{Na/K})_2\text{CO}_3$ fixed in the β - LiAlO_2 matrix) as electrolyte with alloy anode (Ni-Cr-Al) and oxide cathode (based on NiO) and
- (j) *solid oxide fuel cells*, working at about 800 - 900 C (while 600 - 700 C would be preferable) and using oxide electrolyte (Al_2O_3 stabilized by Y_2O_3 , or perspective mixed oxides of the type LaSrGaMg-O) with the cermet anode (based on Ni stabilized by Al_2O_3) and oxide cathode (usually perovskites LaMnO_3 doped by Sr or other prospect types such as CeSm non-stoichiometric oxides).

Both categories classically employ the mixture of H_2 and CO routinely produced from natural gas by steam reformation but potentially counts with the methanol technology. Methanol, however, yet one of easily available solid fuels, must be gasified (encompassing troubles with their appropriate cleaning from sulfur, tar or so). The theoretical thermodynamic efficiency currently exceeds 66% depending on internal losses and current load of the cells with attainable current densities still below 10^3 mA cm⁻². Great potential rests in utilization of waste heats of the produced gases in steam boiler, gas turbine with pressurized systems and in cogeneration of electrical energy and heat. The overall real efficiency of the heat-to-power conversion for such combined systems lies in the neighborhood of 60% .

One of the popularized visions of prospective energetics is often seen in terms of fuel cells allied to the generalized utilization of the so-called 'hydrogen technology'. It is clear that it must be inescapably guaranteed by the perceptible supply of low-cost hydrogen, but it would bring yet unidentified and thus unsolved problems. Although the combustion produces water as the clean exhaust gas, we have in mind that steam is also a strong greenhouse gas so that its huge artificial introduction outside its natural production (oceans) may not be without tribulations. We do not know yet what could happen if the vast amounts of vapor were locally brought into the atmosphere presumably causing unusual regional environmental effects. Besides, the hydrogen storage is yet difficult (low efficiency of liquified hydrogen in suitable vessels often alternated by its absorption in suitable alloys, which, however, is intricate due to the finite cycles of repetitions) and its handling involves irremovable leakage during carriage and feeling. Free hydrogen would rise to very high altitudes, where it can easily react with oxygen producing tiny ice crystals capable to initiate yet inexperienced destruction of ozone layer. Similar questions regarding the greenhouse effect may be faced when dealing with the analogous 'methane technology' particularly when trying to exploit apparently massive deposits of methane-hydrates stabilized under the high pressure deep on the bottom of oceans (which sudden liberation may caused disastrous consequences).

c) Resources of energy – how long they would last

Capital energy reserves to back up conventional heat production

There seems to be a vast amount of energy sources available to the benefit of humanity and we, however, make use of most of them. Let us see the development of energy consumption per capita as recorded for the United States (in 10^3 kWh/year):

1800 (12), 1850 (17), 1900 (32), 1950 (66) and 1990 (100).

The annual energy consumption for the US alone is currently in excess of 10^{13} kWh. For such a large amount of energy a most convenient use is the value of Q , defined as 10^{18} Btu [7] which is 3×10^{14} kWh and which is approximately the amount of energy necessary to bring $5\,000$ km³ of water (contained, e.g., by the Lake Michigan in North America) to the boiling point. Over the past two millennia, the total world energy consumption was approximately $22 Q$ corresponding to average annual use of mere $0.011 Q$. During the period of so-called industrial revolution (the past one-and-half century) some $13 Q$ were consumed. The total world rate of energy consumption has drastically changed, from $Q = 0.01$ in the year 1850, to 0.25 (in 1950's), and to 0.42 expended recently in 1990's. About 20% of this 0.42 value, i.e., $0.085 Q$, was consumed by the US itself. During this period, the world population has violently increased from one to five billions and we can ask *what about our future*. Five potential scenarios can be foreseen:

- A) Turn out to be modest and reduce the world consumption to the limit of the year 1850 (i.e., about 3000 kWh) where the total Q was about 0.05 for five billion people (to range up to 0.1 Q for double population).
- B) Halt the energy consumption at the current level and for the present (unchanging) five billion people, i.e. at 0.45 Q
- C) Maintain the present population of five billions people but let the rest of the world to achieve the living level of the average US citizen. In order to match up the US current consumption per capita, the world annual energy use would increase to 1.7 Q .
- D) Halt the energy consumption at the current level (as in C) but allow the population to increase to 10 billions, yielding the energy use to double, $Q = 3.4$.
- E) Assuming 10 billions (as in D) but letting the previous energy consumption to grow by another 50% to 5.1 Q (is 10 times as in A or 3 times as in C).

Discussing sincerely any reliable energy conservation program we have to see the consequences of extremes. Any crucial change of our lifestyle, dictated by the first degree of energy conservation economy (A), would fundamentally affect the citizens of the industrial nations but would be more courteous to the underdeveloped countries. Therefore, it would be impossible to bargain its anticipation because the history records reveal that any abrupt change is accompanied with major political upheavals [11]. Perhaps we could label such a drastic economical process with suddenly enforced energy crisis or as a result of radical upgrading of efficiency of energy production. It would not be easy at all, as there has been a steady course of action to decrease energy requirements and to search for new energy production technologies, that is factually securing the scenario B. The efficiency of energy exploitation increased from sixties just by few percent to current value close above 30 %, which improvement alone is,

however, not significant enough in the sense of total energy requirements. Let us see more specific numbers:

Oil (petroleum) is the most widely used energy source with the currently estimated world reserves of about 15 Q (with about another 10 Q available from additional sources such as tar sands and oceans shelves. Here, however, one has to be cautious with any estimates, which always depend on many factors, i.e., *how well* do we know the geology of our planet, where the source can be found elsewhere, and if a source could get naturally refilled (recent theories of methane deep-earth diffusion processes possibly to restore depleted gas and even oil wells). Coal is our most plentiful fossil fuel energy source having Q of about 35 and natural gas amount is approximated to about 20 Q (though it is not clear yet what is the origin of natural gas and whether it can be restocked by the outward diffusion of methane yet seen plentiful in the deeper zones of the Earth). Roughly speaking, we have altogether some 80 Q of effectively extractable fossil fuels.

The most important question arises: how many years will those fossil reserves last. If we double or even triple, the above guessed numbers it would provide, more or less, a pragmatic estimate in survival years until the reserves would be factually used up, not too long at all. It goes side by side with another question what about the other conventionally exhaustible sources? A reasonably conservative estimate for the reserves for nuclear fission is about 20 Q if a light-water reactor technology (LWR) is employed and perhaps 600 Q for a scenario involving the use of breeder reactor technology. Use of geothermal energy is more questionable as the present extraction rate is very low, close to mere 0.0005 Q . An estimate for the total recoverable energy from geothermal sources is, however, as high as about 55 Q while the time to exhaustion of the estimated geothermal energy reserves may vary within the range from several thousands to mere hundreds years.

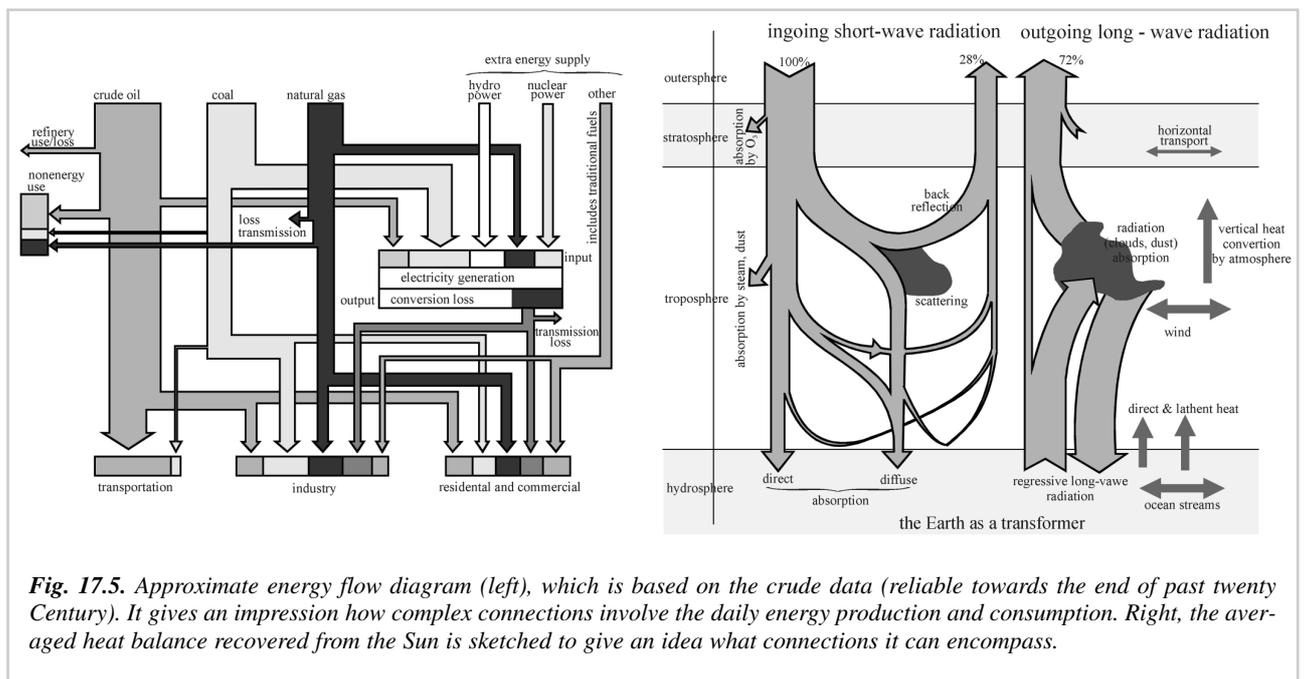


Fig. 17.5. Approximate energy flow diagram (left), which is based on the crude data (reliable towards the end of past twenty Century). It gives an impression how complex connections involve the daily energy production and consumption. Right, the averaged heat balance recovered from the Sun is sketched to give an idea what connections it can encompass.

Not considering fusion, as a hopefully soon available optional source, we have to account for renewable sources of *hydropower* (dams, tidal), *biological* (wood, specialized plants, waste materials) and *solar* (wind, thermal differences and direct thermoelectric and photovoltaic power). There still remains the most conventional source of energy best experienced by mankind, i.e., burning wood, farm wastes and other biological material, now capable of yielding roughly $0.015 Q$ per year. We should note that planting new trees and other plants to replace those we burn is a true income energy source, moreover neutral with respect to the environmental balancing the content of carbon dioxide. It certainly can be summed up with similar kind of hydropower energy which production is estimated to be $0.025 Q$ (and the long-range potential to be about $0.06 Q$). Besides traditional asking for how long the resources should last, we may equally query what is the carrying capacity of the renewable reserves to equally accommodate certain number of human population in near future. The answer is, for scenario A it is about 8 billions, severely decreasing for B close to one, and being the juncture for both C and D down to 0.3 billions. For the most energy demanding scenario E, it goes critically to accommodate tenths of billions people only providing them tolerable life. Even if our estimates are 100 % misguided it still makes available enough warning data to think about!

Solar energy resources

We should not omit the most successful method for generating electricity directly from *income* energy from sun (about $1\ 570 Q$ /year), which is the *solar-thermal-electric conversion* (STEC) system. Traditionally we heat water contained in reservoirs (pipes) with darkened surfaces. We can let sunshine to fall on a large number of mirrors, which reflect and focus rays onto a central receiver (equipped with a heat engine) or we allow natural heating of a large, duly covered area furnished with the central (solar) chimney operational for a hot-air driven turbine. The maximum power density at a sea level on the earth's surface in a very dry cloudless atmosphere is, however, mere 1.07 kW/m^2 . When the Sun is 70° from the zenith, the power density measured by a flat collector is about 0.25 kW/m^2 , which can be improved for the central receiver by adjustable mirrors positioned against the sunlight. A fluid flowing through the thermal receiver is treated classically by a thermodynamic cycle with the associated engine's efficiencies. Therefore, the overall efficiency is difficult to estimate but is unfortunately always low. Climate is among the most important variables; at best, we can assume that about 15% is converted into electrical energy assuming the storage efficiency in neighborhood of 80%. The annual electric generation would not thus exceed 4.65 kWh/m^2 , so that to satisfy the world consumption of $0.85 Q$ (scenario C) would require some 466 000 square kilometers of land to be covered by mirror collectors, which would occupy about 0.3 % of the earth surface area (e.g. 1000 km^2 is about 0.644 % and 1 % equals approximately 1554 km^2). This is technologically next to impossible nowadays, not only

from the viewpoint view of the building costs and construction complications but also from the viewpoint of intricate maintenance of collectors in distant areas (deserts) as well as the other isolation-related issues (e.g. how to realize practical connectivity in delivering electricity to distant users or how to maintain solar surfaces satisfactory clean).

Even the yet imaginary but smart modes of solar cells placed in the 'climatically undisturbed' space, either simply orbiting the Earth or even placed in the '*Lagrange* location' where the gravities of the Earth and Sun are balanced (obviating the need for maintaining the position outside the shadow of the Earth) are not yet without serious doubts. The main problem is the transfer of enormous amounts of energy back to the Earth because there is no experience what the supposed wireless connection, by way of the huge microwave radiation beam, could cause to the Earth aerial weather (both at atmosphere and magnetosphere). Other yet unknown aspects of unidentified leftover liquidation from detached sources of novel origin may always bring new and new surprises to our ecosystem besides the immediate need of very accurate beam localization on the relatively sizeable Earth receivers (even negligible beam misfit destroying everything on the way and becoming even a possible source of terrorist threat when misused). Certainly, the other question is to use all types of alternative sources directly at the spacecrafts where solar cells are so far irreplaceable. Among others, the astronauts can easily improve their electric economy by using oxide-based superconductors naturally operating outside the rocket at the ambient temperature (of about 72 K). The temperature difference between the illuminated and shadow surfaces of the spacecraft is another point of a straightforward exploitation even if the application of some traditional machines may be found surprising (e.g., a rather effective *Stirling* gas-operated engine capable to handle minute gradients).

Nonetheless, any supplementary solar energy systems seem to be very expedient as they directly utilize either the temperature difference (such as flow propensity between heated surfaces and its cooled counterparts) or straightforward sunshine conversion (in semiconductor solar cells). The latter is not a kind of heat engine so that it is not limited by the nightmare of low efficiency of the *Carnot* cycle but follows other physical restrictions of electronic character. These cells, often made from various sorts of silicon, are routinely capable of generating electricity with current efficiencies as high as 24%, and those based on gallium arsenide reaching even 32%. At the contemporary technology level, we can foresee an expectant increase to as much as 50% for some yet undisclosed principles of conversion to come into view soon. Nevertheless, we have to keep conservative estimates to judge the capacities of such resources when facing the present-day reality, in which this energy contribution alternates between, say, 50% directly and 50% after some form of storage with almost 80% efficiency.

The following table may help to envisage the estimate of how long the conservative reserves can last and what is

the present role of novel non-conventional alternative sources of various solar-electric means for the present progress of civilization. We may note that some scenarios require significant occupation of vast land areas (unless we can securely move to outer space) as well as the production of yet very expensive devices requiring, again, much energy to be *a priori* consumed (e.g. solar cells made from GaAs require high input energy, which is hardly repaid during its functional time and bringing another problem of waste disposal of poisonous arsenic if not recycled). Although the data in Table I may not be definite and may get better in view of our disciples (even presumptuous to multiple the exhausting times), the figures remain alarming in the scale of millennia for the civilization to last. They show that the rate at which we exploit our planet is evidently rather insolent and extremely outsized with respect to the planet restoration capacity and we should admit that we live on the environmental credit of our future generations [12–15].

For illustration we would like to add some approximate data for electricity producers trying to include certain ‘ecosystem’ feedbacks, i.e., typical capacity of a power plant against the area exploited:

- (i) Power plant using biomass – output 1 MW at the mean area exploitation of 3 millions m² per one MW,
- (j) solar photovoltaic power plant – output 1 MW with about 50 thousand of m² needed for 1 MW,
- (ii) classical heat power plant fed by coal – output approximately 500 MW with 500 m² compulsory area for one MW and
- (jj) nuclear power plant – output of about 2 GW at the 80 m²/MW.

Certainly, there are other classification measures, e.g., production of wastes (exhaust gases – CO₂, solid wastes such as gypsum, ash – sometimes radioactive) and their elimination as well as the electricity production cost, manufacturing lifetime, cost of the plant disposal, etc. In the overall view, despite all setbacks, the above data uphold a wider employment of nuclear energy as the only reliable solution within the present state of our knowledge.³

d) Heat production as a source of unwanted emission – problem of ‘clean energy’

The most common littering production of civilization is *residual wastes* pointlessly distributed to the atmosphere and even to the outer space. It may be any type of radiation beginning from heat, over light to communication, which is sent to the environment by means of natural attributes of all man-made activities (heat engines, light bulbs, transmitters). This unsheltered activity is not only wasting of energy but also the amplification of polluting framework.

The most common artificial production of heat is also accompanied by surplus emission of gases, namely CO₂. It should be noted, however, that the most important biophysical cycle is the production and consumption of this carbon dioxide. In the plant growth phase, CO₂ is consumed and oxygen released while the reverse process takes place during combustion. Nature has invented a super-sophisticated chemical cycle to safeguard the CO₂ content, while humankind has developed its counterpart, somehow unaware to infringement to the global steady

Table 17.I: Population and energy sources.

<i>scenario:</i>	A extreme conser- vation	B present state	C the same as in the US	D the same for double popul.	E further 50% energy growth
population (10 ⁹)	5	5	5	10	10
consumption energy rate per capita 10 ³ kWh/year	3	25	100	100	150
World-annual need in Q	0.05	0.45	1.7	3.4	5.1
<i>retaining capital energy in years:</i>					
Years until fossil reserves exhaustion	~ 1600	~ 185	~ 45	~ 25	~ 15
Only nuclear reserves (LWR technology)	400	25	5	3	2
The same but with breeder reactors	12000	1500	360	180	120
Geothermal sources as the only energy supply	1100	135	35	20	13
Whole <i>capital</i> energy (exhaustion time in years)	15000	1900	450	230	150
<i>energy supplied by non-capital and non-solar-electric sources:</i>					
Q /year from water, biological and temperature differences	0.18	0.18	0.18	0.18	0.18
Q /year supplied by solar thermal sources	0.01	0.06	0.25	0.50	0.75
<i>income energy:</i>					
% of required solar energy to be contributed, in Q's	0	22.5%	75.5%	80.5%	82.5%
for a given production (kWh/m ² /year) the assumed collector area (10 ³ km ²):					
(4.65) STEC	0	120	800	1700	2600
(1.4) thermoelectric	0	800	2600	5700	8700
(7.45) solar-cells	0	75	500	1100	1650

state. For example, polyp's vigorous utilization of dissolved CO₂ in sea water produces the enormous quantity of corals conserving thus huge amount of CO₂ in solid state as well as plankton itself, whose growth is recently enhanced by sea-fertilization using iron-rich recuperative ('artificial ocean forests'). Perpetual increase of the CO₂-containing surface envelope, shielding the Earth infrared re-radiation, is traditionally called the *greenhouse effect* (of global warming) and sometimes is over-emphasized or misjudged in the view of the eccentricity and periodicity of global stages.

Metabolism of a man-size living creature is in order of a few hundreds of Watts. The development of humankind technological happiness has implied vast burning of fossil fuels so that human consumption rose to several kW. If the total mass of atmosphere is about 10¹⁵ t then about 10⁹ t of CO₂ is sitting in it assuming that CO₂ neither sticks to one place nor react to withdraw. Though the biomass cycle oscillates within one year with amplitude of about 10⁴ t it is assumed with confidence that almost 10⁵ of CO₂ have been inserted into the atmosphere in the past half decade (at the rate of about 0.4% per year) – i.e. the same value which is estimated for the period of 200 years since 1750.

It is known that CO₂ may cultivate plant growth; on the other hand, it is transparent to the incoming solar radiation but opaque (with a high absorption cross-section) to the outgoing radiation transformed by Earth to longer waves. For an idealized Earth spherical shell and the so-called screening *Stefan-Boltzmann* number, δ , assumed at the first approximation to be linearly dependent on the CO₂ concentration we can write the relation $T_{\text{rise}} = T_{\text{fontal}} (\delta/\delta^*)^{1/4}$. Introducing the above data, we can assume a temperature increase of 1.8 K by the year 2005. This is not the only effect, the change of CO₂ may initiate to drive the bifurcations; nobody knows how and where, but it is sure that going across a bifurcation means passing from one dynamical regime to another, possibly to very surprising outcomes, sensitive even to negligible alteration⁴.

In this view the most discussed domain is therefore the CO₂-free production of energy as taking place, e.g., in the *nuclear power plants*. This advantage, however, is often degraded by the fear from radioactive contaminations⁵. It is known that the acting rules allow nuclear power plant

failure to happen less than 10⁻⁶ per year, which means that out of about 500 functioning reactors only one can collide within 2 000 years, which is a very good safety regarding other possible dangers of everyday civilization. Associated problem is a safe deposition of radioactive waste, which can be either

- (i) confined into hard rock deposit-sites (even beneficial for possible later reprocessing),
- (j) recycled by breeding procedure inside the reactor or outside in cyclotron or
- (v) propelled to the sun by rockets.

Despite the latter is the cheapest way requiring only 10⁻⁴ of the produced energy, it would be yet very insecure because the cosmic carriers have a reliability of only 99% comparing with the reactor fail-safe rate of 99.9%). It certainly would also be undesirable to get rid of such precious and factually prospective material, which is suitable for reprocessing by future yet unknown technologies. Moreover the burned nuclear fuel can be even subjected to a direct application in more progressive ranks of nuclear reactors upon the direct fission of their fluoride salts

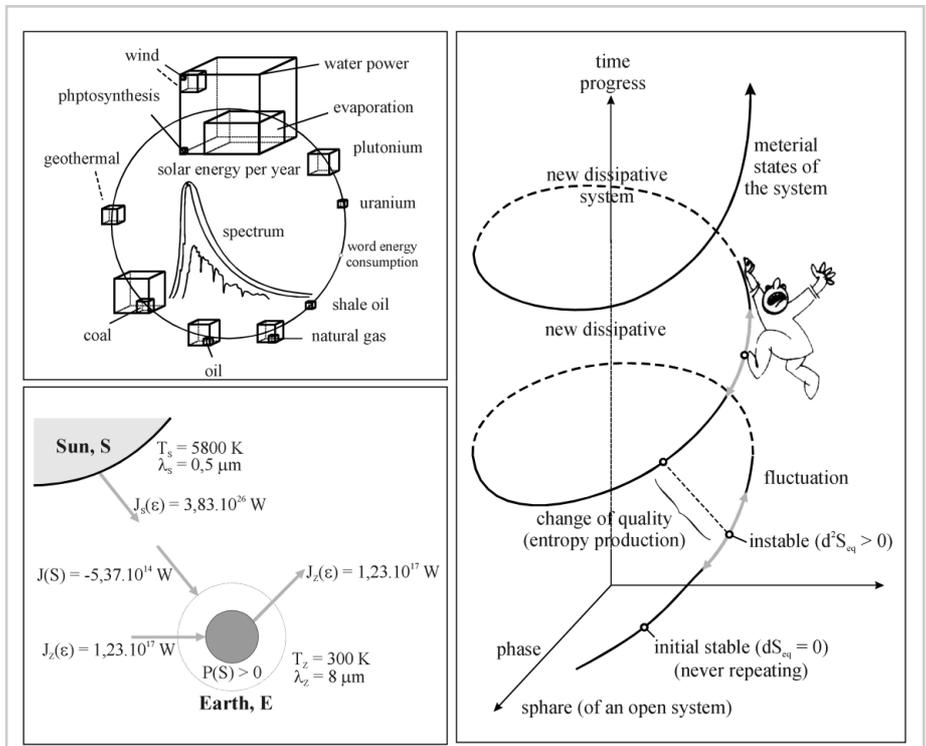


Fig. 17.6. Global view of the income energy delivered from the sun (the inset illustrates the original spectrum launched by the sun and its change while reaching the outside atmosphere and at the sea level) in comparison with the other capital resources of energy available on the Earth schematically shown as the mutually amount-related cubes (upper, left). Below, the entropy relation between the Sun and the Earth is depicted while the left sketch offers the entropy issues, which cause that our world keeps in gradual but repetitively coiled progress.

(actually such a prototype was used as an alternative power source of air-crafts and space-crafts).

However, a wider application of nuclear technology is yet considered intolerable for inexpert public, which is

often kept under prejudiced evaluation of the attitude to possible risk and profitability. Even in short terms, again, the nuclear power looks like the only solution to overcome and even survive the energy crisis and assure sustainable protection of our environment. Nonetheless, in the general scheme of the world energy flows it still represents a negligible portion of our need, see Fig. 17.6 (where the average heat balance recovered from the sunshine is also sketched [17,18]).

Another leftover problem is the waste production of particulate matter, which is normally classified according either to the size (diameter less than 1 μm is dust difficult to settle, behaving as aerosols) or to the source (and/or toxicity). The emission of aerosols represents the most peculiar problem for the weather development as it strongly affects the formation of clouds acting as the condensation centers. This is often described as the aerosol's first effect in which aerosols thicken water droplets. If the droplets are small the cloud 'lives' longer, which is commonly specified as the second (indirect) effect due to the growth conditions (formation of larger droplets may be difficult, being controlled by the aerosol's specific constitution). Besides the total amount of aerosol, its chemical composition and particle size becomes also important. It is rather difficult to account all possible sources such as dust, sand, chemicals (sulfates, nitrates, carbonates), sprinkles of sea water and particularly carbon black, long known as nucleator of ice crystals. Such carbon particles are very curious because of their variety of modifications (porosity, fractality, degree of surface oxidation and the associated hydrophilicity to steam as well as their capacity to easily absorb heat facilitating thus re-evaporation). The final aerosol's effect is very complex: in general, aerosols may have rather cooling than heating consequences (acting against greenhouse effect) but also may increase the rainfalls so that any judgment resists yet a more precise hydrologic cycle evaluation (more difficult than the evaluation of the greenhouse gases). It depends on the neighborhood of pollutant location, altitude of the aerosols to reach momentary and lasting meteorological conditions. It was even estimated that the strength of African monsoons might be sensitive to the amount of anthropogenic aerosols dismissed above Europe as the intensification of drying process at Sahara region coincides with the huge building of coal power plants in the fifties. Their later desulphurization (and also certain reduction), made in the past Eastern block in the nineties, brought already a noticeable improvement for the African monsoons diffusion. A question remains, what happens if the appealed reduction of nuclear power plants leads to the construction of conventional fuel-burning sources, and what consequences we can await reducing burning erosion of equatorials forests, etc.

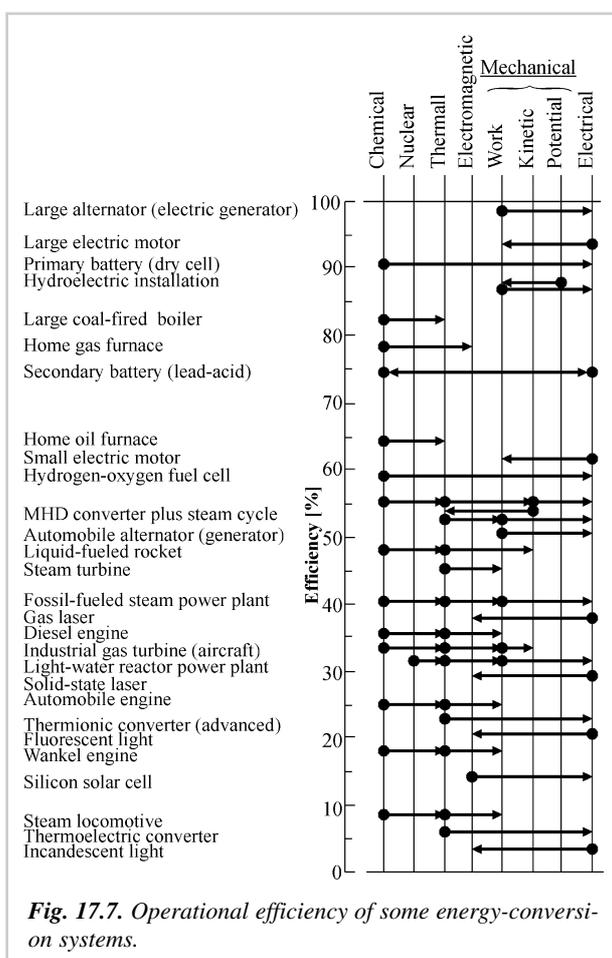
Therefore, the effective removal of particles from the flue gas of coal power plants is very important, which performance parameter is given by *collection efficiency* (mass ratio of dust removed to total). It is based on sudden decrease of gas velocity, change of direction, centrifugal

forces, etc. Very common are electrostatic precipitators and large bughouse units filtering the gas. However, the filters (functioning at about 400 °C) collect all particles including those that may act as catalyzing agents (noble metals), which can eventually take action as catalysts for the undesired synthesis of dioxins from exhaust gases. Wet crabbers are common in chemical industry but have a setback of too high reduction of exhaust temperature and so are used to simultaneously remove another troublesome byproduct – sulfur oxides, which is causing the acid-rain contaminations, often effective on very long distances. Most of the sulfur-emission control systems use some form of *flue-gas desulphurization* in which the sulfur dioxide is removed by wet-scrubbing process. There are two ways of classifying desulphurization: *dry and wet, and regenerative and non-regenerative systems*. In the dry system, the reactant (e.g. huge amount of soon deficient limestone) is mixed with flue gas with as little water as necessary for being sprayed and when such a solution hits the hot exhaust gas, water evaporates and the products are collected as solid powder. In the recovery system, the final product is either sulfuric acid or sulfur (after reduction by carbon); if the reactant is not generated by throwaway system, the final products are sulfur salts of calcium and magnesium. The resulting massive collection of solid wastes provides, however, the large quantities of gypsum (only negligible part is eventually used in the building industry), whose troublemaking surplus must be stored in holding ponds or land fills. There may be even serious traces of often undetected radioactivity, which is particularly painful with ash where radioactivity content can rise to few percent from its initially negligible input amount contained by the raw coal.

Before all, we have to pay attention to prevent rather than consequently treat wastes. We have to be careful to see how "green" are in the reality the so called "green" processes and materials such as naturally disposable plastics because the work required to produce and to prepare may even exceed the recalled (often optimistic) ecological impact when accounting all processing demands. Even the proclaimed biomass conversion may show an inefficient profit if all provisions are made for heat, work and chemicals consumed during the production so that the true final yield may be found negligible.

Another undesirable effect is the formation is NO_x , which is created through an endothermic process and the production of which is thus temperature dependent. More or less, any advanced system of reduction is developed upon the injection of NH_3 into the exhausted gas, which is capable to reduce nitrogen oxides to elementary nitrogen and water. Yet another area of litter worth of mentioning is water pollution due to colloid solids and chemical wastes. Not less important is the above-mentioned discharge of thermal energy into natural waters (and environment generally) above-mentioned as thermal pollution. Chemicals and mere heating of water can change the amount of dissolved gases, and for over 35 °C the oxygen content is even too low to support life.

It is clear that, so far, we cannot avoid thermal pollution if we are to guarantee the energetically apposite progress of our civilization. We just have to think it carefully over, again and again, as to declare what is the acceptable price for our well being and continuing luxuriousness. Quite often, we have to make a choice between two or even more evils with no easy solution. However, it is our infallible duty to decrease any other bypassing pollutants as much as possible, particularly mentioning sulfur and nitrogen gases, aerosols, toxicants, etc. We should not get fooled by various ecological reasons and motivations because they might involve unintentionally subjective views favoring certain aspects of given waste management or energy production or it might even suffer an unseen backing by financial lobbies. We should be conscious that we are continuously hazarding with health



(and even life) as we manufacture more and more chemicals, machineries and technologies producing by-products whose true environmental effect would often become recognized after a delay. Moreover, we are also subjectively alarmed by the prospect of certain danger by offensive propaganda warning not to eat genetically modified food, not to accumulate trash because of radioactive wastes or not to produce injurious gases. However, many will happily keep their bad habits of smoking cigarettes and drinking alcohol, all of which together clearly

amounts to a much eminent health risk. We should be reminiscent that all what we often want is to have our luxury life protected, but prefer if there is someone else to blame for inherent risks.

However, the nature is not benevolent to our life as we know from our not-too-distant geological history – such as the eruptions of volcanoes (CO_2 , SO_2 , CH_4 , dust) or impact of meteorites (extreme heat, spring-out of soil). We can calculate that the impact of a meteorite of the diameter of about 1 km has an annual probability of about 10^{-5} (threatening civilization) and that of 10 km would bring life to extinction each 100 millions of years. Hiroshima atomic bomb sustained the power equivalent to the impact due to a meteorite⁶ with a diameter of about 4 m. Such a catastrophe due to the collision of a cosmic body, threatening any assembly including nuclear power plants, cannot be prevented. Similarly, we cannot avoid other impact accidents geared up by terrorists or triggered by sudden earthquakes. We always have to accept certain risk likewise to our free decision to ride a personal car, being aware of frequent crash accidents. However, similar environmentally disastrous effects, just distributed over a larger time interval, can inadvisably happen with an insensitive construction of power plants with well declared, but factually dubious and under-screened messy policy when producing radioactively-harmless wastes at the cost of huge amounts of otherwise unsafe litters of oversupplied solids or unseen potholes⁷ of CO_2 .

e) Non-equilibrium thermodynamics of fluid systems and our cosmological 'engine'

Ecosystems of planets, in general, are influenced by their positioning in interstellar space [15,16]. Each planet is not a closed system neither is it in contact with two or more thermal baths. Each planet is in contact with a hot radiator (sun ~ 5800 K) and cold radiation sinks (outer space ~ 2.75 K). Each planet therefore realizes a kind of a specific cosmological engine. Being a sphere is crucial because of its rotation and revolution modes with an inclined axis, which are responsible for the richness and complexity in the behavior induced by the solar influx. The atmosphere fluid motion add the spice of chaos so that the thermodynamic events, which take place within a planet, are obviously sustained non-equilibrium flows, which must obey the fundamental laws of non-equilibrium thermodynamics. If our atmosphere were stiff, its thermodynamics would not contain any chaotic phenomena⁸.

Because of a very special nature of the external cosmological state, the boundary conditions for the planets determine the possibility of being an ecosystem, namely a dissipative system with vitality steadily maintained. We can expect that over a planet there is a very complex circulation of availability. We can define a global physical ecosystem to be a system, which satisfies the following properties: it is closed with respect to mass exchange (occupying a finite domain) but is open regarding energy (outgoing flux is matching that which is received) and it

is in a globally steady state for a longer period (energy balanced), see Fig. 6.

So far, the cosmic ecosystem offers only one example, Earth, and it may be its *only* one realization. The Earth has developed as a heterogeneous thermodynamic system with many components in all three phases of gas, liquid and solid, and with their interfacial boundaries of a complex character. Its mathematical solution, even categorically reduced, is infinitely complex, either the simplest one using just the single component and one phase in homogeneous view or another, with two components that do not mix, assuming a heterogeneous concept, or many others including chemical reactions and sophisticated evaluations by finite elements, lattices, etc.. Additional variety of biochemical cycles became as complex as the definition of life itself. The problems of predictability with increasingly complex non-linear models always tremendously inflate.

For example, let us see the temperature field and its reduction, and follow the temperature at a given spatial element. After a period of one year, or averaged in ten years or so, we expect this temperature to repeat itself with certain accuracy. Violations of its expectancy can be attributed to local chaotic interactions (fast irregularities), global chaotic interactions (slow irregularities) and finally to man-made modifications to the energy balance such as occurs by the injection of excess CO₂ on the terrestrial surface. Considering now the density field of other components (SO₂, aerosols) and its finite element reduction, we again expect only small changes; otherwise the Earth would become thermally or chemically poisoned. Certainly, it can become a result of an abrupt volcano eruption or a sudden impact of meteorite but recently it is *steadily* provided by man, who is thus a strange occupant of the Ecosystem and, at the same time, most flexible and very vulnerable. He cannot stand changes of pressure, chemistry of environment and particularly of temperature. The healthy body temperature variation is about one degree and thus man needs a complex body-control system plus a shelter – house and suite. There is an evident difference between the living creature (a self-developed control system) and the entire ecosystem of Earth (determined by solar radiation).

The power per square meter of the Earth's surface is not a large number, but this modest gift is what the Nature has given us. Any particularly stable society could get along with; the generations of dinosaurs lived in equilibrium with this number for a hundred millions years, humankind also managed for several millennia until starting to expand its population and advanced its technology. Finally, in the last thirsty century, a blink with respect to history, a small percentage of humankind has developed a trend for fossil energy consumption, which has become out of tune with the natural orders of magnitude of power that likely the cosmic evolution has decided to give us. Sometimes, it is hard to believe that we are not clever enough, acting without scientific conscience, just simply driven by allurements of increasing growth.

In the first approximation let us consider the Sun as a stable source of Planck's distributed photons at the temperature, $T_S = 5800$ K, at its outer radius R_S . The photons that leave the Sun travel in all directions and without interactions sink at infinity or, better, go into equilibrium with the fossil bath at about 2.7 K. We can define the temperature T_d , at the distance d , which is $T_d = T_S \sqrt{d/R_S} > 1$. For the Sun's entropy emission similar relation holds: $S_d/S_S = \sqrt{d/R_S} > 1$. If the solid Earth were a black rigid sphere with radius R_E , and with transparent atmosphere, the inward and outward fluxes would be given by simple boundary conditions of T 's and R 's. The relative motion of the Earth and the Sun produces a periodic function f , with the period p , which embodies the mass continuity, *Navier-Stokes* equation and energy balance relations for the atmosphere still very far from authenticity. The stationary distribution of the sustained equilibria corresponds to a capacity of mechanical power that may be expressed by a distribution of an infinite number of *Carnot's* engines whose global efficiency can be formulated in general terms by mathematics. It is approximated by the relation, $\eta_{\text{global}} = \int [\lambda (T_1 - T_2)^2 / \max(T_1, T_2)] dS / R^2 \delta T^4$, where λ and δ are respectively the overall Newton thermal conduction (fixed as 8 W/m²K) and *Stefan-Boltzmann* radiation constants (providing $\delta T^4 \cong 1384$ W/m²). The calculated values of η_{global} are in the neighborhood of one hundredth.

The biological network interacts with the thermodynamic ecosystem (is factually 'thermodynamically living') so that it is not a passive stage but a livelihood architecture. The global treatment induces better understanding of the concept of global steadiness governing a distribution of local disequilibria. If the Earth had an irregular orbit, the problem would not admit a globally steady-like solution and if, in addition to the daily and annual periodicity, there were additional irregular movements, there would be neither global steadiness nor the less restrictive property of global periodicity. The ample complication being the variation in either the solar emission or mutual orbit geometry, which imply changes in the input conditions for the Earth ecosystem and which is known to happen in certain often-repeating short (30, 70 or 150 years) or lengthy (thousand and million years) intervals depending chiefly on the Sun, but having also many chaotic components (eruptions). However, within a cosmological scale, the concept of an isolated system becomes no longer practicable because the definition even of our neighborhood boundaries is tricky (as the Sun is enveloped by far reaching dispersion layer full of eddies and horrible jets and our terrestrial atmosphere is diffuse and full of motion, containing rarefied ions with outwards super-fast streams) and the equations of fluid motion fail to hold. These alterations in the input conditions bring about yet new dynamical regime of atmospheric and oceanic motions (apart from changes in composition, structure, etc.). As these modifications are non-linear again, nobody can predict, or know, what could be the resulting effect with respect to what we have experienced or can resolve from history.

Let us move to an example of a renewable engine, and to this purpose consider now thermodynamics of the Earth. This is a system in approximate global steady disequilibrium state, which means that, more or less, inward and outward radiation fluxes balance. We can recall the standard approach (see Chapter 6) to consider a spatial domain, ω , with elementary volume d^3r^{\rightarrow} with coordinates, $r^{\rightarrow}(x,y,z)$, boundary, ω_B , and time, t , assuming that there exist the density, $\pi(r^{\rightarrow},t)$, fluid velocity, $v(r^{\rightarrow},t)$, and temperature, $T(r^{\rightarrow},t)$, which are not all locally stationary. Energy dissipation, w , (irreversibility or entropy production) comes from thermal conduction (∇T) and viscous shear (tensor, σ_{ij}), and is containing a complicated maintained flow of disequilibria to which corresponds a dissipated availability¹⁰ for a *natural* system, w^d :

$$w_n^d = \sigma_{ij} \partial v_i / \partial x_{(k)} + \lambda (\nabla T)^2 / T . \quad 17.1$$

(given in $[W/m^3]$). The power density is constantly created and dissipated and this is the power embedded in the natural motion. If we know the solution of the natural dynamics, we could construct the quantity w , calculate it numerically and this would be the evaluation of the dissipated power of the Earth. Its volume integral would be a fundamental global number qualifying the planet's stationary global conditions, so to say, its 'health'. This is actually an extension of the story previously described for an engine that produces mechanical work, w , and this work is immediately dissipated into heat. Gasoline is solar radiation and ambient coincides with engine, because there is no "outside" to the global ambient. The right-hand-side of eq. 7.1 can be separated into two parts, the first being the shear availability and the second being the *Carnot* availability. For an *active* system (familiarily called 'windmill availability') the second term combines with term of mechanical power to get, $w^a = \lambda (\nabla T)^2 / T + v^{\rightarrow} \nabla P$, which is technically the power source of opportune dams, windmills, etc., constructed by man, while the remaining dissipation, $\sigma_{ij} \partial v_i / \partial x_{(k)}$, apart from a negligible delays, changes nothing from the natural circulation. We can thus see the natural motions as a loop powered by the availability that creates motion, which in turn creates availability, which is in turn dissipated and creates motion again, and so on. The natural and the active systems are different things, indeed. Their joint consideration is equivalent to the consideration of burning a certain amount of gasoline in nature, and see what happens if we burn it inside the

engine. These motions can be periodic (or better chaotic) depending to the temperature gradients. In those places where $(\lambda (\nabla T)^2 / T)$ and $(v^{\rightarrow} \nabla P)$ are particularly large, ejection of mechanical power may occur, typically in the form of the growth bubbles in a pot of hot volcano magma. It teaches us many things. It is known that in a stretched-out period, the solar radiation is not constant and its emission pattern is partly periodic and partly chaotic. The final result is that the Earth ecosystem has an extremely complex thermodynamic configuration with the presence of chaos overlapping a predominant periodicity. It shows the physical fact that the fundamental numbers arose from the pure use of the global formulation; in summary they are predominantly the temperatures of Sun, the separating distance, and the Earth sphericity. The given availability is factually a skin, or better an interface phenomenon particularly when introducing into the model the study of chemical reactions and detailed fluid motion, which come necessarily together because the overwhelming majority of processes take place in the fluid state. It is not clear what number of chemical reactions should be taken into the description, the biophysical cycle of CO_2 (growth $\rightarrow 6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2 \leftarrow$ combustion) being certainly most important. Nature itself has factually invented super-sophisticated chemical cycles and man is now endeavoring in his wealthy empire to develop somehow ignorant and counterpart violations.

It is clear that good ideas for the theory of the ecological human shelter may come from the study of dissipative learning systems, i.e., such adaptive systems that are fit for survival. The Earth has the necessary vitality, complexity and equilibrium-like stability, which is prerequisite for its survival. The hierarchy of interactions may help to formulate the concept that man is not a deterministic system, but rather a finalistic system, or better a control system¹¹. So the species ecosystem has a simpler external interaction and the ecosystem, as a giant engine very complex inside, has its rather simplistic and almost negligible interaction with the Universe itself enabling to see it as yet deterministic world. Therefore, it is the profound mystery to see the existence of islands of order that nurture the possibility of intelligent life. The study and wider application of truly non-equilibrium thermodynamics and the theory of chaos makes sense, but there is a great, unexplored domain beyond that particularly regarding non-equilibrium thermodynamics of the Earth environment itself.

¹ On the contrary, we should mention electrical rectifiers, which are mechanically irreversible as clearly illustrated by a diode transforming alternating current into the direct one, but when being fed with a direct current, it does not produce an alternating one, but only heat. While charging the battery, for illustration, the efficiency depends not only on its input load-current characteristics but also on the form of the external voltage (force) which is rectified. Hence, the property important for the effective rectification vanishes if the current is under backward load (i.e. locking).

- ² Since the fifties, there have been attempts to harness abundant energy innate of nuclear fusion in a peaceful way other than violent nuclear bomb explosion in order to make it functional to produce energy for human use. Its principle is known, we must technically succeed to suitably subjugate the nuclear reaction of hydrogen fusion, by confining protons within a very high magnetic fields while heating the plasma with high-powered radio waves, or powerful lasers, necessary to surmount the repulsive energy forcing thus nuclei to fuse. Such assembly is known as 'Tokamak', which is a 'pocket-size' replica of our Sun, where gravity is replaced by magnetic constraints. Completely different philosophy, however, would provide yet fictitious discovery of 'cold fusion' by *Fleischmann* and *Pons* in 1989, which claimed that deuterium in 'heavy water' (D₂O) would have to fuse to helium in the presence of 'catalyzing' effect of palladium, whose surface, network and fractality can serve as the enforced apposition for the critical 'proximity' of nuclei. It was never proved although the US Office of Naval Research continued study (*Miles*) and revealed that during the electrolysis of such a composition a definite amount of an extra heat is released, which is not associable with any standard (chemical) source. However, the presence of even very local and thus occasional fusion was not approved because no nuclear product (particles) was clearly identified, which is understandable in the presence of noise (e.g., overwhelming cosmic radiation). Some kind of such puzzles can, however, form the basis of future scientific surprises.
- ³ There are many other lines of reasoning, from very rational derived on basis of scientific arguments to intriguingly irrational related more to politics and to often effortless profits laying on behalf that are often environmentally tactless. Warning case is the most recent Czech nuclear power plant 'Temelin', which implementation is under the close watch and protests of various ecological activists, reasoning by the apparent danger of 'nuclear trash' source near to the Austrian border. The anti-nuclear campaign results to repeatedly hold demonstrations, which partakers are often paid on spot from 'unclear' sources just for their role of being the troublemakers. What would happen if 'Temelin' were put off the service? There is a good example just across the border on the riverbank of Danube. A quarter of century ago a completed nuclear power plan in Zwentendorf (by Siemens, single BWR reactor, 730 MW) was sealed and another solid-fueled power plant was build instead about five kilometers away (Dürnrohr, two classical blocks fed by imported Polish coal with the similar power output). The construction cost of ready-build Zwentendorf was about one billion of Euro and its consequent conservation was another quarter of that sum not accounting the every year charge for its maintenance (~ 700 thousand of Euro). This costly decision was the matter of public referendum where mere 0.47 % of participants (about 30 thousand votes out of the 50.47 negative contestants) were responsible for the extra toll amount having been then owned by ten million of taxpayers. The production of enormous amount of greenhouse gas and solid litter was never taken into account nor did its damage evaluate not mentioning the energy squander by coal transportation, waste of human doings, etc. It is an illustration of regretful political decision curiously showed as the nation pride, however, short of reasonableness. In that time, it was affected by the Chernobyl unhappy tragedy caused by the irrational decision of operation staff in the yet-insecure and hand-controlled Chernobyl reactor design, whose nightmare haunts until now. It is, unfortunately, sometimes misused again and again to brainwash the un-informed public.
- ⁴ Certainly, the prediction of changes of global climate can equally be opposed because we really do not yet know whether the CO₂ augmentation is surely bringing this unwanted effect of warming since our previous experience shows that sudden changes of climate can unpredictably happen, caused just by alteration of ocean streams, Earth's magnetism, etc.. We are living in an interglacial period when about 20 000 years ago massive glaciers spread further away from poles. Glaciers have come and gone many times (see next) but the footprints of climate may change even within relatively short phases. For example, in the period 1400-1800 the year-average temperature dropped down to below 8 C (even called as 'little ice age') while within 1910-1940 the global warming was too big to be caused by yet not so assertive 'greenhouse' effect. On the other hand, we have evidence of sudden impacts such as volcano eruptions, etc. Worth of interest is the case of only three days' disconnection of the high-altitude air traffic over the US territory (after September 2001 terrorist attack). It revealed (from the regular measurements of temperatures) an unexpectedly high variance in their maxima and minima differing by more than one degree, which, surprisingly, were suspected to be 'less favorable' to the climate norm (when standard conditions returned afterwards). On the contrary, the wells' burning from horizon to horizon during the 1991 Gulf war looked like an apocalypse with less than 1% of the sun's visible light penetrating through dove-gray plumes rich of NaCl and CaCl₂ crystals and full of uncombusted oil droplets (hydrophobic in nature and immune to cloud scavenging). The plumes were expected to rise to the top of the planetary boundary layer (> 3000m) where smog and other pollutants use to stabilize. According to the atmospheric models, sunshine would heat the black soot, making it rise further through a process called 'self-lofting' (known from extensive natural wildfires) while instead a temperature inversion rode to the rescue. But it turned out that the soot particles had a lot of sulfate mixed in, which makes them to absorb water and act like cloud-condensation nuclei so that a black plume in corner of the Gulf disappeared by the time it got to the Indian Ocean. It is clear that some other oil, with less favorable composition, can possess a great climatic threat if ignited so that we were lucky not to face the effects of out-of-control burning. Certainly we should keep sensitive to any signal evidence of weather changes due to our everyday doings. As for example, we cannot even exclude that the higher frequency of unwanted rainy weekends is caused by gradual collection of dust in the atmosphere during working days, which thus periodically culminates forming nucleation sites and ease consequent vapor condensation. In any case a more violent alteration of weather (extreme windstorms, hurricanes, tornado's) may be a sign of unsuspected changes of whatever likely to come inattentively caused by mankind or nature self.
- ⁵ In general, it is the common contest of the radio-toxicity of ionizing radiation, which is assumed to chemically interact with living cells in the same way as chemically induced toxicity. Curiously, one of the most poisonous substances is pure oxygen that acts in living cells as a strong toxin (originating free radicals), whose effect is similar to the exposure by irradiation. Oxygen can thus be assumed as a 'pollutant' on whose toxicity we got gradually adapted (breathing corresponds to the 30% radiation exposure, which is allowed as a year dose per capita). The life got early experience how to withstand coexistence with radiation, whose natural background is 100 times stronger than that so far introduced by nuclear activity due to man. Some organism (crabs, scorpions) reveal insensitiveness to irradiation. Interesting is the case of operative natural reactors found in African *Gabun*, which about 1.8 million years ago functioned during the period of several hundred thousand years as curiously fed by microorganism that delivered uranium

for its continuous fission from neighboring shallow waters. Since that time radioactive wastes, surprisingly, did not enhance serious contamination of the surrounding soil beyond a tolerable level, giving thus a good indication for the feasibility of a long-term storage of nuclear wastes in natural deposits.

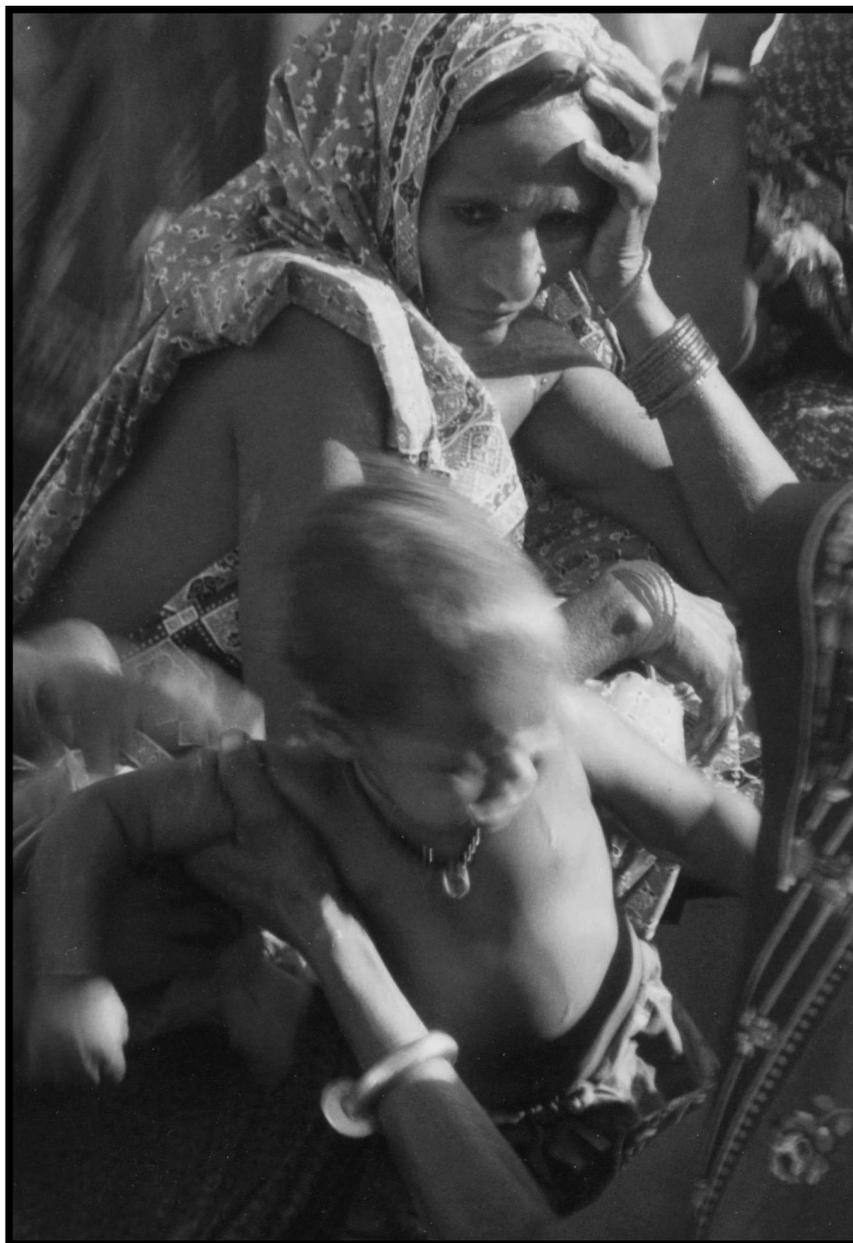
- ⁶ The nuclear load is roughly 500 times cheaper but about 10 million times more effective than the equivalent classical explosives. If the cost of nuclear material is approximately 50 thousand US\$ per kilogram then the same price estimate for one kilogram of the conventional explosive TNT (trinitrotoluene) is mere 1.6 US\$. Evidently, for the same blast-power effect the decisive would not be the low first-cost but other consequences such as spread of radioactivity, infringement of ban-treaty, revenge or other moral blockage (otherwise the ballistic transport is assumed to reach 2 000 US\$ per kilogram regardless the load). Today's store of nuclear weapons is tremendous – about 50 thousand warheads with the concentrated detonation equivalent of about 20 Gt TNT, which can be correlated with the impact power released by a meteorite of the diameter of about half kilometer and with mass of about 100 Mt. In the case that the warheads would be well proportioned over the whole world, it would bring a disastrous result similar to the impact of a meteorite of 10 km in diameter, sufficiently effective to wipe up civilization and inherent life. The cost of such a total destruction would amount to roughly 200 billions of US\$, about the same what US government provides annually for education. (~3% GNP). In order to do it with the conventional TNT explosives it would require TNT production cost corresponding to the whole US annual income for almost 1000 years.
- ⁷ One of the most unfavorable figures for the manufacture release of carbon dioxide provides Czech Republic with CO₂ annual production per capita of about 1.3×10^4 kg with a definitely highest energetically cost of 2.2 USD per one kilogram such created (which is the amount of needed production energy related to the gross national product). These values are closely followed by Poland and Slovak Republic (~ 0.8×10^4 kg at ~1.8 USD/kg). The highest CO₂ production shows USA with almost 2.1×10^4 kg/cap. but at only 0.6 USD/kg followed by Canada and Australia. The most favorable data exhibit Scandinavian countries, Japan and Switzerland with $0.5\text{-}0.8 \times 10^4$ kg/capita at mere 0.1 -0.3 USD/kg. Certainly, it ensues an everlasting inquiry whether such a momentous industrial production of CO₂ (generated by the nature-unexpected continuous combustion of fossil deposits ever-collected through the extended geological history) really effects the crucial circulation of carbon between air, land and water. Terrestrial vegetation uses about 10⁹ tons of carbon a year to grow so that this demand would exhaust CO₂ in the atmosphere if not for constant replenishment through plant respiration and decomposition of organic matter. Only Atlantic Ocean plants keeps removing billions of tons of CO₂ from air and water – not accounting for the further CO₂ dissolution capability and its consequent re-deposition in the form of solid carbonates. However, the presence of CO₂ vigorous sinks is critical to indispensable moderating the human artificially made buildup of CO₂, which has recently increased by about 30% (when comparing with the preindustrial levels). It is well known that major climate shifts of the past half million years, as an alternation of ice ages and interglacial periods, never triggered a spike in atmospheric CO₂ like the one recorded in the past 150 years. In particular, air trapped in ice cores from the Antarctica iceberg were analyzed showing that the CO₂ content approximately oscillated every 100 000 years from about 200 to 280 ppm (parts per million) roughly matching the shift of periods. It is the question if the stable range of CO₂ concentration ended with the modern era's unprecedented burning of petrified fuels, which has currently increased CO₂ content up to the never detected amount of 350 ppm and if it's predicted doubling will be already attained by the year 2100.
- ⁸ If the Earth were a rigid homogeneous sphere with no atmosphere and consequently neither albedo nor downward diffusion, the direct solar influx could be calculated without needing any special experimental measurements. To each point of the surface the solar influx would be a trigonometric factor times the solar constant strictly changing along the exposed face. The neighboring planet Mars is active in this way, so that if we were to colonize it we would need first to create its albedo by manufacturing the retroactively reflecting atmosphere upon introducing CO₂ from mineral sources, or simply by delivering 'Earth-type pollution' (as we use to practice it in our atmosphere) necessary to increase and the surface temperature to enable melting and evaporation of soil-buried water. This process could be relatively brief in comparison to the next step, which should be the creation of livable environment by an appropriate process (planting) in order to introduce oxygen. There, however, are many other obstacles to tackle, such as too high level of dangerous radiation (which is screened out from the Earth by its magnetic field shielding). The surface of the planet Venus is, on the contrary, extremely hot because its atmosphere is dense and opaque due to high concentration of back-reflecting components and particles (containing even droplets of H₂SO₄) exhibiting, therefore, extremely violent atmospheric motion.
- ⁹ The Earth's orbit is fortunately close to a circle but not completely. Its ellipticity varies over the course of the year but its effect is too weak (3 %) to cause the instant seasons but strong enough over its severity, regressing by about one full day every 58 years. The Earth reaches perihelion (closest point towards the Sun) in early January but this date does not remain fixed but slowly regresses. Tropical year is measured between two vernal equinoxes (being the base of our Gregorian calendar) while between two perihelia lies the anomalistic year (about 25 minutes longer), which moves completely through the tropical year in about 21 000 years. Most of this difference is due to the slight change in the direction of the Earth's rotation axis in space, called precession, which is tilted from the normal to the orbit plane at an angle of 23 degrees and precesses once every 23 000 years. The eccentricity of the Earth orbit varies periodically with a time scale of about 100 000 years, so that climatologically it can become imperative if positively modulated together with the 21 000 cycle of perihelion. Another 41 000-years variation is obliquity, which is different from precession. These astronomical phases are often called *Milankovitch* cycles (after the theory of Serbian civil engineer) but their true impact on climate changes is not yet clear.
- ¹⁰ We can even turn to a brief discussion of the properties of background. Neglecting viscosity and assuming T and $v \rightarrow$ zero we can stick on the privileged reference system, fixed to the standard domain, ω , and can derive, after some mathematical manipulations [L. Sertorio "Thermodynamics of Complex Systems" World Science, London 1991], the equation for motion, $\rho \partial v_i / \partial t = - (\nabla P)_i - \rho \partial (v_j v_k) / \partial x_{(k)}$. This equation, in fact, implies that there is a kind of substrate of all phenomena ('ether' as the carrier of electromagnetic field, for instance). It curiously exhibits time reversal symmetry, $t \rightarrow -t$. If the motions are very slow, ($v_{ij} \rightarrow 0$), every fluid loses

its viscosity at that limit so that the viscosity becomes an intermediate concept. Let us recall *Carnot* engine, where the motion of piston is very slow so that $\partial(v_i, v_k)/\partial x_{(k)}$ is also small and we can conserve entropy along the cycle. If, however, a viscous fluid were to perform the job, all the energy fed into the cycle would go into irreversible heat due to the dissipation rather than into work delivered to the shaft.

¹¹In order to secure continuity of our civilization the probability-based models for measuring the threat of natural disasters (cyclones, earthquakes, volcanic eruptions and collision of meteorites, even including the risk of terrorism) must be developed. Certainly it should include all our recent experience with every types of natural phenomena and disastrous effects monitoring all serviceable data (and if unavailable, at least, making, careful guesswork). Equally, the models should pay adequate attention to geological research and the data careful analysis trying to elucidate the estimated figures of the past being attentive to all other sources – even bizarre historical notes. Indeed, the Biblical deluge could have happened if the legend is associated with an intensive ‘tsunami’ which super-high wave might get flooding far away in to the inside land as the result of an imaginable sea impact of a very large meteorite. Giving access to some indistinct evidence such a tale could eventuate some time around the year 350 BC when essential changes in climate and some extinction of a portion of population was indicated for couple of years.

However, in the present thirst for energy we would already need ‘two Earth’s’ to satisfy the US-level luxury equally for all inhabitants and soon the perilous deficiency of drinkable water might rise new serious social violation and armed conflict. In the range of decades or maximum hundreds of years we know how to expect and take in to a serious account the global changes staying behind terrestrial warming and total depletion of the Earth’s capital energy resources. In the view of several hundreds years we may expect critical climatic changes (as is the reverse of the Golf stream or the Earth’s magnetism) along with the impact of another glacial period which may retreat after few millions years. Still in a longer forecast of several hundreds million years we may expect more tyrannical changes of the Earth’s environment such as shifting the Earth plates to form a single super-continent, increased violent contact of falling sunshine, etc. In very long terms of billion of years no less than 10% increase of Sun radiation will gradually extinct life (even the last gasp of microorganisms) during the water intact evaporation thus changing the Earth’s surface to very dry and fiery deserts. The safe oasis of life be necessarily going to move further away to be perceptible on the other planets (e.g., orbiting moons of Jupiter and Saturn), if yet existing. Yet later there would be nobody to be fearful when awaiting the disastrous cosmic-scale collision with the approaching galaxy ‘Andromeda’.

From the viewpoint of our very low-level of civilization, now capable to study of biology at the molecular level, which will surely witness new directions in material design and construction, (not just mimicking biomolecular systems, cf. Chapter 19), but actually moving to use biomolecules themselves in order to construct yet unforeseeable materials. It will succeed the current trend towards smaller, less expensive and more portable devices for the industry, medicine and consumers (unfortunately not yet excluding its traditional driving force through a well-granted military sophistication) that can perform critical functions at these ‘mesoscopic’ scales in which we are trying to stack-up individual particles/molecules directly into a useful shape. We might become advantageous by the enforced control through the “power-of-our-minds” in a similar way to the proteins that are assembled from individual amino-acids. We may even think about the vision of “nanobots”, which foresee the manipulation of small species to actually form miniature engines and automatons. Further on and indeed, we may contemplate the attack to fundamental limits with regards to the information storage and processing, to improve the resistance to chaotic unpredictability, and find new ways to manipulate genes and molecules (possibly steering yet bottomward to tackle the disposition of molecular bonds, and even atoms). It still would assist our civilization (if any), its need and comfort but, perhaps, still little effective in searching our cosmic survival even in shorter terms. This continuance demand would require the further development of our capability to render and uniquely exploit natural laws in order to get closer to the heart of the matter (some kind of yet unknown restructuring, cf. Chapter 20), possibly discovering new germs of some enormous power that would be helpful to convincingly alter the planetary environment. In longer terms, yet outlast humans (if any) could be aspiring to achieve yet higher-level of ability, perhaps, even to the extent of being able to alter or influence an entire solar system by yet unimaginable way, such as reconstructing or changing the planetary system (see also Chapter 2). It may be executed by alternating the Earth’s orbit upon the gravity effect of a large enough asteroid (of about hundreds kilometers in diameter), which will be forcefully brought to pass nearby the Earth periodically pushing by its gravitation the Earth to move slowly but gradually away from the glowing Sun. Another way may be the creation of a special Earth’s radiation shelter in order to escape provisionally the disastrous radiation or the enforcement of other yet unknown resolutions. Here we touch the sphere of science fiction, which, however, would be somehow necessary to effectuate in the same way as the sci-fi vision of our ancestors has been fulfilled today’s, just during our merely momentous being of our civilization.



CHAPTER EIGHTEEN

18. Thermodynamics and society – laws versus feelings

a) Application of thermodynamic laws to society behavior

Recently there arose a remarkable idea that the entire human society can be regarded as a kind of many-celled super-organism [19-23], the cells of which are not cells, but rather we, the human beings, cf. Fig. 1. The Internet might represent a kind of embryonic phase of the neural system of our „if-as organism“ in which a „global brain“ may facilitate the linking up of partial intelligence of the individual users. Later on, perhaps, it may develop its own ideas, strategies and even a consciousness of an unknown order. From a systematic point of view, such a „cyber-space“ [23] is in a similar category as language (the system), but differs in many important respects: such as the temporal scales of all relevant levels in such a cyber-space are similar, the system has a “body (neural network), some participants (system programmers as well as hackers) may deliberately influence the system at all levels, etc. It may become as common a property as “fire” and it may develop a systematic theory such as thermodynamics or thermal physics. We just need to look for some basic links between the mathematical description of particles strictly controlled by the laws of thermodynamics and human beings affected by their feelings. Such correlation of thermodynamic ideas and rules applied to economics was already made by *Lewis* [24] as early as in 1925, and, certainly, it was preceded by pure mathematical consideration rooted back to the time of *Newton*, and his experience while functioning as economist (accountant).

Viewing perceptible activities of the human population on earth’s surface from a greater distance, it may be possible to observe and compare the behavior of societies as a system of thermodynamic-like partners. Metals, a similarly viewed society of different species of atoms, can be described by *functions* derived long ago within the field of thermodynamics, which so far well-determines the state of integration and/or segregation of resulting alloys. By analogy to such a vast variety of problems (known in the associated field of materials science) similar rules can be established to become useful for the application to various problems in segregated societies now governed not by mathematics with its well-defined functions, but by *human feelings* (sociology), as introduced by *Mimkes* in 1993) [20]. For example, important forces may be created by the integration of foreign workers in different states or integration of women in leading positions of politics, business or science. It may help to provide solutions to long-lasting conflicts in binary societies such as Northern Ireland, Africa or the

former Yugoslavia, etc. It may be extended to develop transitional terms of traditional thermodynamics to sociology, economy or even to some military ideas. Societies would exhibit different states depending on the degree of their development and organization. They can show characteristic quantities, which may appear to have a certain similarity to those already known in thermodynamics. The possible arrangements are illustrated in Fig. 2.

Therefore, let us freely move to the matching area of our thermodynamic background, to the previously discussed field of *phase diagrams* (see Chapter 7). The same complication arises when we try to describe the state changes within a society, whose state is connected with the formation of mixtures of independent individuals, i.e., the associations of the original constituent abbreviated as A (x%) and B ((1-x)%). We can recall the chemical analogy described by the change in the Gibbs energy, $\Delta G_{\text{mix}}^s (= \Delta H_{\text{mix}}^s - T \Delta S_{\text{mix}}^s = \Delta G_{\text{mix}}^{\text{ex}} + \Delta G_{\text{mix}}^{\text{id}})$ which is fortuitously composed of two terms. For ideal (id) non-interrelated behavior, ΔH_{mix}^s is zero, and mixing is only governed by the *distribution statistic* of constituents. Such a simple model of the regular mixing of A-B associates is thus conveniently based on the logarithmic law of entropy and can be customarily described by $\Delta G_{\text{mix}}^{\text{id}} = -T \Delta S_{\text{mix}}^{\text{id}} = RT (x \ln x + (1-x) \ln(1-x))$. For the interrelated behavior of constituents in the mixture, ΔH_{mix}^s is either positive or negative and can be conventionally depicted on the basis of the so-called *regular behavior*, where $\Delta G_{\text{mix}}^{\text{ex}} = \omega x(1-x)$. Whereas the *fraction*, x (members, contents or generally concentration) can be directly measured, certain assumptions must be made regarding the *interaction parameter* ω (which must evidently be zero for the mixture exhibiting ideal behavior because the components A and B behave equally).

In addition of this excess term of non-ideality, which is usually dealt with in terms of *cohesive energy*, E, we introduce ϵ to express the *interactions* between the inherent pairs of components A and B, i.e., ($\approx E_{\text{AB}} + E_{\text{BA}} - E_{\text{AA}} - E_{\text{BB}}$). For example, an A-B alloy will be stable if

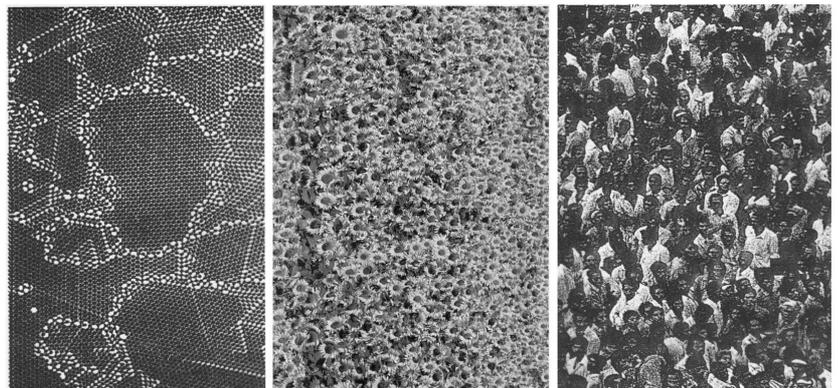
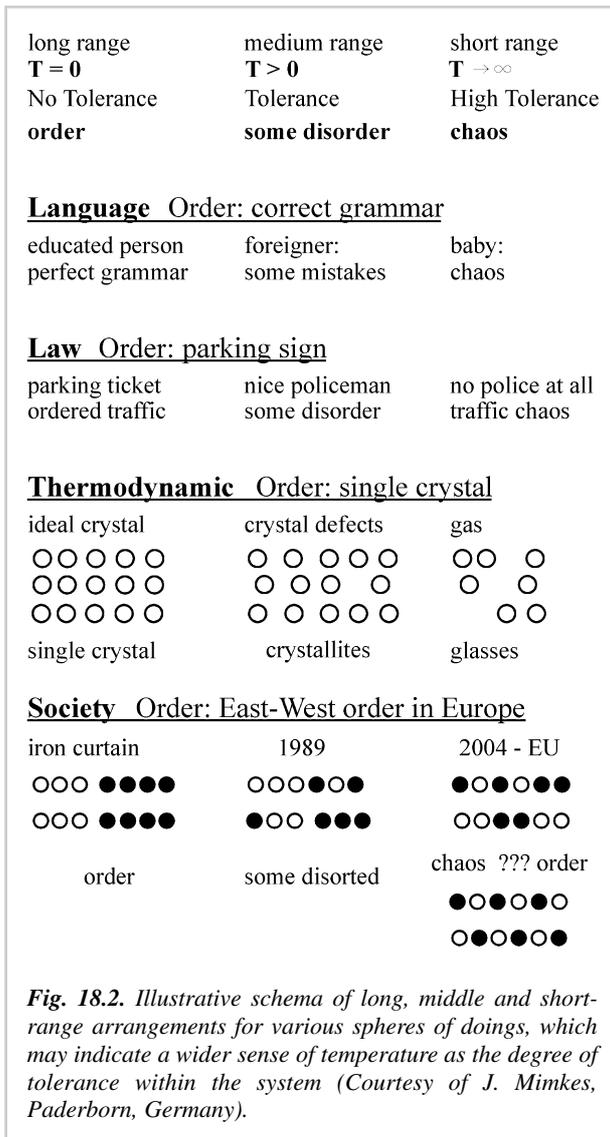


Fig. 18.1. Photos exemplifying some aggregations of variously assumed particles. Left, microscopic picture of the arrangements of atoms, which are homogeneously ordered within microcrystalline domains (separated by whiter interfaces). Middle, macroscopic photo of the plantation field of sunflowers and right, the crowd of people somewhere in India..



ΔG_{mix}^s is at its maximum, which results from either positive or negative interaction energy between the A-A, A-B and B-B neighbors. For a strong A-B interaction, ϵ will be positive while for a strong A-A and/or B-B attraction, it will lead to a negative sign resulting in a limited solubility of the mixture. Surprisingly, Mimkes [22] found statistically well-compiled evidence that such a regular solution model can also be satisfactorily applied to describe the intermarriage data of binary societies consisting of *partners* (= *components*), e.g., girls and boys in different *societies* (= *mixtures*), such as: immigrant foreigners and domestic citizens in the middle Europe, religious Catholics and non-Catholic inhabitants of British islands or African (black) and non-black citizens of the USA. The observed structural analogy is due to the general validity of mathematical laws of statistics of mixing, which allows one to translate the well-established laws of thermodynamics into the social science where the state of binary societies is determined by the above-mentioned feelings, i.e., maximizing mutual *happiness and/or satisfaction*.

Case A – Order and sympathy, $\epsilon > 0$:

Crystal: In rock salt, the attraction of the ion components A (sodium-Na) and B (chlorine-Cl) is much stronger than the attraction between similar pairs of Na-Na and Cl-Cl. The maximum of the (negative) Gibbs energy is given for equal numbers of both components at $x = 0.5$. It is well known that due to the strong Na-Cl attraction, rock salt crystallizes in a well-ordered „...ABABAB..“ – ball-layered structure. This is associated with a negative enthalpy change and accompanied with heat liberation.

Society: A group of English-speaking tourists is visiting a Japanese fair. They are more attracted to English speaking sellers while domestic buyers prefer Japanese-speaking sellers. Mutual happiness (including economic gain) will be low if there are few sellers or few buyers. The maximum of mutual satisfaction will be at equal numbers of all kinds of buyers and sellers. Each group gets a certain degree of excitement from the shopping process when buying and selling; emotion possibly bears a certain analogy with (or relation to) the above-mentioned heat of mixing.

Ancient philosophy: water and wine, fire together with air.

Case B – Disorder, integration, indifference and apathy, $\epsilon = 0$:

Alloys: There are no interactions between the neighbors at all. The Gibbs energy is negative because of entropy disordering effects, only. Such an ideal solution can be illustrated by silicon (Si) and germanium (Ge), in which the arrangement is accidental (random).

Societies: Two kinds of solution can be found:

Indifference: Equal partners are as attractive or repellant as different partners, which leads to

$$(\epsilon =) EAB + EBA - EAA - EBB = 0$$

Apathy: The attraction of all partners is zero so that

$$(\epsilon =) EAB = EBA = EAA = EBB = 0$$

In a downtown supermarket in Kyoto, we will find a random distribution of men and women. For busy shoppers, a short cashier line will be more important than male and/or female neighborhoods. This corresponds to indifference, and the society of shoppers is mixed by chance or is integrated.

Case C – Segregation and antipathy, $\epsilon < 0$:

Alloys: Mixtures of gold (Au) and platinum (Pt) segregate into two different phases. The (negative) Gibbs energy exhibits two maxims, one for Au with few Pt atoms, the other for Pt with few Au atoms. The degree of segregation is not generally a full 100% unless the equilibrium temperature is close to absolute zero. On the other hand there is a $T_{\text{max}}(x)$ temperature needed to completely dissolve or integrate a given composition, x , of two components which can be determined from the derivation dG/dx to yield $T_{\text{max}}(x)$.

Societies: Mutual happiness of a society of, for example, black and white neighbors (or Moslem and Serbian people in the former Yugoslavia) would again show two maxims: one maximum is obtained if the percentage of black

neighbors is low and the white people feel at home; on the contrary, the other maximum is obtained at a high percentage of black neighbors, where blacks feel at home. In order to attain a maximum of happiness, the town (society) will segregate into areas mostly white with just a few black renters and the areas mostly black with a few white renters. In this way both, black and white people, will *feel* mostly at home. In general, the degree of neighborhood segregation will not be 100%. This can happen only if the *tolerance* between different groups is close to zero; resulting in ghettos, e.g., the pure ethnic Moslem and/or Serbia homeland areas.

Ancient philosophy: water and oil, water against fire.

The above grouping can further be discussed in more detail in terms of the extreme values of interactions, such as when the degree of mixing is much greater than zero – this will yield a *hierarchy*, and for highly negative values the situation results in an aggressive society, cf. Fig. 3. On simulating the classical (T-P) phase diagram of matter (solid-liquid-gas), we can define analogous states of societies, i.e., *hierarchy-democracy-anarchy* (see Table 18.I).

Such thermodynamic-like considerations offer a wider source of inspiration: for example, relating P to *political pressure* and V to *freedom*, the constancy of their multiplication (similar to Boyle’s law) shows that for a higher political pressure, the society generates a lower freedom and vice versa. Associating P with the pressure of political relations, then temperature can also be characterized as a measure of the extent of internal proceedings: the warmer the international proceedings, the lower the number of possible collisions. Two neighboring states developing at different rate would mutually interact (the quicker accelerating the slower and vice versa).

b) Some extended thermodynamic thoughts applied to economics

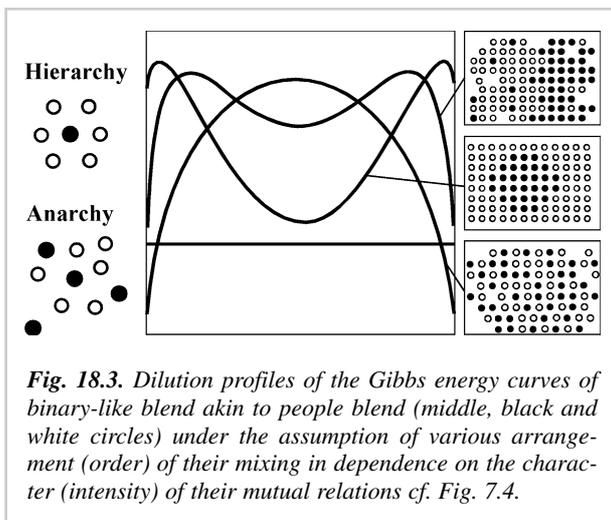
In a similar manner to assuming that feelings govern the behavior of societies, we can broaden our consideration to the field of economics where the achievements of the best prosperity can be assumed similar to the minimum of free energy, see Table I. For example, if two markets with different standards of living are combined (with

Table 18.I: Analogies between the Natural Sciences, Social Sciences, Economics and Military regarding thermodynamic analysis and functions.

Symbols binary	Natural Sciences	Social Sciences	Economics	Military
A-B	gold-platinum	Black-Whites	sell-buy	NATO-Russia
	silicon-germanium	Catholic-Protstant	rich-poor	North-South
	sodium-chlorine	male-female	Europe-USA	SEATO-China
	concentration (%)	minority size (%)	demand/supply	relation of forces
ordering				
$\omega > 0$	compound	sympathy	trade links	military treaty
$\omega = 0$	ideal solution	indifference	free market	neutrality
$\omega < 0$	segregation	antipathy	business/competition	military block
functions				
G	Gibbs energy	satisfaction/happiness	prosperity	security
T	temperature	tolerance to chaos	mean property	reconciliation
Q	heat	self-realization/health	money	weapons
EAA	cohesive E	tradition/heritage	profit/earnings	friendship
$E_{AB} > 0$	binding E	curiosity/love	investment	joint activity
$E_{AB} < 0$	repelling E	distrust/hate	cost	hostility
$E = 0$	indifference	apathy	stagnation	neutrality

stages	
metallurgy	anthropology
disordering/solubility	integration
solubility limit	segregation
phase diagram	itermarriage diagram

⇐ states and state diagrams ⇒		
ancient philosophy	pressure vs temperature	political pressure vs living standard
air	gases	anarchy
water	liquids	democracy
earth	solids	hierarchy



the mean property designated as T , the new standard of living would fall in between the former values. A good case can be shown by the unification of Germany where a uniform standard of living can only be obtained by stirring and mixing partners from both sides. Let us recall the Carnot cycle in Fig.4. Manufacturing products like cars, furniture or other advanced goods from single input parts requires comparable labor (assumed to represent a change in entropy) in any country. The price of merchandise, however, depends on the quality of labor, tools and generally on the living and technology standards, T . This may be pictured in the same diagram as that shown previously in Fig. 17.1. replacing the thermal power cycle by an assumed economy profit cycle. The useful work extracted from the heat Q may then represents money gained by producing in a cheap market and selling in a more affluent market at the difference ΔT (of unequal economies) and (dashed) a non-equilibrium delay caused by transfer of matter replaced by economic hindrance. This implies that the rich become richer ($\epsilon >$) but, on the other hand, job creation or agriculture support may install equalization ($\epsilon <$).

It certainly does not include all inevitable complications when assuming boundary conditions. A material property known in physics as viscosity can be renamed within international relations as *hesitation*, which can be determined as a function of population density, speed of the information flow and the distance between possible collision centers and the places of negotiations (past East-West Germany relations stirred via Moscow communistic administration or Middle East conflicts taking place on the Arab-Jews territories but negotiated as far away as in New York). Understanding the freeway as the mean distance between two potential collision (ignitions), we can pass to the area of transport phenomena observing *inner friction* as hindrance to the streaming forward characteristic, e.g., for migration of people from the East/South to the West. We again can describe such people migration as the problem linked with thermodynamics of diffusion. We can imagine a technology transfer which depends not only on the properties of state boundary (surface energy

standing for the transferred meaning of administration obstacles) but also on the driving force which is proportional to the differences of technology levels (e.g., North and South Korea) bearing in mind that the slower always brakes the quicker and *vice versa*. As with chemistry, nucleation agents (ideas, discoveries, etc.) can help to formulate societal embryos capable of further spontaneous growth. Surfactants are often used to decrease the surface energy, like the methods of implantation of production factories or easing of customs procedures (well-developed Western Europe against post-communistic Eastern Europe). Human society often suffers disintegration, but the overall development can be seen in open loops (or spirals) which finally tend to unification upon increasing the overall *information treasure* of civilization. This is similar to a technological process where raw material first undergoes disintegration followed by separation, flotation and other enrichments to upgrade the quality for an efficient stage of final production of new quality material.

Such examples of brief trips to the nature of sociology could give us certain ideas to improve the art of both the *natural and humanistic sciences whose interconnections were natural until the past century* when the notion of heat was analyzed to become the natural roots of thermodynamics. Researching the analogy of physical chemistry to sociological studies of human societies is a very attrac-

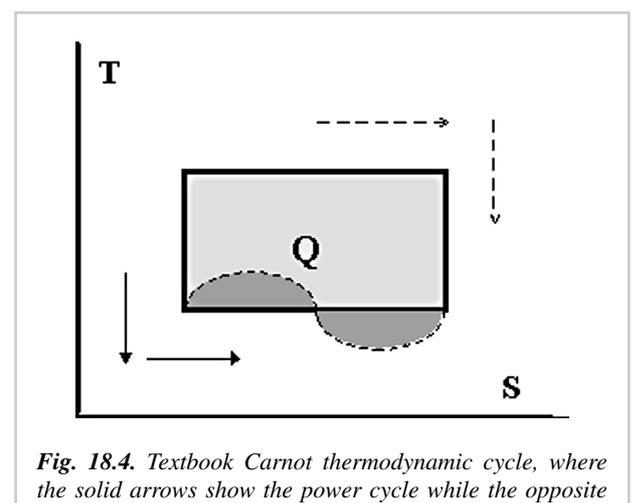


Fig. 18.4. Textbook Carnot thermodynamic cycle, where the solid arrows show the power cycle while the opposite cycle (dashed) shows the reverse heat pump (refrigeration process), is submitted an application to the economy. Similarly, the assumed business cycle, replacing conditions of minimum Gibbs energy by maximum economic prosperity, can be imagined by using a non-conventional representation of T as the mean property of a society, while S , entropy (of society order/disorder), remains the same. Products are manufactured in a cheap (lower T) market and sold in a more affluent market (higher T). The shaded area represents useful work Q (either as heat or money) and the dotted line illustrates the more natural, non-equilibrium processing due to delays caused by, e.g., thermal conductivity (Cruzon-Ahlborn diagram) or business transport obstacles. A similar non-linear backgrounds was shown to be characteristic various thermophysical measurements where, for example, an S-shaped zeros line is obtained for a DTA peak (cf. Chapter 11.).

tive area particularly assuming the role of thermodynamic links, which can be functional until the relation between inherent particles and independent people, is overcome by the conscious actions of humans because people are not so easy classifiable as are mere chemicals. Such a feedback between the human intimate micro-world to the societal macro-state can change the traditional form of thermodynamic functions, which, nevertheless, are here considered only in a preparatory stage of feelings. Therefore this sociology-like contribution can be classified as a very first though rather simplified approach to the problem whose more adequate solution will not, hopefully, take another century as was the development of the understanding of heat and the development of the concept of early elements.

c) Rules of behavior: strategy for survival and evolution

In our previous ‘physico-chemical’ approach, we assumed people as unvarying ‘thermodynamic’ particles without accounting for their own ‘human’ self-determination. The interactions of such ‘sedentary’ particles are given by their inherent nature (internal state, charge), properties of the host matrices (neighboring energetic) and can be reinforced by their collaborative integration (collective execution, stimulated amplification) in the set-up vicinity. On the other hand, in the diluted intermediates, where a few impurity particles are scattered in a uniform lattice of the other host atoms, such visitants prefer to cooperate with each other, or align in a mutually favorable way, and the nearest-neighbor reciprocated ‘orientation’ can be positive or negative. That is, for example, the case of magnetic spins tending to be aligned antiparallel for the typical case of antiferromagnetic arrangement. Problems occur if an odd number of such aligned atoms are arranged in a loop, impossible to satisfy globally the desire of all spins to align in a definitely opposite way to one another (characteristic for a trimerous or pentamerous network). Unfulfilled compensation and resulting competition between the various types of interactions can lead to the effect of frustration, well known in the concrete case of ‘spin glasses’. It may be generalized for a rolling landscape under-peopled by inhabitants representing thus a very complicated free-energy terrain showing the locations of the global maxims (peaks) and minims (valleys). How easily the occupants of neighboring valleys can communicate will depend on the

towardness of environment (e.g., temperature excitations or tolerability conditions needed to facilitate flipping across the separating barriers). It is clear that the nature is rich even when accounting insensible inorganic world (cf. Chapter 16).

Certainly, there are works concentrating on a plausible cooperation between people as (genetically) unrelated individuals aimed to show their reciprocal strategies of behavior that can emerge spontaneously as a result of the same blind driving forces of survival [26,27]. This subject has been investigated using a branch of mathematics that today is called ‘game theory’. It aspires to determine the strategies that individuals (or their whole groups – organizations) should adopt in their search for premium valuation or loss compensation for their doing when the outcome is uncertain and depends crucially on what strategies the other counter-partners may adopt. Von Neumann is the founding father of this matter, which can be traced back to 1928. It involves the evaluation of risks and benefits of all strategies in games (as well as in rea-

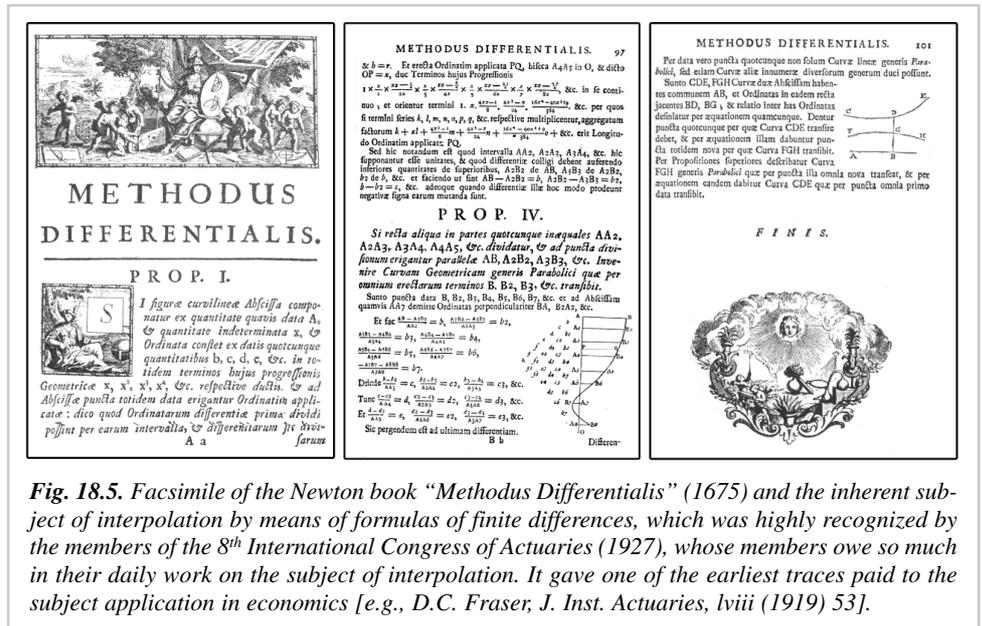


Fig. 18.5. Facsimile of the Newton book “Methodus Differentialis” (1675) and the inherent subject of interpolation by means of formulas of finite differences, which was highly recognized by the members of the 8th International Congress of Actuaries (1927), whose members owe so much in their daily work on the subject of interpolation. It gave one of the earliest traces paid to the subject application in economics [e.g., D.C. Fraser, J. Inst. Actuaries, lviii (1919) 53].

listic actions of wars, economics, endurance) or whatever we can account as describable in its ongoing competitive advancement. It is known to have important impact not only on economics but also on mathematics, which is enriched through the advances simultaneously made in combinatorics (i.e., the theory of arrangements of sets of objects) [28]. The drawn-in principles are found applicable to human societies in better understanding how cooperation emerges within the world of egocentric self-seekers, whatever they are politicians or private individuals, superpowers or small societies, where there is no strictly applied central authority to rigorously police their actions. Later in 1970s it was found functional in the sphere of biology [29,30] for understanding the group behavior and so-called ‘reciprocity cooperation’, which is concerned with symbiosis, often accounted even between different species.

The most instructive and widely exercised computer model (by mathematicians, social scientists or biologists) is a simple game called 'Prisoner's Dilemma'. The idea of this approach is to simulate the conflicts that exist in a real situation between the selfish desire of each player to pursue the 'winner-takes-all' philosophy, and the necessity for cooperation and compromise to advance that self-same need. It is similar to the previously mentioned problem of 'spin glasses' looking for the determination of the lowest energy state or, in general, the optimal solution for the traveling salesman's problem to find the most favorable scheme that must be solved in the presence of conflicting constraints. The two counter-partner actors can choose to cooperate with each other or not. If yes, they receive some bonus, if only one does ('bum-sucker') he receives nothing while the other ('defector') gets a reward though the bonus is smaller. If both defect, each gets a minor reward. Even though each player inevitably gains if both cooperate, there is always a temptation to defect, both to maximize the profit and avoid being betrayed.

The dilemma 'of what strategy is better' often results in the so-called 'tit-for-tat' ('blow-for-blow') policy, i.e., the signalization of willingness to cooperate at first and then retaliating to whenever the opponent defects. It includes the property of forgiveness, which is perpetually making available the opportunity of re-establishing the trust between the opponents; if the counter-partner is conciliatory, it forgives, and both reap the greater reward of cooperation. In conclusion, however, it does not seem too clever as any highly complex strategy seems to be incomprehensible; if one appears irresponsible, the other's adversary has no incentive to cooperate. Let us mention the biological context where one can interpret the reward and penalty offered in the game in terms of the ability of individuals of different species to survive through reproduction – the reward is simply the numbers of offspring produced during the breeding season. In terms of ecosystem, this strategy of retaliation in kind is vigorous and does well when playing a wide variety of other tactics. Though no strategy is evolutionarily stable, it turns out that 'tit-for-tat' cannot be invaded and displaced by all-out defectors in a long-term relationship. The detection that retaliation is a common strategy sends an optimistic message to all those who fear that human nature is founded on greed and self-interested alone, hopeful that nice people do not have to finish at last.

Economics straddles the divide between science and the humanities. The world's economies possess nonlinear features characteristic of complex dynamical systems, although the marketplace is rather associated with a form of financial survival of the fittest. There are objective measures of economical and financial success, whether of nations or companies, such as gross product, budget deficit, market share, revenues or stock prices, however, yet many factors may or will be seen ill defined. For decades, the central dogma of economics revolved around decayed equilibrium principles in a manner entirely analogous to the application of equilibrium thermodynamics. As mentioned, it was pioneered by *Lewis* [24] and, surely, *Newton* paved the way by the first use of exact mathematical evaluation directed to economic accounts, see Fig. 5.

Recent Nobel Prize was awarded in the sphere of establishing game theory as a powerful tool with applications ranging from the industrial economics to international trade and monetary policy. It may be simply illustrated on the strategy, which a monopolizing company must consider in a bid to prevent a would-be competitor from encroaching on its market. Engagement in a price war may inflict losses on rivals and persuasion of a more welcoming strategy (cartel) may assure profits for both companies, but often agreeing illegitimately high prices. It may also help answering the trade-off dilemma between cheap, high-polluting transport and expensive green alternatives.

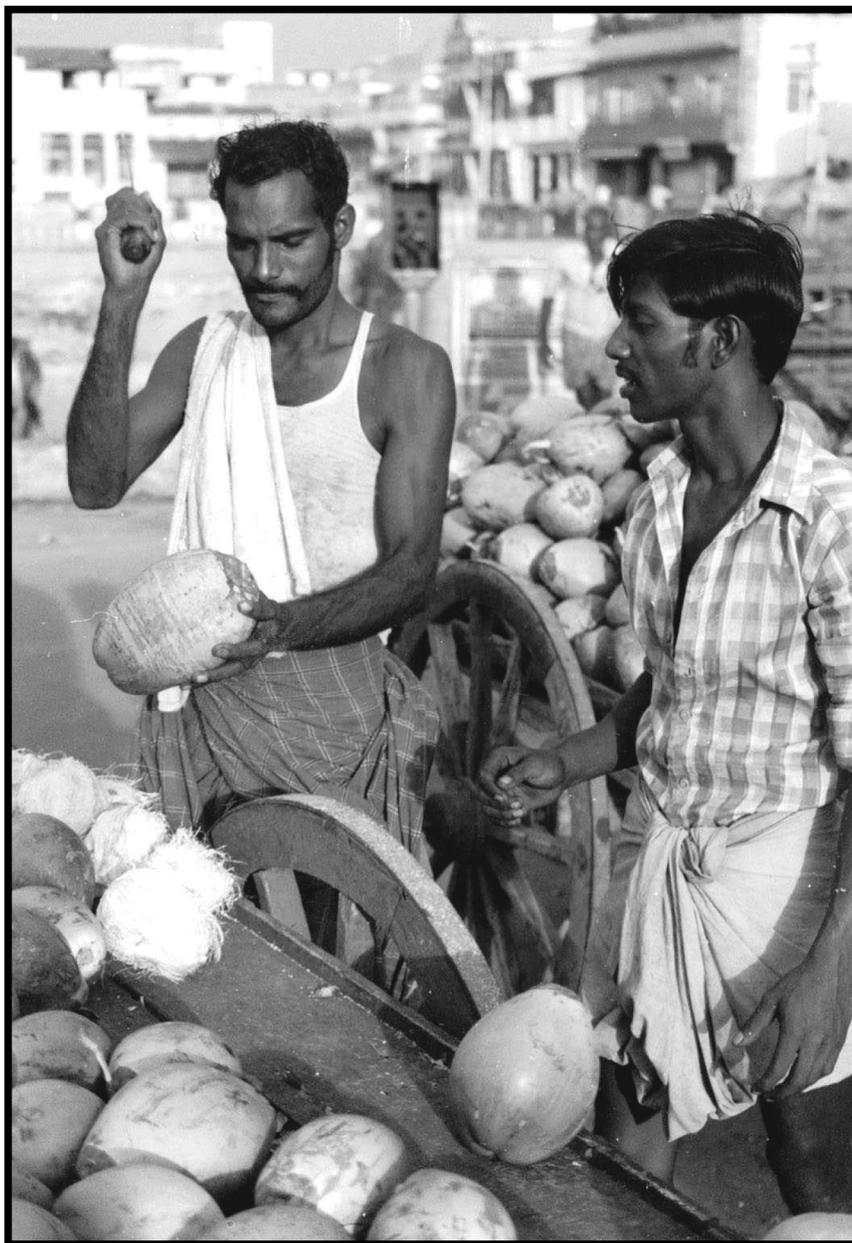
Certainly, we can draw yet other analogies between the crisis points associated with self-organization and chaos that occur in inanimate processes, from ordered chemical reactions through certain phenomena that arises within human societies (revolutions) and behavior of people. It is worth mentioning that there always remains an intriguing question concerning the distinction between computer simulation and reality. In many cases, a simulation of a physical or chemical process on a computer could not be confused with the process itself, i.e., a computer simulation of self-organized chemical waves is not the reaction in nature. For the scientists, who are deciphering the wide-ranging complexity, it places renewed emphasis on interdisciplinary research in the over and done Renaissance style, and helps to underline the symbiosis between the science, technology, economy and humanities.

¹ Certainly, we are not considering here further complications, what it could be the so called „oil-and-water“ model, where one group, the water, wants to get rid of the other group, the oil, while oil does not particularly want to be with its own kind and would stay mixed with water, as happens when an *emulsifier* is used to change the interaction conditions.

² In order to change the interaction behavior of inorganic mixtures we can add admixtures, surface reactants, dopants, etc., so that the appropriately adjusted composition matches the lowest value of the system's Gibbs energy. For living organism it is far more complicated to intervene its "chemical factory" in order to achieve desired feeling of maximal satisfaction or happiness. The primary chemical in charge of the living function is surprisingly nitric oxide. It's a vascular traffic cop, activating the muscles that control the expansion and contraction of blood vessels. If the mind is in the mood the body appropriately responds. Alike the interaction of differently charged molecules the interaction between two heterosexual beings is controlled by hormones: male testosterone and female estrogen, which triggers desire by stimulating the release of neurotransmitters in the brain. These chemical are ultimately responsible

for our moods, emotions and attitudes. Most important seems be dopamine, partly responsible for making external stimuli arousing, among other things, from drug addiction or sport/work/hobby or other activity holism. Dopamin-enhancing drugs (antidepressants) can increase desire and erection as well as apomorphine. Another neurotransmitter almost certainly involved in the biochemistry of attraction and desire is serotonin, which, like dopamine, plays a significant role in feelings of satisfaction. Another imperative hormone is oxytocin, which is in charge of feel-good factor, e.g., for couples holding their hands, watching romantic movies or grouping with the same leisure time as well as melanocyte-stimulating hormone with a dual effect of giving men erections and heightening their interest in sex and attractiveness. Probably the most controversial issue on the chemistry of attraction and sexuality is the role of pheromones, so far only used by perfumemakers that have latched market by pheromone-based scents. Therefore the mutual attraction and associated sexual desire is yet seen as a sort of magic, a phenomenon filled with delightful mystery thus for long outside of a rigorous description in any thermodynamic language.

³ Nevertheless, it is worth mentioning that evolutionary games generate irregular or better the regularly shifting mosaic, where strategies of cooperation and defection are both maintained. The outcome is milling chaos, with clusters expanding, colliding and fragmenting with both preeminent and nastiest persisting. The term of punctuated equilibrium is also mentioned saying that the evolutionary changes occurred usually in shorter bursts separated by longer periods of stability. Catalyzing any replication of a molecule is a form of giving a self-support, with each link feeding back on itself, which would be the earliest instance of mutual aid, and in this sense, cooperation could be older than life itself. Remarkably enough, the genetic algorithm use to evolve from a random initial point and became a dominant member whose rule base was just as successful as the 'tit-for-tat' strategy that won the tournament. Indeed, most of the rules are shared, but some are better. One is the kind of sexual reproduction, in which the chromosomes of two parent solutions are recombined. It means that the population still evolved towards rules that performed about as well as 'tit-for-tat', but they were only half as likely as in the sexual case to produce rules substantially better than that for retaliation. Besides the importance of sex, the strategic environment itself was changing and was taken to be the evolving population of chromosomes moving away from cooperation and subsequently reversing back again. Eventually, the reciprocators spread to dominate the entire population. The computer simulations showed that sex helped a population to explore the multidimensional space and so find the gene combinations with the greatest fitness; that there became a trade-off in evolution between the gains to be had from flexibility (advantageous for a long run) and the specialization (for immediate survival).



CHAPTER NINETEEN

19. Modern materials and society

a) Intelligent processing and manufacturing of advanced materials

Thermodynamic studies and broader application of thermal methods of analysis have played an important role in the development of new materials and in the material headway, which assisted the civilization to move forward [31]. It has simultaneously taken place on macroscopic and microscopic scales [32–34], which can be exemplified by the building structure as a matter of construction fashion, cf. Fig. 1 [35], by the building's internal equipment (standard furniture, luxury belongings, communication instruments, etc.) [36] and by the functional property of individual materials involved, see next paragraphs.

Herewith, we would like to show the three examples of proficient materials based on the author's studies performed during the past twenty years [36]. As expected, the chosen cases can be of broad interest, which can give readers certain insight to the problematic issues of advanced materials, particularly pretentious for the current need to master material's quenched states, structure and stoichiometry as well as possible chemical and morphological compatibility with living tissues. With a deeper analysis, we just can become jealous of how the Nature designs hierarchical structures to satisfy complex requirements in the mastery of both the non-living inorganic and biological organic systems.

Until recently, scientists were doubtful whether higher complexity can produce qualitatively new behavior and whether the discovery of very complex materials has somehow broken a conceptual barrier opening active research in broader classes of multicomponent (and now even low-dimensional) systems. It touches equally the research of quantum states with their auspicious optical and scattering characteristics as well as the use of unexpected technologies, such as novel heat-convection-free experiments performed under microgravity [37]. Besides yet more and more sophisticated technologies we also restore old-manufacturing practices now re-applied to modern processing, such as the calendar as rolling machine for rapid quenching [36,38]. The goal of progress is to obtain such materials that would, on one hand, allow the effects and the properties of materials used to date to be produced with much better parameters tomorrow and, on the other hand, grant material capability to act as ready-to-use reserves when new effects and properties are discovered and exploited in the next-generation technology.

A common drawback is the insufficient cross-disciplinary transfer of specialized skill from branches that are not directly related though they could mutually serve as inspiration. We can see that the building design, architectural styles, applied materials, decorations, etc., have for long served in the fortitude of civilization, which spontaneously included the design aspects of traditional (Euclidean) and sensational (fractal) geometry, the application need for natural and artificial materials, etc., cf. Fig. 1, [33–35]. There is also a non-negligible tendency to underestimate the importance of the search for people

gifted for science and ready to undertake its missionary vocation and student's subsequent inter-disciplinary education with respect to learn both the 'feeling' of material and the 'tactility' for experimentation.

It is well known that major discoveries in materials and their engineering have driven the progress of civilization. Such a process was complex as the art of processing was passed down from generation to generation but little of the ancient knowledge survived major historical population shifts and cultural transformation. Much of the art was rediscovered in different eras and parts of the world. We, for example, can recognize with amazement the sophistication of Damascene sword steel, the maturity of 3000 years old blast furnaces discovered in Africa and the perfection and durability of Roman aqueducts, some being still in use today. Transistor, among other revolutionary changes in the second half of the 20th Century (such as the associated quantum Hall effect, integration, optoelectronics, and oxide superconductivity) upshot the growth of electronics. The transparency of silica glass improved only slowly over centuries, until studies on optical fibers were begun in earnest, so that the transparency subsequently increased by orders of magnitude within just a few years. However, for the generation that witnessed the emergence and rapid ascent of new materials in the fifties, the name of 'materials science' was unknown and slowly accepted in the titles of Universities over the sixties becoming, however, the sign of smartness in nineties.

Recently it has achieved the new state of a joint approach within the scope of the so-called field of '*intelligent processing and manufacturing of materials*' [39], which tries to cover the three necessary aspects of a fruitful progress¹:

- (i) tailoring the quality functional material,
- (j) constructing and producing the material under the most economical (and ecological) conditions and
- (ij) assuring the material's promotion, distribution and marketing as well as its enhancement for a yet wider demand (along with the attention to an acceptable impact on sustainable level of civilization).

Novel applications of *fuzzy logic* often assist its satisfactory solution [35]. Moreover, the new products achieve success through a combination of sound technical pattern and imaginative industrial design. Such an amalgam creates so-called '*product character*', which is the way and process used to provide functionality, usability, and satisfaction of ownership. In particular, the satisfaction is greatly influenced by the aesthetics, association, and perception that the products carry a combination that we can refer to as product personality. The overall character of the product is a synthesis of its loveliness, functionality, usability, personality and economy.

Smart composite structures with built-in diagnostics can soon appear on the market in order to substitute the traditional use of standard materials (metals, various polymers). Functional ceramics is expected to become significant in view of possible integration into future 'smart' systems (intelligent automata) to be composed of sensors (information sources), actuators (movement),

batteries (power) and computers (coordination and decision).

Progressive tailoring of magnetic as well as of mechanical, ferroelectric and dielectric properties is for long in the center of attention. Currently, their elaboration respects the so-called ‘medium’ ordering states [40] popularized under the generalized term of ‘nanomaterials’ and ‘nanotechnologies’ [41]. For example, the extent of magnetic exchange interactions is effective across a given width of magnetic domain walls, and the disordered nano-crystallites of a subcritical domain size (*‘fine-metals’*) would thus appear as magnetically disordered in a similar way as truly non-crystalline, yet classical glasses (*‘metglasses’*). It may similarly bring new dimensions to nonlinear optoelectronics where again nanocrystalline based waveguides play important role in infrared optics. Silica glass fibers alone could cause the frequency doubling of infrared laser beams suggesting those even non-crystalline solids can have large second-order susceptibilities. Such oxide glasses [40] can also serve as useful transparent matrices for semiconductor and metals nano-crystallites to form nano-composites (formerly known as colloids, e.g., ruby glass containing gold) with large third-order susceptibilities. Controlled uniform size distribution of such nano-particles is needed for nonlinear devices and soliton switching as well as for waveguide lasers while non-uniformity is required in the applications for optical data storage.

Order-disorder phenomena in the system with lower dimensions are another separate and well-emerging category providing new boundary problems such as nanometer range phase separation in the thin amorphous films prepared by CVD as is known, e.g., for germanium. It touches non-stoichiometric semiconductors prepared via non-equilibrium MBE or MOCVD. Such a matrix can be generally understood as being a submerged disordered

system of defects with nano-crystalline dimensions. When the system’s characteristic dimension is comparable with the electron wavelength, the quantum electron phenomena (i.e. dimensional absence of electron resistance) become important and such derived materials are known as quantum wells, wires and/or dots. If for an appropriate thickness of a semiconductor layer the disorder of the interface is controlled by remote doping, a high mobility transistor function can be achieved. Quantum-sized dots can also be conventionally formed by dispersion in a suitable matrix, their optimum size to be estimated on the basis of the ratio of material permittivity over the effective mass.

Oxide gels and organically modified silicate gels (*‘ormosils’*) can serve as hosts for such semiconductor nano-crystallites as well as for other inorganic materials and polymers. Submicron sized halides in composite glassy electrolytes can essentially increase ionic conductivity, and nanometric (*‘pinning’*) centers can improve superconductivity of complex cuprates. Nano-crystallization of porous silicon can play an important role in the better management of photoluminescence when taking into account the role of separating interfaces of silicon grains, which was recently shown to be responsible for the blue photoluminescence. The quality was dependent on the remaining (nanosized) separating layers, as revealed by the early studies carried out on inorganic and organic silanes.

To speak about the neighboring domain of superalloys, we can briefly cite the importance of inhibition during the sub-critical formation of nuclei. Similar considerations apply to the embryo’s generation in such diverse spheres as is the preventive medicine, which deals with the growth of viruses and/or diseases (cancer) as well as environmental sciences, which pays attention to the formation of smog, rain or snow. Resistivity of plants against the

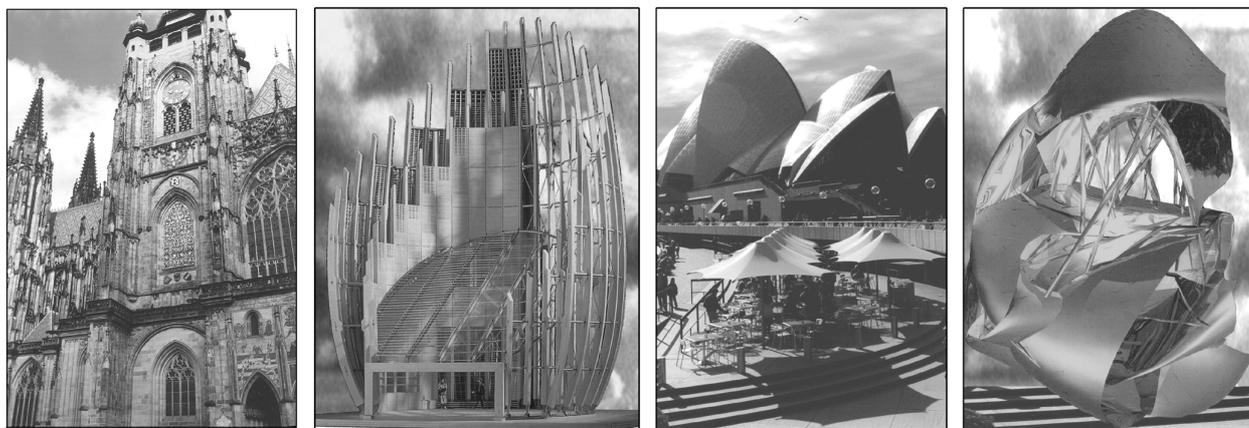


Fig. 19.1. Living objects as compositional constructions are lengthily rewarded together with the aptitude of human imagination and design as well as the building capacity of applied materials then available. From left: Stone, fractal-like composition of the side portal of the gothic jewel of the St. Vitus cathedral in Prague (Czechia) founded by Charles IV in the middle of fourteenth Century (Architect Matyáš of Arras replaced in 1352 by Petr Parléř); Cultural Centrum J.-M. Tjibaou in Noumea (New Caledonia, 1994); Opera in Sydney (New South Wales, 1973, Bjorn Utzon) and a new design proposed by Marcus Novak (2002, USA) showing liquid-like architecture (trans-architecture) made of conjoined lamina and cross-fade linkage [P. Zellner “Hybrid Space” Thames & Hudson, London 1999].

damage due to ice crystals formed upon freezing of aqueous solutions belongs to this category and is aided by presence of low-molecular carbohydrates (sugar). Self-protection is accomplished by raising the body's liquid supersaturation to high viscosity, which is then capable to undergo vitrification. Formation of glassy (freeze-concentrated) phase may also improve the stability of frozen food and is equally important in cryopreservation of human implants in liquid nitrogen and shelf life in general. The stability can be naturally and artificially improved by the additions of 'cryoprotectors'. They avoid damages caused by inappropriate cooling as experienced at too slow rates, where cells can be killed by overly lifted salt concentration owing to intracellular water loss as a result of osmosis. At faster rates, cells can be destroyed by intracellular ice formation due to insufficient water flow-out or the undesirable phase separation of lipids and proteins in membranes (protecting their mesomorphic liquid-crystalline state capable to commence a glass transition).

Biological materials from both the human natural and non-human synthetic sources have significant medical applications. These may include processed tissue from porcine heart valves, bovine carotid arteries, human umbilical veins, hyaluronic acid or chitosans, and is completed by wide range of synthetic non-degradable, bio-absorbable and soluble polymers, which require yet deeper studies of the effects of enzymes and other biologically active materials, absorbability, degradability and degradation products equally important for inorganic metals, ceramics and glasses exhibiting some phenomena to meet criteria for biomedical use. They invoke additional questions of electrochemical corrosion, durability of passive layers and their self-production on certain surfaces. Worth noting is the growth of the pre-treated TiO_2 layers proficient to yield biocompatibility and to exhibit the capability to elicit immune and hypersensitive reactions, interactions with biological pathways, processing and sterilization on biodegradation or even self-sterilization effects (anti-bacteriologic action of TiO_2 -treated surfaces, which are kept under ultraviolet light).

Understanding the mechanisms underlying the mystery of the order-disorder transitions from nonliving to living offers hope for prolonging the quality of life by, e.g., helping to design better therapeutic treatments for diseases of the skeletal system or perhaps even dietary supplements, which inhibit the onset of diseases. An important step is seen in the osteogenic properties of bioactive glass-ceramics capable to release soluble (hydrated) silicon, which activates bone cells to produce growth factors. Formation of ordered proteins (DNA-like structures) on inorganic bioactive substrates (clays) could not be solved on mere entropy concepts as it may involve a mechanistic solution based on the order-disorder paradox of life. Namely, hydrated (three-member) silica rings can be easily formed on the activated silica surfaces (fractured or otherwise bio-stimulated) creating thus pentacoordinated silica atoms in a metastable transition state due to the aminoacid interaction with trisiloxane rings. Such a Si-OH complex can act like an inorganic enzyme by providing a favorable reaction pathway for polypeptide synthesis².

b) Metallic glasses

In the late seventies, the metallic glasses represented a new class of materials [43], whose physical properties and non-traditional technology of manufacturing became the subject of an intensive research. Although the involved method of rapid quenching enables the products to be obtained only in the form of powders, wires, layers and ribbons, this technology substantially decreases the energy consumption and supplies materials with the properties unknown until recently. Additional ways were proposed how to form bulk materials from such limiting, almost 'one- or two-dimensional' samples, usually by pressing them together often to form composites. T-T diagrams useful to depict the quenching processes were discussed in Chapter 8 (cf. Fig. 2).

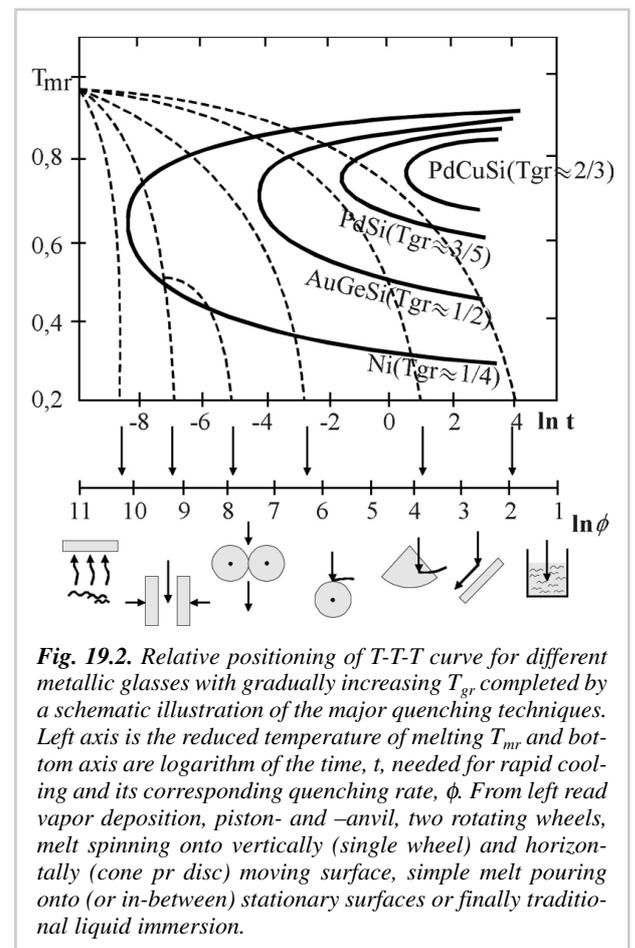


Fig. 19.2. Relative positioning of T-T curve for different metallic glasses with gradually increasing T_{gr} completed by a schematic illustration of the major quenching techniques. Left axis is the reduced temperature of melting T_{mr} and bottom axis are logarithm of the time, t , needed for rapid cooling and its corresponding quenching rate, ϕ . From left read vapor deposition, piston- and -anvil, two rotating wheels, melt spinning onto vertically (single wheel) and horizontally (cone pr disc) moving surface, simple melt pouring onto (or in-between) stationary surfaces or finally traditional liquid immersion.

Most metallic glasses, with hardness of about 1000 HV and strength up to 3000 MPa, are magnetically soft. Their good permeability, low coercive field, low attenuation of acoustic signals, good magnetostriction constant and low losses give a good basis for broad applications in electronics (pulse transformers, magnetic amplifiers, switching cascades, data heads), electrical engineering (transformers, rotating machines, inductive current limiters, ground fault interrupters, tunable delay lines), sensors (deformation, pressure, temperature, acceleration) and magnetic shielding. Originally, the massive application of metallic glasses in distribution transformers was

foreseen, which could economize as much as 1/3 of lost electric energy. However, the obvious questions of manufacturers, how stable such glasses are and how long they can act in full service was never successfully answered – even if a relatively inexpensive $\text{Fe}_{80}\text{B}_{20}$ with high magnetization and low losses is capable to withstand its damage due to crystallization for about 25 years at temperatures below 200 °C. The lack of more precise estimates became the main hindrance for the glass worldwide utilization though the glass found exploitation even at increased frequencies in small mobile and air-borne transformers where the size is a decisive factor.

Metallic glasses also exhibit some other extraordinary property as superconductivity ($\text{Mo}_{64}\text{Re}_{16}\text{P}_{10}\text{B}_{10}$ with $T_c \sim 8.7$ K) or technological utility ($\text{Ni}_{78}\text{Si}_8\text{B}_{14}$ as a hard solder for turbine casings, AgCuTiB for joining ceramics or $\text{Fe}_{72}\text{Cr}_8\text{P}_{13}\text{C}_7$ as corrosion resistant). At high hardness and tensile strength, they are relatively ductile. This was the reason for their exploitation as reinforcing materials for special tires, high pressure tubes, conveyor belts or huge flywheels (accumulators of mechanical energy), or eventually as a prospective material for building purposes (concrete reinforcement).

Consequent development of fine metals with the crystalline size of about 10 nm, either distributed within glassy matrix or representing the middle-range ordering of matrices, made possible to improve magnetic inductance and permeability and lower magnetostriction. The typical composition of such nano-crystalline materials is $\text{Fe}_{74}\text{CuSi}_{13}\text{B}_9\text{Nb}_3$ (in comparison with the classical, commercially available ‘metglass’ $\text{Co}_{67}\text{Fe}_4\text{Cr}_2\text{Si}_6\text{B}_{14}$). Equally interesting are the issues of ‘quasi-crystals’ with unusual pentagonal symmetry, neither exactly crystalline nor non-crystalline, where their order is not consistent with heretofore accepted rules defining the allowable symmetries of crystals (cf. previous Fig.10.11). They can be grown as large as a few centimeters from glasses with typical composition of $\text{Al}_{64}\text{Cu}_3\text{Li}_{27}$ or GaMn_2Zn_3 .

Practically every review begins with a reference to the paper by *Gubanov* [43] who showed that magnetic ordering below a well-defined critical temperature may exist even in systems possessing fluctuations, which are typical amorphous mixtures characterized by various degree of topological disorder and absence of translation symmetry. Most easily they can be prepared by melt quenching of compositions in the neighborhood of deep eutectics, such as 80% of metals (Fe,Ni,Co,Mo,Cu,Cr) combined with 20% of glass-forming metalloids (B,Si,P,C,Ge) or other admixtures (Zr,Hf, Nb,Ta or even Be).

Glassy alloys exhibit a continuous series of compositions without any sudden change of topology whereas the crystalline counterparts habitually reveal transitions to another structure, accompanied sometimes by the miscibility gaps, and resulting in a marked discontinuity and character changes of properties. On the other hand, an essential complication is faced due to the finite size of the metalloids present in the alloy and the problem of the possible chemical bonding between the metal and the metalloid affecting the magnetic moment, which becomes even

more complicated with the (Zr,Hf)-type interactions. The magnetic glasses do not manifest magnetocrystalline anisotropy and its intrinsic absence is why these glasses have been regarded as candidates for extremely magnetically soft materials. The magnitude of magnetostriction constant is important for the magnetic properties because of enormous stresses resulting from quenching. It can be diminished by thermal annealing and is little changed when the relative amount or composition of metalloids is altered. From the composition diagrams of metals we can also find the line where the magnetostriction is zero, which helps to determine the alloy composition, whose magnetic properties are least affected by the mechanical state of material. The coercivity field in metallic glasses is similar to the case of crystalline materials, depending

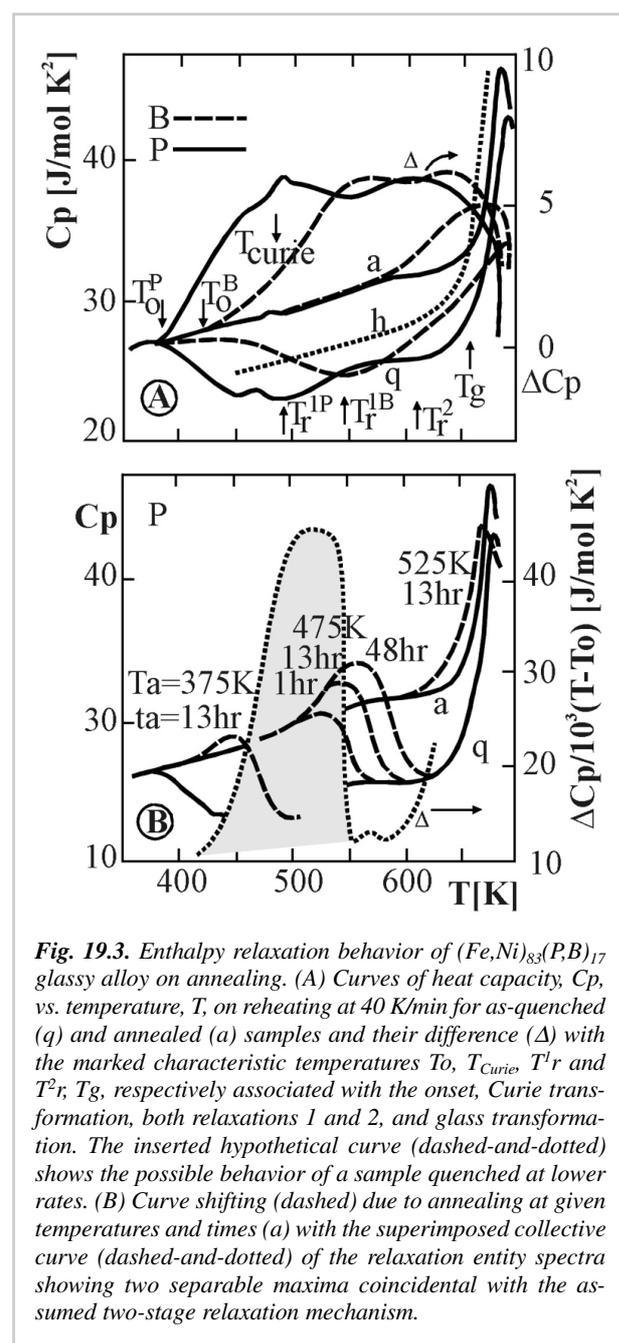


Fig. 19.3. Enthalpy relaxation behavior of $(\text{Fe,Ni})_{83}(\text{P,B})_{17}$ glassy alloy on annealing. (A) Curves of heat capacity, C_p , vs. temperature, T , on reheating at 40 K/min for as-quenched (q) and annealed (a) samples and their difference (Δ) with the marked characteristic temperatures T_o , T_{Curie} , T^1_r and T^2_r ; T_g , respectively associated with the onset, Curie transformation, both relaxations 1 and 2, and glass transformation. The inserted hypothetical curve (dashed-and-dotted) shows the possible behavior of a sample quenched at lower rates. (B) Curve shifting (dashed) due to annealing at given temperatures and times (a) with the superimposed collective curve (dashed-and-dotted) of the relaxation entity spectra showing two separable maxima coincidental with the assumed two-stage relaxation mechanism.

on local structural arrangements, fluctuation of chemical short-range order, surface defects and irregularities, and pinning of domain walls on defects or stress sites.

The magnetization losses in ac-fields are one of the most important characteristics for applications in electronics. Their extent depend on eddy-current losses (the time dependence of the field, degree of magnetization and the associated deformation of domain walls, the thickness and resistivity of the material) and anomalous losses (number of domain walls and their non-sinusoidal, non-uniform and irreversible displacement). The number of walls is relatively much lower than in crystalline counterpart so that they have to travel relatively smaller distances during the change of magnetization. Even the precipitation less than one percent of fine particles may considerably lower the losses and increase the permeability at high frequencies by creating the nuclei of additional domain walls. From the point of view of the saturation magnetization, the $\text{Fe}_{30}\text{B}_{20}$ -type glasses can lower the induction to working values from 1.8 to 1.4 T for the certain metalloid-metalloid ratio (e.g., $\text{Si}_{0.4}\text{B}_{0.6}$). The effective permeability is usually achieved in association with the easiness of compositional glass-formation, which decreases the degree of structural inhomogeneities.

Upon a consequent heating at temperatures below the beginning of crystallization, quenched metallic alloys can gradually lower their free energy towards a more stable configuration. This phenomenon is called *structural relaxation* and is manifested by continuous change in all physical properties. From the comparison between thermal expansion and DSC measurements, it was concluded that the annealing-out of the excess free volume explains the densification of the sample glass and contributes mainly to the exothermic effect detected during the first heating. In general, relaxation processes can be defined as any thermally activated rearrangements of all constitutional species and can be of three types [38]:

(i) topological short-range ordering, at which the structural defects may relax and disappear at temperatures close below T_g , where the collective motion is prevalent characterized by the logarithmic type of

kinetics of the changes of the measured thermophysical quantity,

- (ii) compositional short-range ordering during which the chemically similar atoms (e.g. Ni, Co, Fe and/or B, Si, C) can exchange their mutual positions. This arrangement of neighboring atoms may be manifested by the changes of the Curie temperature, magnetic field-induced anisotropy or Young's modulus, and
- (iii) diffusional ordering, which, again, is connected with the existence of persisting structural defects, but especially dependent on the thermal history of the glass preparation, i.e., structural freeze-in during the ribbon formation.

Calorimetric studies proved themselves as a very sensitive indicator of the relaxation state of the glasses and they can also supply direct evidence of the relaxation processes of the first and second types. Therefore the above classification was considered too strict when calorimetric data were analyzed for the annealing-induced relaxation of metal-metalloid glasses, see Fig. 3 [44,45]. In accordance with the percolation model [45,46], the excess endothermic peak occurring above the temperature of annealing and evolving reversibly in a continuous manner was attributed to irreversible/reversible processes, which consist of

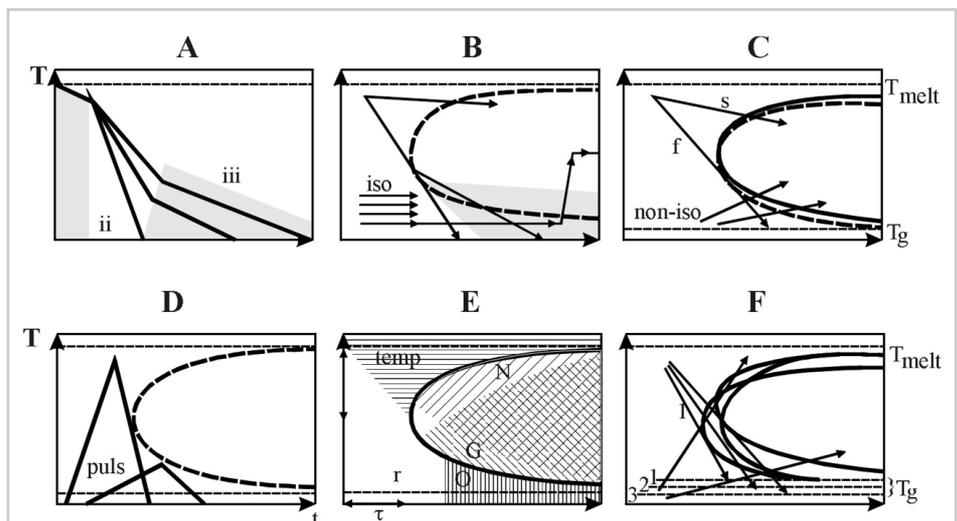


Fig. 19.4. Hypothetical T - T - T diagrams as tools for establishing possible courses of thermal treatment: (A) approximate cooling lines in the T - t coordinates with the three typical stages marked as (I) fusing or tempering and transporting melt to the place of processing when the sample temperature is controlled by self-cooling (hatched), (II) rapid cooling through the controlled heat conduction into tempering support and (III) free cooling after the termination of the effective tempering contact with heat sink (hatched). (B) Two stage cooling provided by the two rollers technique marked together with a T - T - T boundary line (dashed) showing their possible interaction during the low-temperature cooling when the sample separates from the rollers (hatched). Traditional isothermal annealing with a common two-stage treatment is also marked by horizontal lines. (C) T - T - T diagram with two overlapping crystallization processes illustrating the possibility of formation of two different phases on slow (s) and fast (f) cooling. (D) Flash annealing by electric heat pulses introduced in the front of the nose of the T - T - T curve for such a short time period not interfere with the crystallization. (E) T - T - T diagram with the shaded areas marked for the different rate-controlling processes, customarily Nucleation (N), growth (G), quenched-in nuclei (Q), and areas of dominant processes taking place during relaxation (r) and tempering ($temp$). (F) A model of possible overlap of three crystallization curves of three phases with different degrees of metastability to show that the crystallization products can be affected by the different rates of cooling and/or reheating.

- i) local and medium-range rearrangements, which occur by interactions involving only larger metal atoms and
- ii) long-range regrouping, which takes place through interactions and diffusion between all constituents and their clusters.

In order to achieve the most advantageous performance of the annealing at higher temperatures, a heating rate as high as possible is required to ensure that the stress relief occurs at the desirably highest temperature and not too early during the time of heating. This requirement was reflected through a special technique called *flush annealing* in which heat is delivered to the sample in distinct pulses – see Fig. 4 [47]. In practice, such a treatment is essentially accomplished in two ways.

- i) Continuously, where the glassy ribbon is pulled under a constant tension from a supply spool so as to pass over an intensive heater and immediately cooled rapidly from both sides, usually by a jet of helium or by contact with cooling block.
- ii) Discontinuously by resistivity heating with short dc or ac electric current pulses flowing directly through the ribbon conventionally immersed in the cooling medium (such as oil).

The first procedure provides heating rates up to 10^2 K/s up to maximum peak temperature of about $500\text{ }^\circ\text{C}$, whereas the second method appears to heat samples to about $800\text{ }^\circ\text{C}$ as fast as 10^4 K/s, exceeding and leaving critical temperatures without causing undesirable crystallization.

It is assumed that the bond orientation anisotropy gives rise to the observable magnetic anisotropy. A closer inspection of the magnetic domain structure shows that besides the in-plane magnetization there also exists a domain whose magnetization is oriented perpendicularly to the ribbon plane. This is a standard interpretation of the fine labyrinth-like structure visible by SEM [48] (see previous Figs. 10.11 and 10.12). The easy-magnetization direction lies essentially along the ribbon and the stress direction.

c) Ceramic high-temperature superconductors

Superconductivity, one of the most fascinating phenomena in solid-state physics was discovered in 1911 by *Kamerlingh-Onnes* [49] for low-temperature conductivity measurement of mercury but it was not until 1957 that a satisfactory microscopic theory of the effect became available, i.e., one by *Bardeen, Cooper and Schrieffer* and known as BCS theory [50]. The special relationship responsible for superconductivity are ‘pair correlations’, which in the presence of certain electron ‘attraction’ leads to the formation of electron pairs, often called *Cooper pairs* [51]. Each pair can be considered as a bound state of two electrons with opposite spins and momenta and may form even if the interactions are repulsive due to certain stringent requirements (i.e., the interactions must be much less repulsive for electrons near the *Fermi* surface than away from it and the electron pairs can be treated as being independent of each other but entangled).

The crucial impulse for advanced superconductivity studies was the year 1989 where the surprising discovery

by *Miller and Bednorz* [52] revealed that a ceramic sample, i.e., a barium-doped lanthanum copper oxide, becomes superconducting at 36 K, some 12 K above the previous record temperature for traditional transition metals alloys. The escalation of thermochemical research in the nineties became a main engine in the search for yet a new sort of ceramic superconducting material, generally called the *high- T_c superconductors* (HTSC). Specialized thermo-physical studies at low temperatures became a useful tool in depicting their characteristic behavior and the subsequent quest for the other promising cuprates yielded materials with transition temperature (T_c) far above the boiling temperature of nitrogen (77 K) so that they could be used with cheaply available coolant rather than expensive liquid helium, cf. Fig. 5. Although the research boom

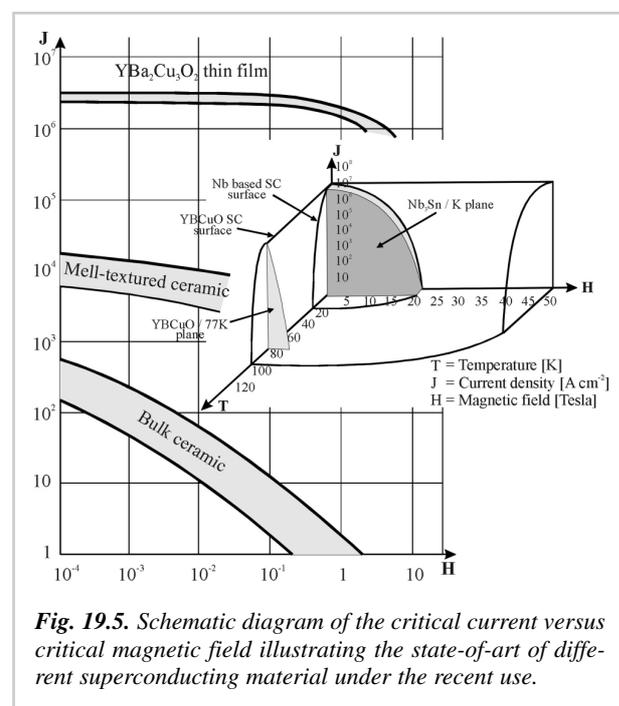


Fig. 19.5. Schematic diagram of the critical current versus critical magnetic field illustrating the state-of-art of different superconducting material under the recent use.

is gradually expiring the commercial applications have been too slow to take off and the early promise of magnetically-levitated trains, powerful electric motors or super-efficient power transmission has not yet been fulfilled³.

We are happy to mention that in our mother Institute of Physics we took an early part in the worldwide development of HTSC having been interested in various aspects of structural and preparative thermochemistry, thermodynamics and even preparative technology of phases as well as, more recently, in certain theoretical aspects of superconductivity. Among others the investigations near the beginning were: the early crystallographic characterization of the famous phase, $\text{YBa}_2\text{Cu}_3\text{O}_x$, conveniently abbreviated as ‘123’ [53], initial studies in quenched ‘123’-based compositions, which we, unfortunately, did not completed to develop practical utilization for HTSC wire texturing (while drowned by means of fast melt solidification and glass-pattern re-crystallization [54–57]) though we constructed the first ‘guesstimate’ of its T-T

diagram – see Fig. 6. The early description of kinetic and topological problems associated with the formation and decomposition of the ‘123’ phase [58], see Fig. 7, was also the target of our research, not mentioning the growth of single crystals and various methods of powder technologies.

The thermochemical research evidently played a decisive role, so that it became also reflected in extended publication activity in relevant journals, not excluding *J. Thermal Analysis and Thermochimica Acta*, where even special issues [59,60] were published. Here the progress of HTSC was associated with better understanding of phase diagrams, starting from the oxide (Cu, Ba, Y), their binaries [61–63] through pseudo-binaries to the Y-Ba-Cu-O pseudo-ternaries, yielding an improvement in the construction of phase diagrams. The research finally moved to the novel families of HTSC systems (Bi-Ca-Sr-Cu-O) and the determination of their thermodynamic properties [64–67] as well as the innovative Hg-Ca-Ba-Cu-O system [68]), cf. Fig. 8. We paid increased attention to the improvement of calculation methods and simulation procedures (cf. preceding Fig. 6.3) of the phases involved and finally published a series of improved thermodynamic data [64–67] – see Table I. More than twenty-years’ experience with the construction of various types of phase diagrams [69] and encouragement with using specific calculation procedures in order to estimate the related thermodynamic properties were summarized in our previous reports [70,71] and were also mentioned in the previous Chapters 6 and 7 (such as a simulation method [66,67] by means of the linear appreciative rule shown in Fig. 6.3 and the modified *Richardson and Jefferson* plot [58], cf. Fig. 7.3, adopted for the description of temperature dependence of the oxygen pressure for various phases occurring in the system represented by multiparty formulae $Y_xBa_yCu_zO_\delta$).

In contradiction to the structural models we could hypothetically account just for the stoichiometric subsistence of various phases yet unknown by formally extending the cation ratios to ranges of yet undetermined compounds [68,71], but suitable for thermodynamic estimates. Such hypothetical changes of ratios $(Y+Ba)/Cu = \xi$ (from $\xi \leq 1$, through $\xi \approx 2$ to $\xi \geq 2.5$) can be derived, on one hand, from the basic superconductor $YBa_2Cu_3O_x$ (‘123’, $\xi = 1$), and on the other hand, from the non-

superconducting ‘green phase’ Y_2BaCuO_x (‘211’, $\xi = 3$). We can also extract partial values for the formation enthalpy in such homological series. For example, according to the stoichiometry changes along the line $YBa_2Cu_3O_7 \rightarrow YBa_2Cu_4O_8 \rightarrow YBa_2Cu_5O_9 \rightarrow (1/2)Y_2Ba_4Cu_7O_{15}$ we can estimate that each adding of a single CuO conveys 19.8 kJ/mol, while that for Cu_2O is 12.13 kJ/mol and the multiplication of BaO layers provides the value between 29–32 kJ/mol [72].

Impurity atoms in most materials are usually viewed as a problem because they can result in properties deviating from those ideally assumed. However, they can be sometimes used to advantage when attempting to understand

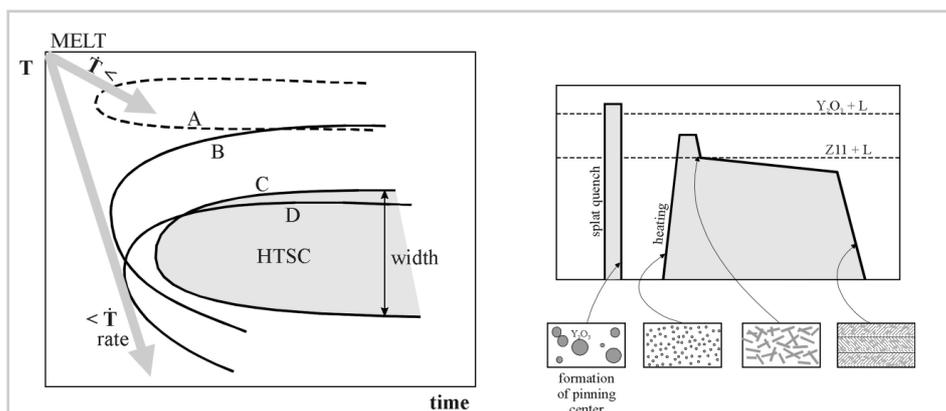


Fig. 19.6. Hypothetical T - T - T diagram (left) suggested for the rapidly quenched HTSC in the $YBaCu-O$ and $BiCaSrCu-O$ systems (expressed in the simplified cation ratios):

Initial comp.	ϕ_{crit} K/s	T_{melt} °C	Precipitating phases				ΔT^C_{per} °C	T^C_{per} °C
‘123’	10^7	~1400	‘100’	‘211’	‘123’	‘011’	~200	~1000
‘2223’	10^3	~900	‘001’	‘2212’	‘2223’	‘2021’	<10	~840

The formation of the superconducting phase ‘C’ precedes likely the polymorphic crystallization where the non-superconducting phase ‘B’ and ‘D’ develop first from the low- and/or non-crystallized matrix latter re-reacting to form the desired superconducting phase ‘C’. Indisposition of the system to provide directly the phase ‘C’ on mere quenching is exploited for a trick needed to prepare technically applicable HTSC in two-step melting and cooling (right diagram) without achieving the total melting. As shown by shaded area the first sharp melting assures certain leftover of fine unmelted particles of Y_2O_3 (which later serve as vital pinning centers) while the second broad melting and controlled cooling provides the required peritectic formation of superconducting phases and alignment of its microcrystallites.

new complex materials. This is because the interaction of such doping atoms with the matrix can reveal detailed information on the local electronic environment, which is the case of HTSC. Here the electron-electron attractive interactions occur in the degenerated electron gas as a result in the formation of the above-mentioned *Cooper* pairs. The superconducting ground state represents ‘condensation’ of these *Cooper* pairs into a single macroscopic quantum state – a process analogous to the fundamental *Bose-Einstein* condensation. The order parameter associated with this groundstate has d-wave symmetry. The typical examples of these HTSC materials are shown in Table I. Whereas in these systems the conduction is due to holes while in the other, electron-doped systems of $Nd_{2-x}Ce_xCuO_4$ ($T_c \approx 20$ K), this is different.

The common structural features of all HTSC is a perovskite network $MMeO_3$ [73] formed by densely

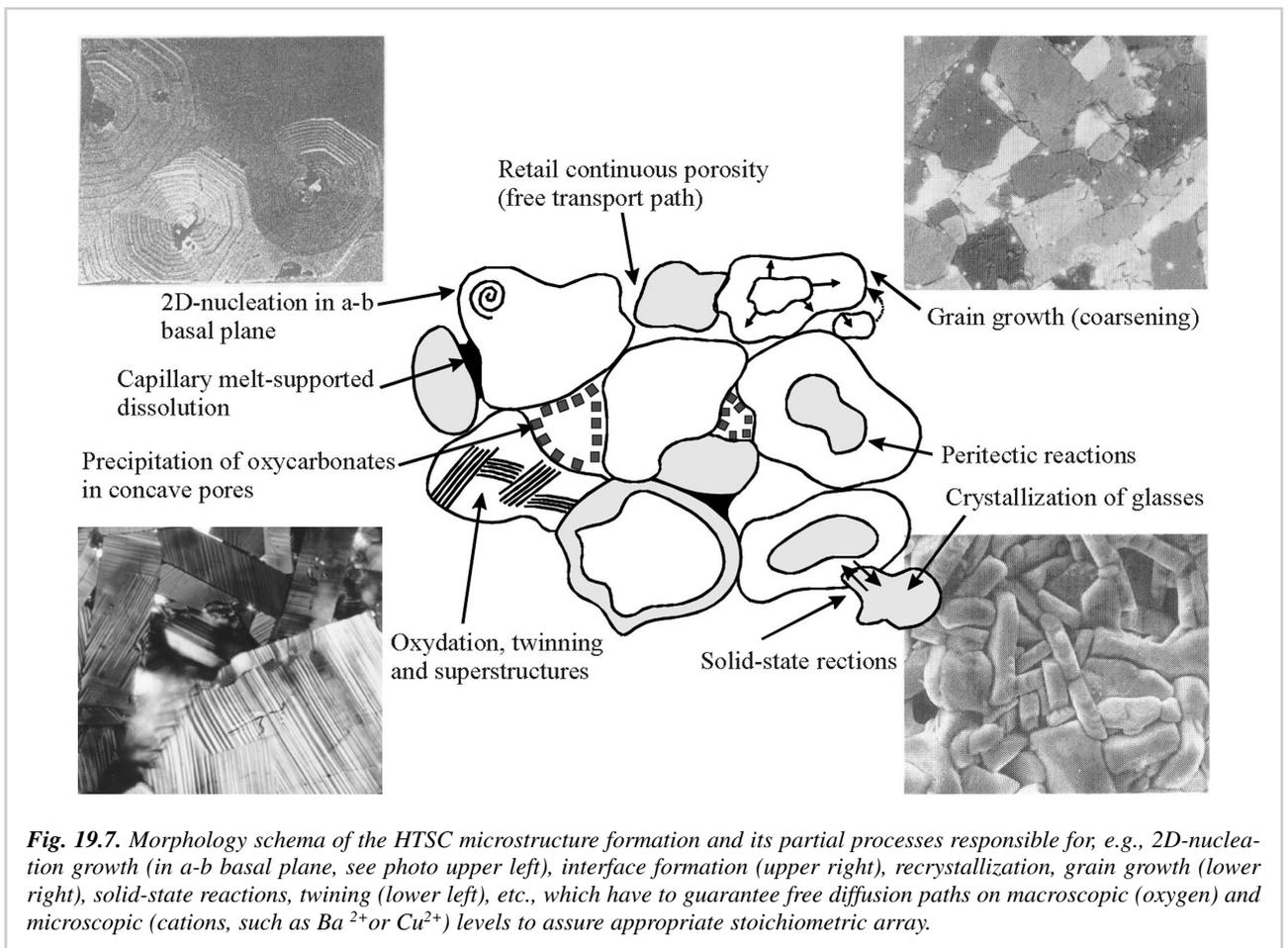
Table 19.I: Thermodynamic data calculated for oxides superconductors.

Oxide	ΔH_{298}^0 kJ mol ⁻¹	S_{298}^0 J K ⁻¹ mol ⁻¹	$H_{298}^0 - H_0^0$ J mol ⁻¹	cp = a+b.10 ⁻³ T - c.10 ⁵ T ⁻² J K ⁻¹ mol ⁻¹			$T_{ph.tr}$ K	$\Delta H_{ph.tr}$ kJ mol ⁻¹	$c_{p,ph.tr}$ J K ⁻¹ mol ⁻¹
				A	B	C			
Sr ₆ Bi ₂ O ₉	-42.07,4	471	68900	399,4	68,3	32	1238	267,7	534,7
Sr ₃ Bi ₂ O ₆	-2443,4	310,2	45065	254,4	46,8	18,6	1483	199,9	356,6
Sr ₂ Bi ₂ O ₅	-1860,3	265,5	37110	206	39,8	14,3	1213	132,5	280,6
Sr ₁₈ Bi ₂₂ O ₅₁	-17928,9	2607	376330	2072,1	411	139,7	1076	1099,5	2777
Sr ₆ Bi ₁₄ O ₂₇	-7927,6	1365,7	196020	1054,8	221,5	64,4	922	516,7	1392
SrBi ₄ O ₇	-1803,5	351,7	50310	266,8	58,7	15,4	800	113,5	346,8
Sr ₂ Bi ₆ O ₇	-3029,6	554,5	79450	424,4	90,5	25	864	194,9	555,7
SrBi ₂ O ₄	-1224,2	202,8	2914	157,6	32,9	9,9	1213	101,5	217,8
Sr ₈ Bi ₁₀ O ₂₃	-8033,1	1175,3	169620	933,1	185,6	62,7	1070	529,8	1250
Sr ₈ Bi ₂ O ₁₁	-5387,5	578,1	84770	496,2	82,9	40,9	1335	350,3	670,2
Sr ₅ Bi ₆ O ₁₄	-4902,7	700	101975	565,9	112,6	38,4	1213	366,6	775,4
Sr ₆ Bi ₂ O ₁₁	-4391,4	471	68900	399,4	68,3	32	1238	261,7	534,7
Sr ₆ Bi ₄ O ₁₅	-5162,7	620,4	90130	508,7	93,6	37,4	1200	323,4	685,8
Sr ₂₄ Bi ₁₄ O ₅₂	-19201,2	2332,3	339290	1925,4	347,8	143,5	1224	1248,4	2594
Sr ₂ Bi ₂ Cu ₆ O ₆	-2095,7	303,3	44,5	247,8	66	20,3	1372	156,7	384,1
Sr ₈ Bi ₄ Cu ₅ O ₁₉	-7243	956,5	142,2	849,9	174,2	95,8	1819	661,4	1254,9
Sr ₃ Bi ₂ Cu ₂ O ₈	-2906,4	401,5	59,5	348,5	78,4	35,9	1772	254,1	522,1
Sr ₁₈ Bi ₂₂ Cu ₁₀ O ₆₁	-20384	3072. 1	449,6	2469	698,3	182,5	1676	1438,7	3850,4
Sr ₉ Bi ₄ Cu ₁₆ O ₁₆	-7097,7	841	120,8	708	150,6	74,2	2018	547,2	1077,8
Sr ₇ Bi ₂ Cu ₂ O ₁₂	-5384,4	623,1	91,9	557,2	99	68,9	2001	477,8	813,2

Oxide x:y:z:δ	ΔH_{298}^0 kJ mol ⁻¹	S_{298}^0 J K ⁻¹ mol ⁻¹	$H_{298}^0 - H_0^0$ J mol ⁻¹	cp = a+b.10 ⁻³ T - c.10 ⁵ T ⁻² J K ⁻¹ mol ⁻¹			$T_{ph.tr}$ °C	$\Delta H_{ph.tr}$ J mol ⁻¹	$c_{p,ph.tr}$ J K ⁻¹ mol ⁻¹
				A	B	C			
for Y _x Ba _y Cu _z O ₈									
123-O6	-2586.817.9	319,86	49352	307,48	76,28	26,213	1373	1370	362,12
123-O7	-2706.3+2.4	323,06	51107	315,29	54,47	42,45	1288	110900	418,1
123.5-O7.5	-2794.513.5	345,15	54040	305,12	84,56	22,064	1190	23400	416,6
124-O8	-2881.215.7	367,24	57750	356,72	45,74	42,47	1110	9200	445,8
125-O9	-3055.2110.5	411,42	65610	363,27	114,67	22,064	1023	8900	498,2
143-O8.5	-3828.3114.2	454,15	70016	312,96	41,07	42,81	1170	156500	357,9
211-O5	-2712.012.6	223	35344	206,1	35,2	20,925	1543	31200	262
YCu ₂	-1038.6124.3	98,81	15677	92,9	16,36	8,05	1843	64500	125,6
Y ₂ Cu ₂ O ₅	-2214.815.1	200,83	31360	201,65	41,85	18,155	1428	1430	265,14
Y ₂ Ba ₄ O ₄	-2533.5+0.7	178,81	28128	164,65	20,53	20,32	1673	9800	198,37
Y ₂ Ba ₂ O ₅	-3131.016.4	245,16	37905	227,88	22,05	36,734	1313	10200	249,27
Y ₂ Ba ₄ O ₇	-4314.117.5	377,84	57346	335,28	24,6	52,44	1413	28100	386,75
Y ₄ Ba ₃ O ₉	-5666.615.3	424	66049	393,75	48,23	44,915	2433	245700	510,18
BaCuO ₂	-782.0121.4	110,52	17020	91,45	24,42	7,245	1318	28300	122,46
BaCu ₂ O ₂	-807.017.4	151,51	22707	118,3	27,09	8,01	1500	42800	163,76
Ba ₂ CuO ₃	-1409,1129	176,87	26730	145,32	28,77	16,594	1123	4300	176
BaCu ₅ O ₈	-2656.4+4.9	420	65590	354,18	113,42	24,9	1073	3100	445,05

Table 19.II: Structural layer ordering in the superconducting cuprates and their associated critical temperatures [K] for $n = 1-4$.

	n = 1	n = 2	n = 3	n = 4
Y-cuprates $\text{YBa}_2\text{Cu}_{2+n}\text{O}_{5+n+\delta}$ $\downarrow \delta$ $\uparrow e^-$ $[\text{CuO}_8]^{2(1-\delta)+} [\text{BaO}]^0 [\text{CuO}_2]^{2-} [\text{Y}]^{3+} [\text{CuO}]^{2-} [\text{BaO}]^0 [\text{CuO}_8]^{2(1-\delta)+}$	93	80	-	-
Bi-cuprates $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ $\downarrow \delta$ $\uparrow e^-$ $[\text{BiO}]^+ [\text{BiO}]^+ [\text{SrO}]^0 [\text{CuO}_2]^{2-} [\text{Ca}]^{2+} [\text{CuO}_2]^{2-} [\text{SrO}]^0 [\text{BiO}]^+ [\text{BiO}]^+$	12	85	108	-
Tl-cuprates $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ $\uparrow \text{Tl}$ $\uparrow e^-$ $[\text{TlO}]^+ [\text{TlO}]^+ [\text{BaO}]^0 [\text{CuO}_2]^{2-} [\text{Ca}]^{2+} [\text{CuO}_2]^{2-} [\text{BaO}]^0 [\text{TlO}]^+ [\text{TlO}]^+$ $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3+\delta}$ $\uparrow \delta$ $\downarrow e^-$ $[\text{TlO}]^+ [\text{BaO}]^0 [\text{CuO}_2]^{1.66-} [\text{Ca}]^{2+} [\text{CuO}_2]^{1.66-} [\text{BaO}]^0 [\text{TlO}]^+$	95	118	125	-
Hg-cuprates $\text{Hg}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ $\downarrow \delta$ $\uparrow e^-$ $[\text{HgO}_8]^{(2-2\delta)+} [\text{BaO}]^0 [\text{CuO}_2]^{2-} [\text{Ca}]^{2+} [\text{CuO}_2]^{2-} [\text{BaO}]^0 [\text{HgO}_8]^{(2-2\delta)+}$	98	120	135	118



coordinated oxygens being the source of two sublattices, one with the large M (= Ba, Sr) cations of 12-coordination and the other with small Me (= Cu) cations of 6-coordination. The most important structural elements are the copper-oxide planes with a unit cell CuO_2 , which are formed from octahedra, pyramids or squares. Examples are $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, where the planes are formed from octahedra, in $\text{YBa}_2\text{Cu}_3\text{O}_7$ from pyramids and in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ from squares. The electron transport and the physical processes leading to superconductivity are believed to take place within these planes. In the simplest case of LaCuO_4 , the CuO_6 octahedra are elongated due to the *Jahn-Teller* distortion, lifting the degeneracy of the Cu-*d* orbitals, which is two- and three-fold. This leaves for Cu a valency of 2+ implying a $3d^9$ configuration. The hole in the 3*d* shell is placed into the highest antibonding Cu-O state, which has predominantly $3d_{x^2-y^2}$ character. With one hole per formula unit of LaCuO_4 , one can expect its metallic character with a half-filled conduction band. La_2CuO_4 can be doped with holes by partial replacement of La^{3+} by Sr^{2+} , similarly Nd_2CuO_4 can be doped with electrons by replacement of Nd^{3+} by $\text{Ce}^{3.5+}$. The Cu-O planes of $\text{YBa}_2\text{Cu}_3\text{O}_7$ contains holes without further modification because the charge is moved from the planes into the chains (so called ‘self-doping’) formed from CuO_4 squares sharing an oxygen atom.

Among the most suitable cuprates are those fulfilling the relation $d_{\text{M-O}} \leq \sqrt{2} d_{\text{Me-O}}$ and containing one (or preferably more) crystal planes per unit cell that consist of only Cu and O atoms in a planar square lattice, cf. Table II. In order to maintain electroneutrality, the MO must be strictly 2+, which determines the choice of M-cation. The cations with the formal charge 4+ exhibit only small ionic

radius and thus can bear an insufficient number of neighboring oxygens. The solution grants access to structures either showing anion deficiency ($\text{YBa}_2\text{Cu}_3\text{O}_x$) or exhibiting a more complex constitution (Tl, Hg-based structures). Basic configuration reveal three parallel layers, $[\text{CuO}_2][\text{MO}][\text{M}'\text{O}]$, necessarily associated with overlapping of electron orbitals ($\text{Cu} - 3d_{x^2-y^2}$ and $\text{O} - 2p_{x,z}$). As mentioned, superconductivity originates from the strongly interacting electrons in these CuO_2 planes (Cu atoms are believed to be in the $\text{Cu}^{2+} - 3d^9$ configuration with the spin 1/2 so that the overall electronic state is the antiferromagnetic *Mott* insulator). Doping these insulating CuO_2 layers with holes (or electrons) causes the appearance of new electronically ordered state, which includes that of superconductivity because the mutual hopping of electrons from Cu to Cu becomes possible. A generally known schematic phase diagram of such cuprates reveals ‘optimum’ hole-doping near the hole concentration about 0.2 per Cu atom (with inter-atomic distance of about 0.3 nm, the *Fermi* wavelength of about 1 nm and superconducting coherence length of about 1.5 nm).

The complex ‘ceramic’ morphology of these materials plays an important role. Most HTSC are composed of grains (expected to be oriented along the current), the interface of which is responsible for the composition adjustments by enabling desirable easy-interaction with surrounding oxygen – cf. Fig. 7. Therefore, we can expect an intimate relation between HTSC properties and the material morphology depending on the way of foregoing technological treatment. We try to avoid the formation of insulating layers, the contamination by reactive gases (CO_2 , H_2O) or the incorporation of impurities from the sample holders (Pt, Al) or precursors, although some

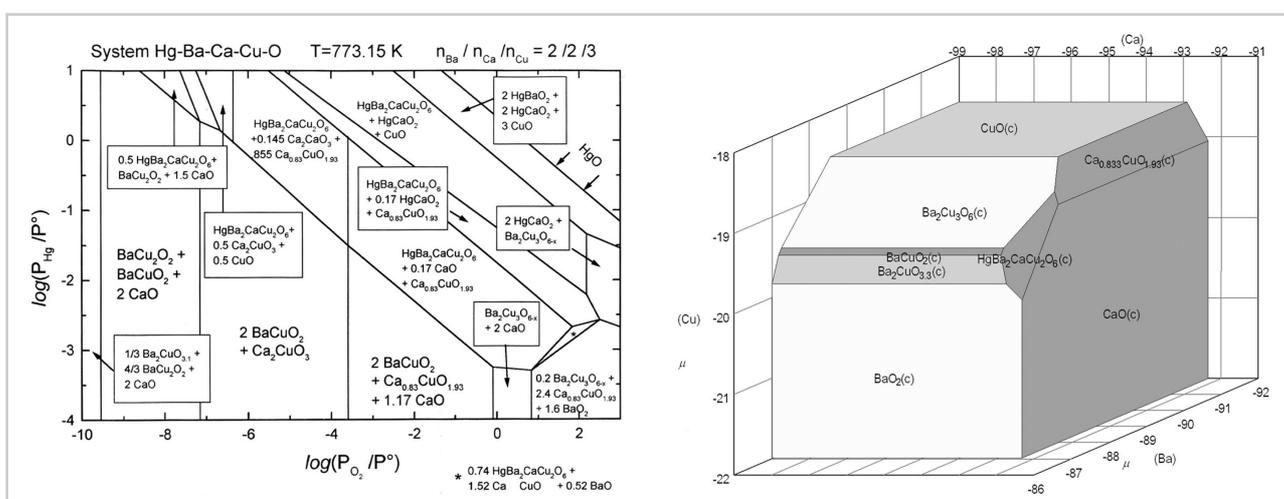


Fig. 19.8. The HTSC phase diagrams are revealed here as a typical portrayal suitable to illustrate two expedient methods of thermodynamic calculation accounting on plausible phases and their stoichiometry to occur in the system Ba-Ca-Cu-Hg-O. Left: Conventional minimization of the total Gibbs energy to satisfy the material balance conditions (conveyed on under constrains of fixed partial pressure – chemical potentials of oxygen and mercury (courtesy of D. Sedmidubský, Praha, Czechia). Right: Application of the concept of chemical activity makes it possible to treat as many as three metallic elements equivalency in a specific 3-dimentional representation, which is capable to depict the behavior of volatile phases, O_2 and Hg, enabling the construction of so-called chemical potential phase diagrams [23]. It is illustrated by the plot of chemical potential (μ) for three metals involved (Ba-Ca-Cu) in their conservative stage (c) assuming two gaseous components (g) at the temperature $T=773$ K and pressure $P=1\text{atm}$ (courtesy of H. Yokakawa, Tsukuba, Japan).

impurities may turn out desirable when serving as pinning centers (such as unreacted Y_2O_3 itself) for super-current vortices. Therefore, it is often welcome to increase the population of dislocations and suitable defects in order to provide easy vortex pinning to get an increase in the critical current, J_c . Indeed, their core size dimensions should match that of the correlation length and the vortices; they must be inbuilt while such ceramics is ductile. The extreme brittleness of the ceramics and the tendency to the formation of non-stoichiometric stacking faults, occurring as the precursor of the relatively more stable $YBa_2Cu_4O_8$ phase under the form of additional CuO layer, makes it difficult. Thermomechanical treatment, such as cold isostatic pressing (joining the effect of high oxygen pressure and plastic deformation) helps the built up of favored internal, chemical and mechanical stresses. Under these conditions, crack nucleation is minimized and the dislocation and stacking faults densities can be adjusted to get significant diminution of the correlation length along the vortices, which leads to diminishing the activation energy of their motion.

Beside standard low-temperature measurements used to determine superconductivity, we can employ other very specific thermoanalytical technique to elucidate special features of the HTSC structural behavior. One of such yet unusual technique is that of emanation thermal analysis (ETA) helpful in determining fine oxygen changes [74], cf. Fig. 9., or sorptometric measurements aimed to analyze the surface/bulk heterogeneity revealing its true

fractal-like dimensions [75]. For example, the pore size distribution of $HgBa_2Ca_2Cu_3O_{8+\delta}$ was calculated from nitrogen-adsorption (obtained over the size range between 1.7 to 300 nm) and the related fractal dimension value was calculated to lie close to 2.5. Another type of the experimental evidence of the oxygen ordering is the microscopic observation of the interface boundary between the $123_{ortho} \leftrightarrow 123_{tetra}$ transformation in polarized light. The diffusing oxygen forms orthorhombic domains with ordered Cu-O chains growing in the $[1\bar{1}0]$ direction where the domain thickens is being limited by elastic energy. After the critical thickness is reached, the chains start to grow in perpendicular direction, thus forming a twin structure, as illustrated in Fig. 10.

Another awkward effect can be found in the HTSC vicinity layer of super-current channels where cation stoichiometry may not stay stable but its intimate links can be strongly modified [76]. In this approach we can conceptually suppose that the real (123) composition at $x = 6.85$ can contain both the two- and tri-valent cations of copper as well as holes (\square), such as $YBa_2Cu_{2.6}Cu_{0.4}\square_{0.15}O_{6.85}$. Under the effect of negative-charge of super-current flow on the very thin neighboring layers it may induce not only the phase structure deformation but also certain chemical changes due to the possible absorption of some species, likely Ba^{2+} and \square^{2+} , that can migrate from the internal body of HTSC. The intact interface composition can then vary through a curiously wide range of stoichiometry, e.g., $YBa_{3.03-3.09}Cu_{0.392-0.26}Cu_{0.40}\square_{223-0.226}O_{5.744-5.677}$.

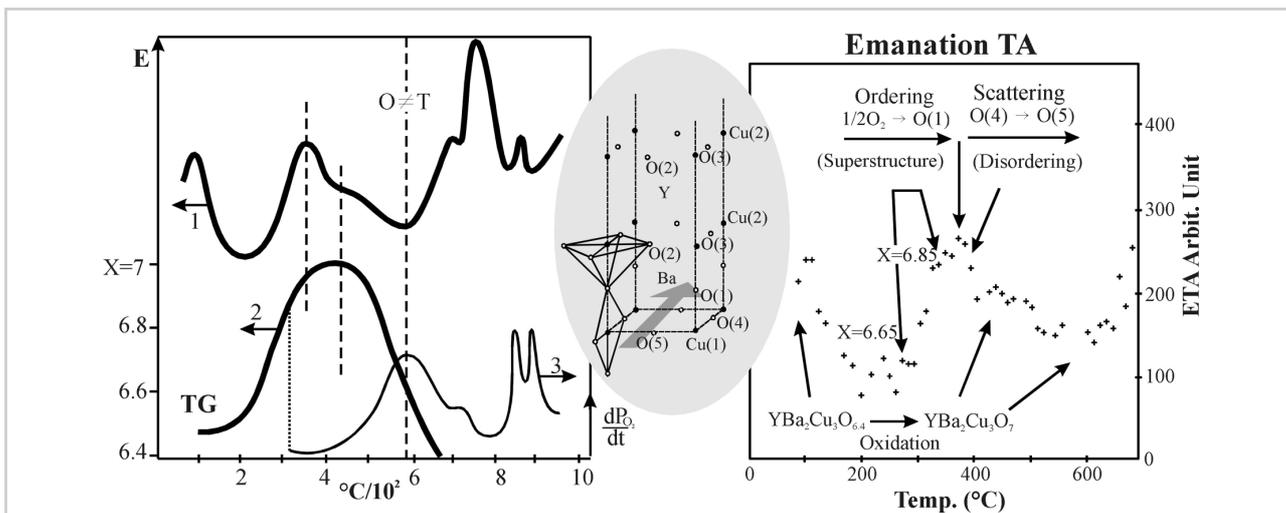


Fig. 19.9. Beside the traditional methods of mass changes detection (TG or EGA, see left, thick curves) and their capacity to profit rather insensitive traces, the method of emanation thermal analysis (ETA, right) brings into play another evaluative possibility. The sample is labeled by radioactive thorium, which is acting as a recurring source for argon that escapes and serves as a penetrating probe. Argon diffusion pathway, forced through to get out from the sample bulk, must be receptive and big enough to accommodate such an spacious atom, which is twice as big as oxygen. The best passage is certainly provided by defects (cracks, interfaces) but network 'corridors' can suit likewise such as the vacant chains formed by O(5) voids, see the inset, structure in the middle. The gradual oxygen occupation, which increases along the O(4) voids, can be seen as step-wise as the ordered transitional structures (or better superstructures) are gradually formed. It shows that the basic structure of '123' is more complicated and is closely related to the environmental conditions (temperature, pressure, transport delays). It follows that intermediate configurations can exist between the familiar fully oxygenated (ortho-) and deoxygenated (tetra-) structures, i.e., the superlattice associates with $\delta = 6.55$ [2/500] and $x = 6.85$ [1/300] having full occupation every two in five or every second chain. Later on, owing to temperature scattering, oxygen also tends to occupy some forbidden O(5) sites, essentially restricting thus the diffusivity free path of probing argon through the lattice, left..

Although we are used to take care about off-stoichiometry and the occurrence of second phases in the bulk HTSC, we have to be also careful about the peculiarities of composition on the interfaces, where high curvature of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystallites may even change the local oxygen stoichiometry, x , by depletion of oxygen on surface stress sites with consequent formation of weak links (see Fig. 10). Tentatively, it may result in the drift of the low-temperature curve tails, experimentally measured on the plot of relative conductivity versus temperature. Similar consequences were earlier studied by the electric field effect resulting in the field-driven oxygen rearrangement [77] arising from the field-driven movement of the mobile charge carriers in HTSC, being thus a generic property of these superconductors.

Yet another source of curiosity may be established when making SQUID measurements on the $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystals [63], where we can witness stepwise sequences of gradual transfer of dimensionality from the 2-D to 3-D superconducting state, see Fig. 11. Although first indication of superconductivity turns up at a temperature as high as 92 K, the internal dissipation processes hold back its instantaneous progress down to 85 K. It is because the $[\text{CuO}_2]^{2-}$ layers turn more easily to the superconducting state on cooling (already at $T_1 = 91.2$ K) while 2 K lower the same is done by whole blocks of $([\text{CuO}_2]^{2-} [\text{Y}]^{3+} [\text{CuO}]^2)$ until the whole-bulk superconductivity is achieved at yet 4 K lower temperature via tunneling Ba-CuO-Ba barriers. This behavior, however, does not comply with the classical BCS theory but seems to be more correlative to the antiferromagnetic arrangement in 2-dimensional systems.

Onset of superconductivity bears special features because all linear dc transport coefficients disappear. Material parameters are thus deduced rather from equilibrium properties, would they be of the thermodynamic nature, or from spectral measurements. Apparently, the HTCS escape the traditional BCS [50] theory including its generalization by *Eliashberg* to strongly coupled superconductors. The critical temperature is nearly by an order of magnitude larger than it is common for the conventional superconductors of comparable electronic density of states. Moreover, the critical values of temperature, T_c , magnetic field, H_c , and magnetostriction, dV/dH , the thermal capacity, c_p , the discontinuity of c_p at the critical point, and the energy gap are not interrelated by ratios found in conventional superconductors. This

fact immediately boosted a search for a new mechanism of the superconductivity.

Moreover the HTSC have a much shorter coherence length, ξ , which is the spatial separation between electrons in the *Cooper* pairs, typically of the order of nanometers in comparison with conventional superconductors exhibiting $\xi \sim 10\text{--}100$ nm. The coherence length is for HTSC shorter than the magnetic penetration depth, λ , which is a measure of how effectively the super-currents screen the magnetic field as it tries to penetrate the mate-

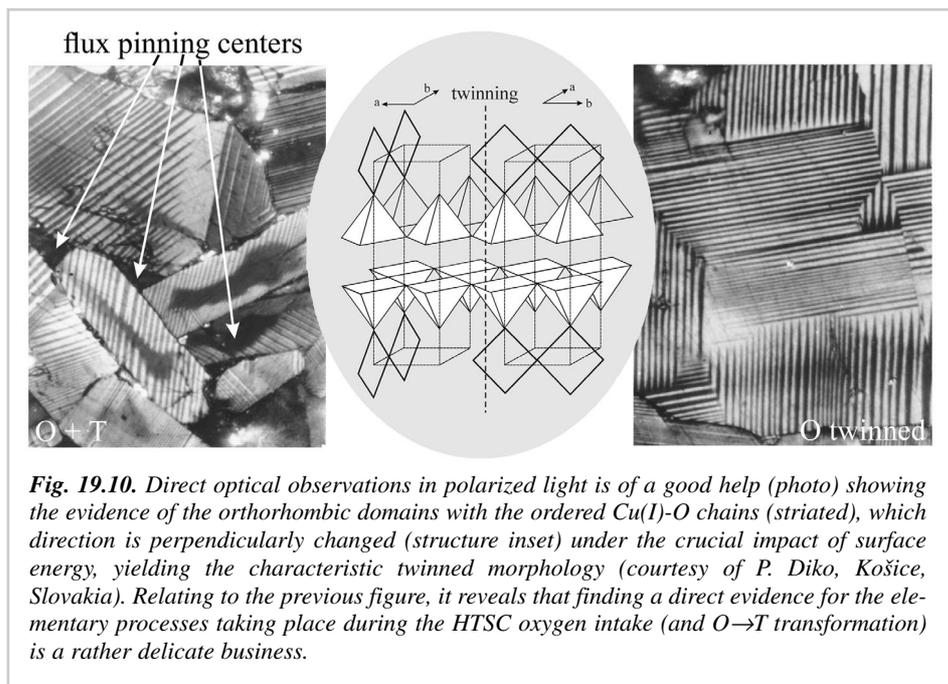


Fig. 19.10. Direct optical observations in polarized light is of a good help (photo) showing the evidence of the orthorhombic domains with the ordered Cu(I-O) chains (striated), which direction is perpendicularly changed (structure inset) under the crucial impact of surface energy, yielding the characteristic twinned morphology (courtesy of P. Diko, Košice, Slovakia). Relating to the previous figure, it reveals that finding a direct evidence for the elementary processes taking place during the HTSC oxygen intake (and $\text{O} \rightarrow \text{T}$ transformation) is a rather delicate business.

rial. The value of ξ determines the size of the normally conducting core of the vortex line and for HTSC the vortices are more weakly pinned on defects. Important is the larger impact of thermal fluctuations in oxides because the vortex lines are more easily disturbed, reminding elastic bands running through the layered structure that are not very taut and do not have a strong restoring force.

While in the study of conventional superconductors the major headway was made possible by physical measurements (discovery of the superconductivity itself, the *Meissner* effect, the isotope effect, the energy gap seen first in the specific heat and later in the tunneling, and so on), in the case of HTSC the most important test of new theories was provided by a large variety of materials in which the CuO_2 planes are embedded in quite different ionic backgrounds. Chain-free materials soon ruled out the very first theories based on the superconductivity of CuO chains, only. Similarly, materials in which the assumed ingredient is missing eliminated the ionization of the apical oxygen, the orthorhombic distortion, the breathing phonon mode, and other coupling mechanisms. The crucial test for the theories based on the dominant role of CuO_2 planes was the sensitivity of the critical temperature to the substitution of electronically neighboring zinc into Cu(2) positions.

The physical measurements turned in a large part towards magnetic properties of the HTSC. In the conventional isotropic superconductors the magnetic field either is expelled or forms the *Abrikosov* vortex lattice. The THSC materials are, in general, highly anisotropic with the anisotropy ratio ranging from moderate values leading to the anisotropic three-dimensional behavior to large values showing clear two-dimensional features. These regimes make possible to achieve new phases of the vortex matter would they be the vortex liquid, braking of vortices into pancakes, or the system of mutually orthogonal *Josephson* and *Abrikosov* vortices penetrating each other in two-dimensional-like systems. Though rearrangements of the vortex matter correspond to rather small changes of the free energy, these transitions are detectable in the specific heat. Such thermodynamic measurements together with magnetic measurements, neutron diffraction and direct observation of the structure via vortex decoration provide the experimental background for the vortex matter comparable to the early studies of phase transitions in solids. The theory has followed this step back into the history as the interest has shifted from the microscopic treatment towards the phenomenological approach of *Ginzburg-Landau* type. Some advanced calculations were done in studying the electrostatic potential in a superconductor applying the *Maxwell* equation for the vector potential, the *Schrödinger* equation for the wave function and the *Poisson* equation for the electrostatic potential. It follows that the electrostatic and the thermodynamic potential largely compensate each other, resulting in an effective potential acting on the superconducting condensate [68].

d) Bio-compatible glass-ceramics as mimetic materials for the bone tissue substitution

Degeneration of a human skeletal system in time results in dysfunction of bones, teeth and joints and is one of the most troublesome issues. Extensive bone defects, left after the removal of tumors, infections or as a result of injuries, are ideally replaced by 'autogenous' bone tissue. As the amount of this material for the patient is limited and the use of 'allogenic' bone is accompanied by biological, mechanical and sociological difficulties, there is a great need for alternate non-human synthetic sources.

Merely four decades ago, it was considered inconceivable that a man-made material could bond to living tissues in view of the deep-rooted experience that it would result in a foreign body reaction and the formation of non-adherent scar tissue at the interface with inserted material. This understanding was irreversibly altered when a special composition of soda-lime-phosphate-silica glass was synthesized by *Hench* [80,81] and successfully implanted in the femurs of rats. About 6% of P_2O_5 was added to simulate the Ca/P constituents of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, that is the inorganic mineral phase naturally existing in bones. Therefore, the bone-like apatite formation on the surface of implant is of a key importance during the physical and chemical processes leading to the formation of a sufficiently firm connection between the implanted material and the newly formed bone tissue. Its comprehension bears all general aspects of compositional and nucleation-growth phenomena discussed for glasses in Chapters 7 and 8 and specified to oxide systems [81–84].

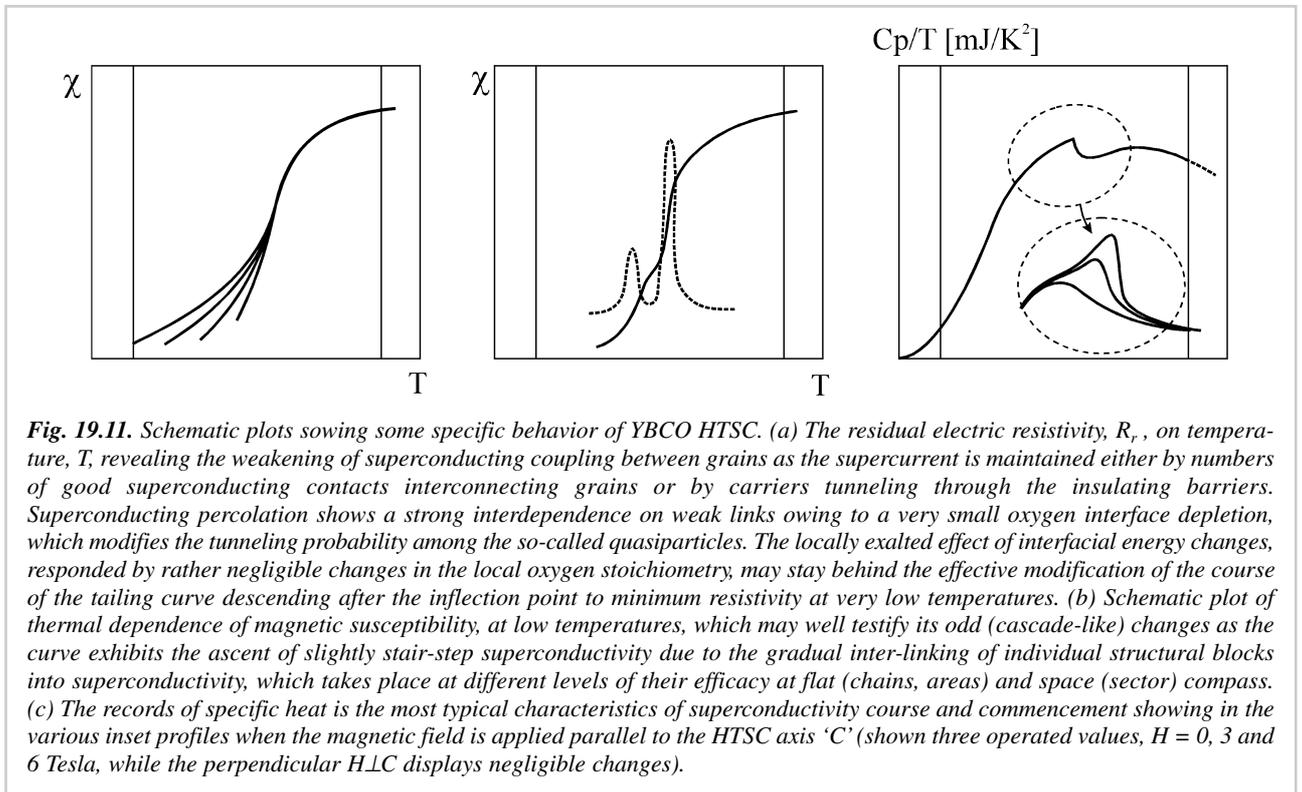
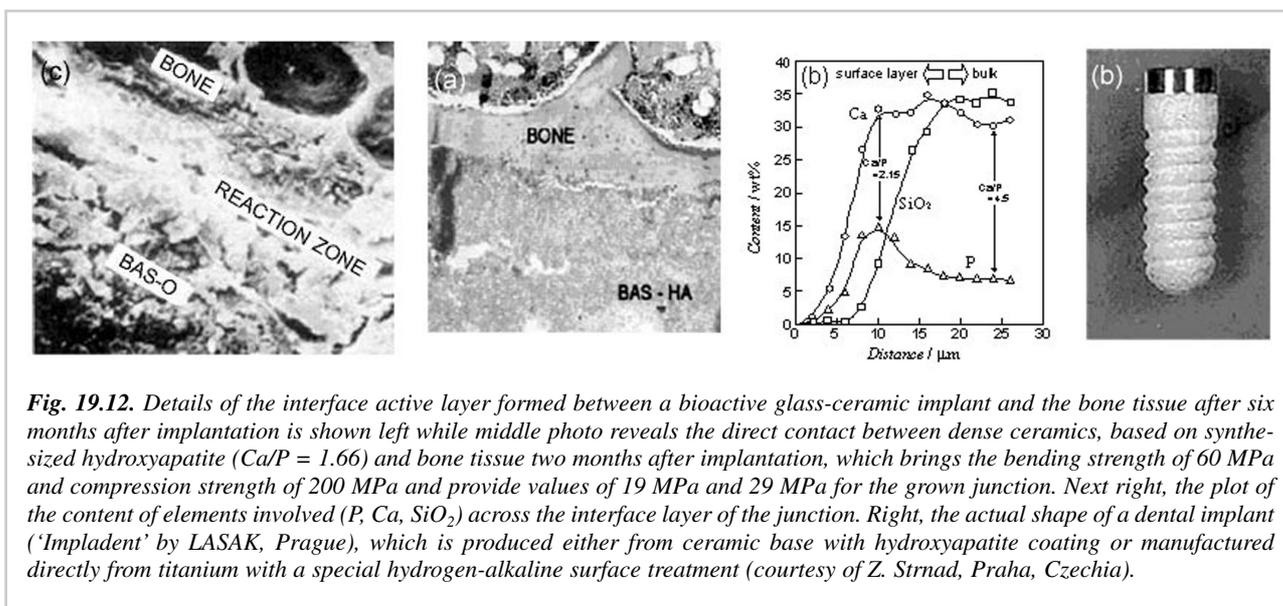


Fig. 19.11. Schematic plots showing some specific behavior of YBCO HTSC. (a) The residual electric resistivity, R_r , on temperature, T , revealing the weakening of superconducting coupling between grains as the supercurrent is maintained either by numbers of good superconducting contacts interconnecting grains or by carriers tunneling through the insulating barriers. Superconducting percolation shows a strong interdependence on weak links owing to a very small oxygen interface depletion, which modifies the tunneling probability among the so-called quasiparticles. The locally exalted effect of interfacial energy changes, responded by rather negligible changes in the local oxygen stoichiometry, may stay behind the effective modification of the course of the tailing curve descending after the inflection point to minimum resistivity at very low temperatures. (b) Schematic plot of thermal dependence of magnetic susceptibility, at low temperatures, which may well testify its odd (cascade-like) changes as the curve exhibits the ascent of slightly stair-step superconductivity due to the gradual inter-linking of individual structural blocks into superconductivity, which takes place at different levels of their efficacy at flat (chains, areas) and space (sector) compass. (c) The records of specific heat is the most typical characteristics of superconductivity course and commencement showing in the various inset profiles when the magnetic field is applied parallel to the HTSC axis 'C' (shown three operated values, $H = 0, 3$ and 6 Tesla, while the perpendicular $H \perp C$ displays negligible changes).



The bioactivity [84] leads to both the osteoconduction and osteoproduction because of rapid reaction on the bioactive glass surface, cf. Fig. 12. The surface reactions [84–87] involve ionic dissolution of critical concentrations of soluble Si , Ca , P and Na ions that give rise to both the intracellular and extracellular responses at the interfaces of the glass with its physiological environment. The smartness of such a mimetic process⁴ is likely hidden in the activity of oxygen characterized by the action of silanol groups ($Si-OH$). They likely serve as nucleation sites for the bio-compatible interface formation capable to co-exist between the original tissue and the implants, which can be expediently made from glass, glass-ceramics, ceramics or cements. Other composites (polymers) as well as particularly treated metals (etched titanium) can be used if the set-in conditions of its suitable surface reactivity are esteemed.

Bioactivity has since attracted increased attention being aimed to further molecular manipulation (doping surfactants), particularly by micro-additives of various organic molecules such as proteins, glyco-proteins and polysaccharides (useful in easier mine-realization), and the intelligent response by host organism is evaluated in order to achieve well-tailored implants. Bio-glass-ceramics that activate genes offer the possibilities of repairing, or perhaps even preventing, many disease states, such as osteoporosis, in which a large fraction of women lose a substantial amount of bone mass as they age. They can be also used as a second phase in a composite that mimics the structure and properties of bone. In future the implication of glass activation of genes it may be possible to design therapeutic treatments or food additives that will inhibit the deterioration of connective tissues with age. Further understanding bioactivity may even help in better perception of the creation of life [88]. It shows a great variability in the application of different glasses (and the importance of amorphous materials in general) in many fields of human activities [36,42,80,83–85].

Most recent research shows that the integration of bio-materials implicates a series of cellular and extra cellular matrix events, some of which take place at the tissue-implant interface and reflect the host response to the bulk and surface characteristics of the implanted material. As a part of this process, the most frequently implanted material, such as etched titanium, glass-ceramics, calcium phosphates and cellular culture substrates, become coated with a layer of electron-dense material, which has been referred to as 'lamina limitans' or 'cement lines' customarily consisting of proteins (sialoproteins, osteocalcins, osteopontins, etc.) that naturally circulate in the blood stream (certainly, in very low concentrations only). It was found that there are several potential sources for such proteins, which have a tendency to accumulate at the reaction interface. It was also proposed that osteoclasts express and secrete some non-collagenous bone-matrix proteins onto the bone surface. The differential deposition of matrix constituents by osteoblasts at the beginning and end of the bone deposition cycle is now believed to be the major source of interfacial proteins at natural bone and bone-implant interfaces. It is in line of general understanding of life-based building of firm and well-structured inorganic constructions (various shells, cf. Chapter 16) where obviously both the morphology and the composition (structure) play a part of crucial and inseparable responsibility.

Earlier studies revealed the concept staying behind the incorporation of micro porous bioceramic materials. Namely, it is the intergrowth of tissue into pores in the surface layer or its integration throughout the implant. This is often termed as 'biological fixation', which is capable of withstanding more-complex stress states than implants that achieve only mechanical attachment, i.e., 'morphological fixation'. The limitation associated with porous implants is the size of the pores, optimally as large as 100–150 μm , which can only assure that the implant remains viable and healthy, remembering the importance

of fractality discussed in Chapter 13. The large interfacial area, required for such porosity, is due to the need to provide an uninhibited blood supply to the ingrown connective tissue. Therefore, the vascular tissue does not appear in pores that measure below 100 μm and without sufficient blood supply such tissue expires or inflammation ensues, which practically destroys interfacial stability and implant sufficient in-fixation. On the other hand, the fraction of larger porosity, required for successful bone growth in any materials, degrades the strength of the material applied. Consequently, it has fashioned a successful approach for solving the suitable interfacial stability, which is best achieved when the firm body material is used with well-sticking porous coatings, conveniently

liquid. The reaction layers enhance adsorption and desorption of growth factors, and influence the length of time for macrophages that are required to prepare the implant sites for the tissue repair. It was shown that a Ca- and P-rich layer is also formed on various surfaces that are deficient of these cations. This happens when the surface is exposed to solutions containing these actions (e.g., body or simulated body liquids). The behavior of some additives was also investigated showing, for example, that when F-ions are present they also get incorporated in hydroxyapatite crystals distorting, however, the crystal structure by formation of fluorapatite and the addition of multivalent ions delays bonding so that even their small amounts may reduce bioactivity⁵.

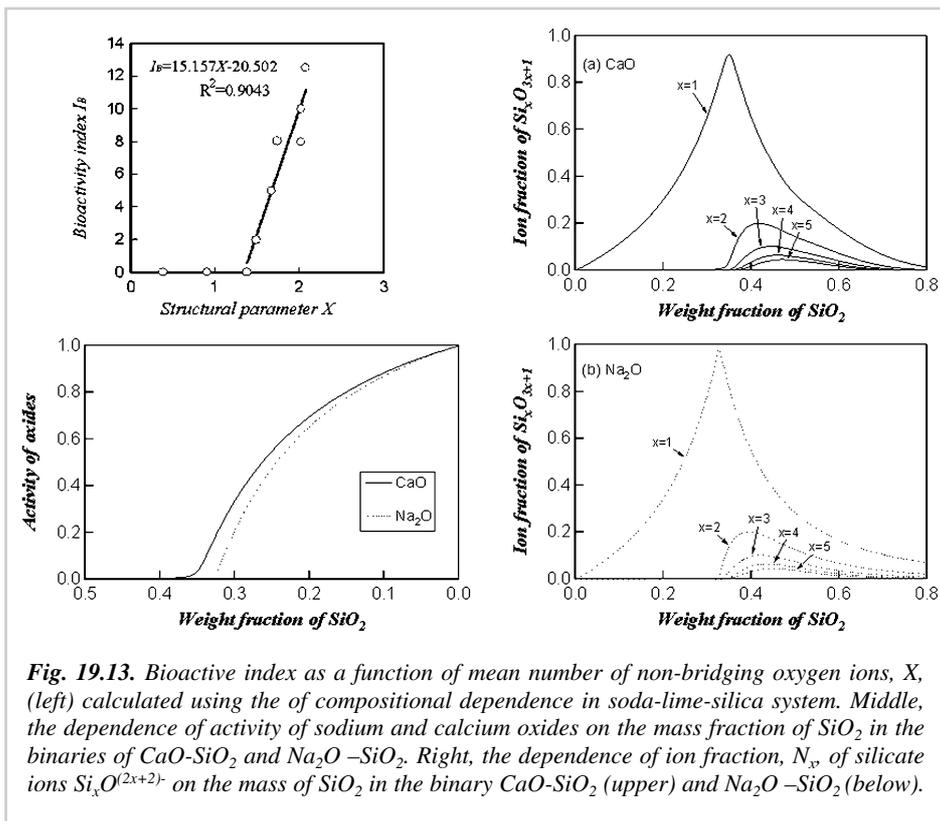


Fig. 19.13. Bioactive index as a function of mean number of non-bridging oxygen ions, X , (left) calculated using the of compositional dependence in soda-lime-silica system. Middle, the dependence of activity of sodium and calcium oxides on the mass fraction of SiO₂ in the binaries of CaO-SiO₂ and Na₂O-SiO₂. Right, the dependence of ion fraction, N_x , of silicate ions Si_xO_{(2x+2)⁻} on the mass of SiO₂ in the binary CaO-SiO₂ (upper) and Na₂O-SiO₂ (below).

on surgical metal alloys or as unloaded fillers for bone ingrowths.

Very important is good understanding of reactions that occur at the surface of glassy implants of silica-specialized composition. First, there is a rapid release of soluble ionic species and the formation of a high surface area of hydrated silica and polycrystalline hydroxy-carbonate apatite bi-layer. It was experimentally observed that the alkali-hydrogen ion exchange and the network dissolution rapidly reduce the amount of the Si-O-Si and Si-O-Ca modes and replace them with Si-OH bonds having so-called *non-bridging oxygen* [91-96]. Single non-bridging oxygen modes are then gradually replaced by more spherical OH-Si-OH. As early as within several minutes, a P-O bending vibration, associated with formation of an amorphous calcium phosphate layer, appears due to straightforward precipitation from the solution of body

The index of bioactivity, I_B , for an active implant depends on both the rate of calcium phosphate film formation and time of crystallization to hydroxyl-carbonate apatite and the selective absorption on the growing hydroxyapatite layer of extracellular proteins that control cellular attachment, differentiation and growth. The defect structure of the growing hydroxyapatite crystals is likely to be responsible for the preferential adsorption of the growth factors. Metastable hydrated silica species, such as penta-coordinated silicon ions, Si(OH)₅⁻, which is present during the silanol-condensation reaction, may be associated with the enhanced progress of crystallization on surfaces providing, in the same time, specific bonding sites for biological moieties.

The simplified concept of the glass structure of silicate glasses has been used for evaluation of the mean number of non-bridging (X) and bridging (Y) oxygens per polyhedron in the glass lattice. The correlation between these structural parameters, X and Y , and the bioactivity index has been tested for prediction of bioactivity in the soda-lime-silica glasses. The values of $\langle X, Y \rangle$ vary from $\langle 0, 4 \rangle$ (pure silica glass), to $\langle 1, 3 \rangle$ (pseudo-binary Na₂O.2SiO₂ glass) to $\langle 2, 2 \rangle$ (pseudo-ternary CaO.Na₂O.2SiO₂ glass). When $X > 2$ and $Y < 2$, the glasses are commonly called as 'invert glasses' [82]. When two glasses have the same value of $\langle Y, X \rangle$ they may be said to be „structurally similar“.

Empirical index of bioactivity, I_B , was introduced by Hench [80] as $I_B = 100/t_{0.5bb}$, where $t_{0.5bb}$ is the time for more than 50% of the implant interface to be bonded to bone. By reading the values of I_B at various typical points of glass composition from the so far reported iso- I_B plots

in Na₂O-CaO-SiO₂ ternary system, the structural parameters X and Y can be derived on basis of the molar composition, cf. Fig. 13. When X1,5 (Y2,5), the glass loses its bioactivity and bioactivity index comes close to I_B~0. The value of X1,5 (and Y2,5) indicates the actual range of bioactive glasses where I_B>0. Essentially linear dependence with negative intercept has been found between the mean number of non-bridging oxygen ions and bioactivity index. Our recent studies on Na₂O-CaO(MgO)-SiO₂-P₂O₅ systems evaluated its behavior by both assessments, in-vitro test of mutual bonding after soaking in simulated body liquids and in-vivo tests of implantation in dog tibia [85]. Both tests were well correlated with the parameter Y and revealed that the value of Y must be close to the value 2 to assure its suitable bioactivity but loosing it while exceeding the value of 3.

The compositional dependence of relative proportion of non-bridging oxygens [O¹⁻] in the soda-lime-silica system has been also calculated applying methods currently used in the chemistry of organic polymers. It was assumed that the silicate ions are present as linear and branched chains of general formula Si_xO_{3x+1}^{(2x+2)-}. The calculated relative proportion of [O¹⁻] in the Na₂O-CaO-SiO₂ glasses has been compared with their ability to form the surface calcium phosphate layer in the simulated body liquid, which indicates its bioactivity, see Fig. 13.

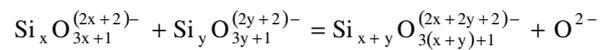
The concept of non-bridging oxygens has been applied for various cases and treated under different theories [90–96]. Earlier, we effectively evaluated the oxygen states in the iron-rich borate glasses [96] in reference to the model proposed by *Toop* and *Samis* [93]. For this case of bioactivity, however, we employed *Stevl's* parameters, X and Y, [86,92] expressing respectively the mean number of non-bridging (O¹⁻) and bridging (O⁰) oxygen ions per polyhedron in the glass lattice. We accredited it as a simple and useful way for the description of bio-glass compositions and their structures. These parameters can be readily calculated from the molar composition of glass

assuming that Y = 2Z – 2R and X = 2R – Z where Z is the mean number of all types of oxygen per polyhedron, i.e., the mean coordination number of the glass-forming cations, and R is the ratio of the total number of oxygens to the total number of glass-forming cations in glass.

The correlation between glass properties and structural parameters has been found for many glasses so that the bioactivity data of the soda-lime-silica glasses containing about 6 wt% P₂O₅ were compiled from literature and plotted as a function of calculated structural parameter X, as revealed in Fig. 13. Since this model considers only non-bridging and bridging oxygen ions, it cannot hold in any more general regime (X>>2) where the free oxygen ions reach an appreciable concentration. Therefore, we can propose the dominant reaction in the formation of silicate solution (glass): O⁰ + O²⁻ = 2O¹⁻ where O²⁻ refers to the free oxygen ions.

Consistently with *Masson* [91,94], we applied the following assumptions [86] to derive the anionic distribution in MO-SiO₂ glass forming melts:

the silicate ions are presented exclusively as linear and branched chains of general formula: Si_xO_{3x+1}^{(2x+2)-}. These species may arise by the poly-condensation reactions expressed generally according to the following equation:



- i) The equilibrium constant k_{xy} of above equation can be approximated using that for the lowest k -members k_{11} , i.e., $x = 1$ and $y = 1$.
- ii) The above equation may be written in a more general form, $2\text{O}^{1-} = \text{O}^0 + \text{O}^{2-}$, where O¹⁻, O⁰ and O²⁻ are the non-bridging oxygen, bridging oxygen and free oxygen ions, respectively.
- ja) According to the *Tyemkin's* equation [95], the activity of the MO oxide in the MO-SiO₂ binary melt a_{MO} is equated to the ion fraction of the ion fraction of free oxide ion $N_{\text{O}^{2-}}$, where $a_{\text{MO}} = N_{\text{O}^{2-}}$

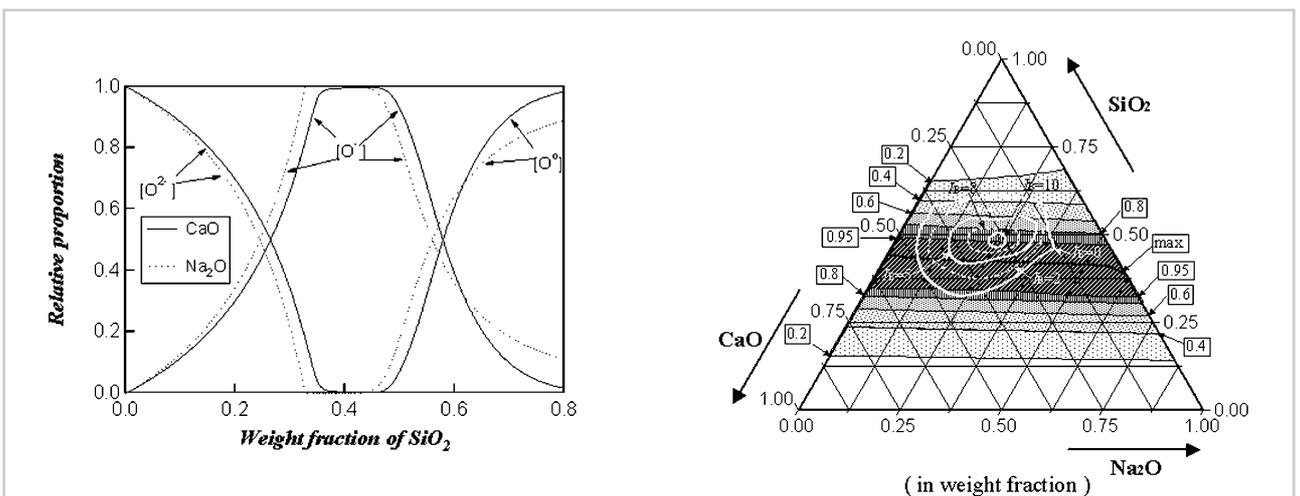


Fig. 19.14. Relative proportions of non-bridging, O¹⁻, bridging, O⁰, ad free, O²⁻, oxygen ions in the binary CaO-SiO₂ and Na₂O -SiO₂ systems (left). Right, a comparison of the relative proportion of non-bridging oxygen ions, O¹⁻, in the Na₂O-CaO-SiO₂ ternary system calculated in the present chapter with the I_B plots for the system with 6 mass % of P₂O₅

- jj) For linear and branched chains, the a_{MO} has the following relation with respect to the mole fraction of SiO_2 , i.e., $1/X_{SiO_2} - 2 + 1/(1 - a_{MO}) - 3/\{1 + a_{MO}(3/k_{11} - 1)\}$
- ij) Knowing the value of k_{11} for the binary system $MO-SiO_2$, the ion fraction N_x of any silicate ion is given by complex relationship [85] as a function of x and a_{MO} .

The ion fraction of non-bridging oxide N_O can be approximated by the summation of N_x using x up to 50, i.e., $\sum_{x=1}^{50} N_x$. The ion fraction of bridging oxide N_O^o is then obtained by $N_{Oo} = 1 - N_{O2} - N_{O1}$.

Taking the literature values for $k_{11} = 0.0016$ and $= 8 \times 10^{-8}$ for $CaO-SiO_2$ and Na_2O-SiO_2 binary melts, respectively, the X_{SiO_2} dependence of a_{MO} can be calculated. Fig. 14 shows the compositional dependence of a_{MO} at different weight fraction of SiO_2 . The ion fraction N_x is obtained according to $2O^{1-} = O^o + O^{2-}$. The calculated ion fractions N_x is represented in this diagram as a function of weight fraction of SiO_2 . According to the conventional pseudo-binary assumption, the compositional dependence of the relative proportion of O^{1-} in $Na_2O-CaO-SiO_2$ ternary melts were obtained using the values for the binary melts shown in Fig. 14.

The compositional dependence of the calculated relative proportion of O^{1-} in the $Na_2O-CaO-SiO_2$ ternary melts is shown in Fig. 13. For example, the maximum of the relative proportion of O^{1-} in the $aNa_2O-aCaO-(1-2a)SiO_2$ series was observed at the SiO_2 weight fraction of 0.43. The calculated relative proportion of O^{1-} in the $Na_2O-CaO-SiO_2$ glasses can be compared with their ability to form the surface calcium phosphate layer in the simulated body liquid. The region of the remarkable high bioactivity, $I_B > 8$ can be observed in the compositional region characterized by the higher relative proportion of non-bridging oxygen ions (< 0.8) in the side of SiO_2 -rich composition where an appreciable concentration of bridging oxygen ions can subsist, cf. Fig. 14. It is worth mentioning that the ability to form the bone-like apatite layer

after soaking even P_2O_5 -free $Na_2O-CaO-SiO_2$ glasses in the simulated body liquid was found similar to that containing 6% of P_2O_5 [97]. It approved the assumption that the bone-like apatite formation depends largely on the properties of basic $Na_2O-CaO-SiO_2$ ternary glasses, given by their structural property characterized by the activity of oxygen ions structurally involved, porous morphology and its audible bioactivity.

We may conclude that today's bio-glass-ceramics are used in a broad field of devices functional inside the human body. This is possible mainly due to their good biocompatibility and possibility to adjust their biocompatibility on basis of prefixed glass composition optimized upon the calculation of non-bridging oxygens in the glass lattice when taking up the assumingly polymeric character of the common matrix silicate glass. Among the ceramic materials used for bone replacement, bioactive glass-ceramics appears, therefore, particularly promising because of their ability to form the reactive but stable interfaces with living host tissue. However, the major problem of these materials, which inhibits their application on several types of implants, is their poor match of mechanical behavior of the implant with the tissue to be replaced. As mentioned above, their use for surface coating, for composite and porous-structured materials as well as new resorbable materials are promising ways for the next development, where thermochemistry, thermodynamics, thermal analysis and fractal morphology would clearly possess their incommutable assistance. No one has succeeded, however, in finding such a material, which would fully correspond to bone or other living parts of the body. Its development is the task of a growing number of researchers and institutions working in the field of both organic and inorganic bioactive composites to design a further improvement of material's structure and performance. We also should not forget that the nature is still a much better engineer than we are, so that we have to be patient facing our great task to learn how to make and imitate the appropriate synthesis.

¹ Intelligent Processing and Manufacturing of Materials (IPMM) is an informal international community of people interested in intelligent software and hardware applications and solutions to problems that exist in the creation and manufacturing of minerals, metals, ceramics, plastics and other materials and products. IPMM holds an international conference every two years: Golden Coast (Australia 1997), Honolulu (Hawaii 1999), Vancouver (Canada 2001) and Sendai (Japan 2003). The technical program covers such a wide range of topics that includes knowledge engineering, fuzzy logic and systems, artificial neural network, genetic algorithm, first-principle modeling, finite-element-analysis, material engineering, simulation and hybrid modeling, automation, robotics and holonics, vision systems, real-time monitoring as well as material design and property prediction, powder and surface technology, molding, forming, rolling, casting and rapid solidification, nanotechnology, biological and biomedical applications, environmental topics, microstructural and thermodynamic modeling and eco-economics. In this respect we should hark back the importance of such a more global manufacturing and economic approach. We could remind that socialism likely collapsed because it did not allow prices to tell the economic truth. Similarly we may even expect that capitalism may also collapse because it does not allow prices to tell the ecological truth

² Uniform surface of silica glasses has been effectively employed in various topic subjects. For example, it is an accustomed requisite in the domain of chromogenics, which covers any visibly switchable technology useful for glazing, mirrors, transparent displays such as electrically powered technologies of electrochromics, suspended particle devices known as electrophoretic media, phase dispersed liquid crystals and cholesteric liquid crystals. Related effect is known as thermochromism exhibiting the change of color with temperature useful in aerospace industry to change the emissivity of surfaces upon heating or as traditional temperature indicators. Increasing the troublesome fracture toughness of silica glasses can be achieved not only by traditional increase of the surface ten-

sion by incorporating the large cations (K, Ca) through the vapor cation exchange but also by artificial forming a composite surface layer with two-phase microstructure. It can be made either by reinforcement of a ductile crystalline phase (nanoparticles of ZrO_2 or other ceramic nanofibers) or by *in situ* precipitation of Zr-rich dendrites (such as the formation of ductile β -phase of ZrTi precipitating directly from the alloy Zr-Ti-Nb-Cu-Ni-Be glassy matrix). Relative accessibility of improved flow mobility along the glass surfaces can be conceivably used to achieve yet visionary strategy of unusual computer architectonics and self-design. Nanometer-sized processors are spread discretionary in the surface thin suspension layer and their network interconnection is allowed to diffusely self-adjust and mutually link according to the minute need of job processing and data evaluation. It would give first step towards the new generation of a self-installed computer hardware, which would be adaptable to the kind of applied tasks and activated environmental conditions. Besides, this solid, homogeneous, relatively inert, mechanically smooth and chemically impermeable support is indispensable to establish links to the organic biological molecules, which again is best completed by a sort of inorganic silicates that can thus assist to array biomolecular probes suited for necessary hybridization. A simple microscopic slide can provide exciting potential for rapidly mapping and sequencing the human genome, which has even led to promises of high-tech clinics with the ability to prescribe drugs based on the genetic make-up of the patient. It would need the creation of a library of chart knowledge (of sequenced genes) that would allow researchers to take an active, discovery-focused approach to understanding human physiology at the molecular level possibly replacing and/or providing synergies to the trial-and-error methods that are presently used for drug discovery in high-throughput laboratories. In particular, such an inquiry DNA microarray consists of a glassy silicate substrate with an organic coating – customarily an organo-functional alkoxylane. During silanization, which is typically achieved by dip coating or thermal chemical vapor deposition, the silanol group reacts covalently with silica glass surface via hydrolysis and condensation reactions. Once attached, the silane molecule can extend from the glass surface, which, thereupon, provides its necessary organic functionality. Such a coated glass is then grafted with various known DNA probes at predetermined locations and the DNA microarray is then thought of as a glass-based, biological sensor that can contain over 10^4 distinct, known probes at personalized locations. Such a glass-based biological sensor can provide researchers with the ability to characterize the human genomic state fully with a single, miniature experiment, possibly managerial in near future.

³ A major difficulty with the ceramic HTSC is that such complex metal oxides have high mechanical fragility, so that their ability to bend is severely limited. Although this has been overcome by surrounding its filaments with highly pliable metals (Ag), there is a ceiling on the amount of current that can be carried and on the level of magnetic field in which the system can be operated. Other efforts to bond cuprate superconductors to substrates has a target: melt and liquid coating methods, in the hope to cut the cost and ease production. Most progressive seems to be the growth of buffer layers directly onto a Ni-alloy where the intermediate NiO layer exhibits good compatibility with HTSC. Such a liquid phase epitaxy (LPE), with no need of high-vacuum components, is cheaper to build as compared with traditional chemical vapor deposition (CVD) and provides higher growth rates. Electrical engineers are looking forward to some of such processes that can help to reduce the capital and operating costs by using HTSC. For example, whereas conventional large copper-wire-based power transformers are cooled by oil and require location outside on hard standings, massive enough to support their weight, HTSC equivalents would use liquid nitrogen, which is a widely available commodity, cheap enough and intrinsically secure, making available much lighter units that could be safely installed indoors, near the point of power use. The process of entire HTSC applicability seems to replicate another similar case of above-mentioned metallic glasses, equally innovative and promising material of the seventies, that never get actually in practical use in transformers due to unanswered intricacy of their thermodynamic instability where thermochemical research equally contributed most influential function. Nevertheless, worth mentioning is the first important HTSC application as a security switch in high power electric circuits, where the massive rod of HTSC is coupled in-between and kept near the critical current state to avoid shortcut explosions that often happen when using classical fuses.

⁴ The uniqueness of such surface-activated materials is their high bioactivity, which opens qualitatively new application fields, especially for anchoring the implant in a host tissue, with practical use in orthopedics, stomatology, neurosurgery, oncology, craniofacial surgery and possibly other fields. We are proud to mention that we have taken part in the research progress of bioactive materials since early eighties. This matured in their actual appliance in practical implantology under the trademark IMPLADENT (particularly successful within oral implants [Z. Strnad, *Biomaterials*, 13 (1992) 317] produced commercially by 'LASAK'). Fig. 19.12 illustrates, for example, the actions of BAS-O implant, which is based on inorganic polycrystalline materials prepared by controlled crystallization of glass, whose main components are CaO, P_2O_5 , SiO_2 and MgO. During the crystallization process, the glassy material is converted to a glass-ceramic material whose main crystalline phases are apatite and wollastonite. BAS-O granules and ground material are used to fill cysts, defects left by injuries, defects left by excochleation of benign tumors, and can be of help to reconstruct extensive acetabular defects. Compact, wedge-shaped blocks (with various heights and surfaces) became useful for, e.g., condyle elevation. Individually shaped implants can be used in neurosurgery to cover defects left from cranial trepanation and as inlays in plastic surgery. Another case of biomaterial is abbreviated as BAS-HA (hydroxyapatite) which is synthesized from aqueous solutions under precisely defined pH, temperature and other physical parameters, which ensure reproducible preparation of a highly pure, crystallographically defined product, which does not contain any unwanted calcium phosphates. Its structure and composition are similar to bio-apatite, which is the main inorganic component of living bone tissue. Implants form a strong bond between the bone tissue and the implant material without any intermediate fibrous layer. Final product is the BAS-R, which is the surface bioactive, resorbable, inorganic, crystalline material based on tricalcium phosphate.

⁵ Equally important, however, are biomimetic processes called 'surface-induced mineralization', which uses self-assembled monolayers as a template for tailored nucleation. For example, this method is currently subjected to tungsten as a mechanically strong substrate material. In contrast to depositional methods of affixed coating the as-cast Ti-surface is first subjected to the acid etching (TiH-formation) and then to the NaOH treatment, followed by subsequent thermal annealing, which results in formation of a gel layer that is composed of an amorphous sodium titanate. When further exposed to the simulated body liquid, Na^+ ions are released from

the surface layer via ion exchange with H_3O^+ , which enhances the formation of Ti-OH groups ready to induce apatite nucleation. It helps that a large number of apatite nuclei are formed directly on the metal surface, which spontaneously grow into a dense uniform surface. We should append that there are many different approaches for producing the specially layered or CaP-coated implant devices, each of which has its own intrinsic materials and properties. The effect of variation of these properties on the clinical performance of each device is not yet known, but it induces creative access to novel therapeutic coatings. Entire surface treatments have a dual beneficial effect: better strength of devices and improved osteoconductive properties combined with the ability to deliver therapeutic agents, proteins, and other growth factors directly into the coating. Novel materials may thus offer the magnified capability to stimulate bone growth, combat infection, and, ultimately increase implant lifetime.

Adjustment of chemical composition and associated morphology requirements together with the application of suitable tailoring to achieve matching structure of appropriate fractality of contact interfaces, is still only half a way to the so called "tissue engineering" though the micro-additives of various organic molecules enable easier mineralization (such as proteins, glycoproteins and polysaccharides). The procedures described above are still following the natural way of our organism self-reparation, such as a bone fracture and injured skin undergo repair but, even when this does occur, this usually involves nonspecific reparative tissue rather than the regeneration of the specific functional tissue that has been affected. The new philosophy of tissue engineering would involve the use of technologies of molecular and cell biology, combined with those of advanced materials science and processing, in order to produce tissue regeneration in situations where evolution has determined that adult humans no longer have innate powers of regeneration. Tissue engineering will certainly become an interdisciplinary and multidisciplinary field that would show a great promise in generating living alternatives for harvested tissues and organs for the advanced transplantation and reconstructive surgery. Tissue engineering is based on the creation of new tissues *in vitro* followed by surgical placement in the body or the stimulation of normal repair *in situ* using bioartificial constructs or implants of living cells introduced in or near the area of damage. In addition to the physiological, medical, and genetic diagnosis of the patient, it would require that the doctor needs to collect three-dimensional image of the patient's remaining tooth or leg (in the case of seriously damage or lost) with detailed anatomical structure (bone, cartilage, tendons, ligaments, blood, vessels, muscles, nerves, skin, and so forth) and the external shape. The doctor may also collect the patient's saliva or other body fluids to extract genetic material (DNA) and also a tiny piece of tissue or bone marrow to obtained seeding cells for expansion. It is already seen in the light of "cell sheet engineering" avoiding the limitation of tissue reconstruction using biodegradable scaffolds or single cell suspension injection. Such a concept, however, does not aim to use mere single cell but cell sheets, which are prepared using the temperature-responsive culture dishes. Suitable polymers are covalently grafted onto the dishes, allowing various types of cells to adhere and proliferate at about 37 °C. The cells spontaneously detach when the temperature is reduced below 32 °C without the need for proteolytic enzymes. The confluent cells are noninvasively harvested as contiguous cell sheets with intact cell-cell junctions and deposited extracellular matrix. The target point is the use of biodegradable polymer scaffolds, performed on the target tissue shape, for cell ceding, as already demonstrated in 1980s on reconstructing the cartilage tissues for the growth of human ears on mice.



CHAPTER TWENTY

20. Advanced trends in understanding our Universe

a) Bartoli's thermal engine and zero-point radiation

In the year 1874, the Italian experimental physicists *Bartoli* [98] put forward an idea of bringing electrodynamics and thermodynamics into the treatment of heat radiation, which is often thought to become a major source of inspiration for the later concept of *Stefan-Boltzmann* Law of blackbody radiation [99]. Light pressure, however, was not a new subject and played important role with respect to the competing theories of light: the corpuscular emission was taken to imply the existence of light pressure whereas the wave theory was usually regarded as incompatible with such a pressure. In 1870, *Crookes* constructed his 'light mill' (radiometer) and interpreted its motion by result of mechanical energy of radiant heat. In 1873, *Maxwell* noticed in his new electromagnetic theory that "in a medium in which waves are propagated there is a pressure in the direction normal to the waves ... and that falling rays might perhaps produce an observable mechanical effect on delicately suspended things in vacuum...and he calculated that for the maximum sunlight to be about $8.82 \cdot 10^{-8} \text{ lb per square foot}$ "¹.

Examination of light balances rather than light mills was actually due to the need to distinguish between the direct action of radiation and the indirect action caused by convection currents in the residual molecules in vacuum, resulting from heating. *Bartoli* adopted the *Clausius* version of the second law of thermodynamics restricting heat transfer from a colder to a warmer body without a compensating amount of mechanical work being performed². Such a qualitative thought experiment seems merely to have served as a heuristic guide for *Bartoli* to consider the existence of light pressure. Later he approved this highly artificial construction by a more realistic variant in which the spherical shells were replaced with a classical cylinder (with permeable and reflecting walls) operculated with crest and tail lids (fixed as blackbody) and operating with two moving pistons as heat reflectors [99]. The net result is again a transfer of heat between the cylinder's closures assuming the amount of heat, q , to be proportional to $K r S / v$ where S is the surface of lids with the emissive power K , piston diameter r and radiant heat velocity, v ($\equiv c$). Consequently, *Bartoli* derived the relation for radiation pressure, $p = 2 Q E / v$, where Q is the power received by the unit area and E is the mechanical equivalent of heat, enabling him to calculate the solar pressure to have the value $8.4 \cdot 10^{-4} \text{ g/m}^2$ (which, however, was about 2000 times less than required to power a radiometer). Few years later, *Bartoli* gave up his original idea deciding that there is no light pressure after all.

The absolute validity of the second law of thermodynamics was for long a hot topic for discussion and particularly *Maxwell*, *Boltzmann* or *Loschmidt* concentrated on the principle necessary for a mechanical explanation, in general, not referring to particular processes such as

radiant heat, which might violate the law. In 1882, the US astronomer *Eddy* argued in a thought experiment of a system of apertures distributed equidistantly around three concentric cylinders ('siren') that radiant heat (having presumably a finite velocity) could apparently be an exception. He evidently viewed his result as providing the support for the *Maxwell-Boltzmann* hypothesis, which in *Eddy's* interpretation stated that 'the second law was merely the mean result emerging from the laws of probability' and which was an escape from the pessimistic prediction of the prognoses of heat death of the Universe.

Boltzmann raised later critique against the details of *Bartoli's* process arguing by necessity to have to modify it to become reversible and adopted the assumption of radiation pressure as well as the validity of the second law of thermodynamics (implicitly rejecting *Eddy's* claim). He conveyed the relation $p(T) = (\pi/c) T \int \phi(T) dT / T^2$, where ϕ is the energy flux and T is the absolute temperature, and confirmed experimentally *Stefan's* Law of radiation energy in the form $p(T) = (\pi/3c) \phi(T)$ and $\phi(T) \approx T^4$ [90]. It literally followed *Maxwell's* old result written as $p(T) = (1/3) \psi(T)$, where ψ is the energy density. In 1893, *Wien* derived his displacement law by extending *Boltzmann's* reasoning to cover the separate wavelengths of the blackbody radiation (scaling) so that $u_\omega = \omega^3 f(T/\omega)$, where f is a universal function and ω is the frequency. Both these relations were temperature dependent so that at the absolute zero they would vanish, which would bring somehow 'disastrous' consequences on the stability of atoms factually leading to body's collapse³ [101].

This has brought into serious consideration the concept of zero-point (ZP) energy of electromagnetic field background, which was originally introduced into physics for the sake of consistency of experimentally observed spectral composition of the blackbody radiation with the assumption of discontinuous light emission [102]. In modern quantum electrodynamics, the zero-point energy arises rather from the non-commutativity of operators corresponding to the wave amplitudes of electromagnetic field [103]. The spectral distribution of the blackbody radiation, which conforms to this requirement, is represented by a complete *Planck's* formula:

$$u_{\omega T} = (\omega^2/\pi^2 c^3) \{ \hbar \omega / [\exp(\hbar \omega / kT) - 1] + \hbar \omega / 2 \} \quad 1$$

This formula consists of two additive terms, the first describing the purely thermal (i.e. conventionally temperature dependent) part of the blackbody radiation. The other one corresponds to the radiation surviving even at absolute zero temperature, down to the so-called zero-point radiation. Using homogeneity arguments, there is only one possible form of the spectral energy density, u_ω , which is *Lorentz* invariant; it reads⁴:

$$u_\omega = (\hbar \omega^3 / 2\pi^2 c^3) . \quad 2$$

This relation, which describes isotropic zero-point radiation, has two significant properties: namely, it is

Lorentz invariant and, in contrast to the temperature dependent term in the previous equation, its integral taken over all admissible frequencies is divergent.

Serious disadvantage of this formula is obviously due to its divergence with respect of the integration over the infinite frequency range. In order to obtain a physically more meaningful figure a rather laborious work with infinities and/or the introduction rather arbitrary cut-off frequency is required. Moreover, any macroscopic model of partitions involved in thermodynamic thought experiments with electromagnetic radiation should not a priori ignore their microscopic atomic structure without serious danger of introducing a bath by ZP radiation⁵. Physically, the ZP radiation can be interpreted as a random, highly pervasive background field existing due to the incoherent vibrations of distant charges dispersed somewhere in and over the Universe. It is exclusively responsible for the quantum behavior of minute particles (often called ‘*Zitterbewegung*’). Hence, the zero-point radiation (ZPR) ensures the stability of ordinary matter by precluding the devastating effect of the Coulomb interaction.

b) Energy in vacuum and Casimir forces

The force between uncharged conducting surfaces, the so-called ‘*Casimir force*’ was described as one of the least intuitive consequences of quantum electrody-

determined by r , to frequency, while the *Planck* constant, \hbar , converts the frequency to energy. The *Casimir* effect results, thus, from changes in the ground-state fluctuations of a quantified field that occurs because of boundary conditions. It occurs for all quantum fields and can arise from the choice of topology, too.

Thus, it was considered for various shapes of cavities (hollow space surfaces) where the vacuum stress outside the cavity exerts a force that tends to pull the sphere apart. Apparently, there are a greater number of modes on the cavity surface that in the free space; hence, as the diameter increases, the rate at which new modes appear on the surface is greater than the rate at which free-space modes disappear. This force is applied to a number of long-range interactions, such as those between an atom and a material surface or between bulk material bodies⁶. One of the most important manifestations is the interaction between atoms and molecules called *van der Waals* bonds. This is the force of attraction between dielectric bodies, which, in the case of tenuous media, can be interpreted as arising from the retarded ($1/r^7$) and *van der Waals* short-range ($1/r^6$) potentials, which occurs between the molecules that make up the bodies. When two bodies are sufficiently dense, it is no longer valid to consider molecule-molecule interactions alone, and one must take into account the boundary conditions for the electromag-

netic field at the material surface. *Lifshitz* (1956) [110] made the calculation on the basis of charge and current fluctuations in a material body so that the *Casimir* and *Lifshitz* approaches represented different realization of the same phenomenon although showing some common points; perhaps, the fluctuating field could be associated with the zero-point motion of electrons within the body.

Above all, the *Casimir* effect is of considerable theoretical interest and may find wide applications in quantum chromodynamics, quantum electrodynamics and/or strong-field gravitational effects. We can recall its basis arising from the

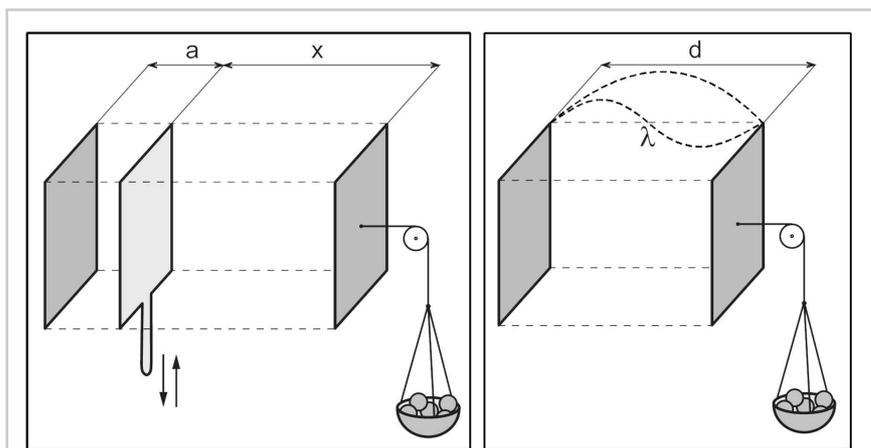


Fig. 20.1. Alternative models for two optional approaches for the estimation of *Casimir* forces between the conducting plates.

states of a one-dimensional harmonic oscillator, which can be raised or lowered in units n of $\hbar\omega$ where \hbar is the *Planck* constant (in J s, i.e., h divided by 2π) and ω is the angular frequency. The excited states have energy $E_n \rightarrow (n + 1/2) \hbar\omega$, a relation which is known to lead to acceptable results in quantum-mechanical calculations for $n \geq 0$. However, if the kinetic energy of the system (or alternatively the temperature) goes to zero, there remains a zero-point energy of $\hbar\omega/2$, responsible for matter not to cave-in. This, summed over frequencies, represents a zero-point field with a large energy density.

The quantum and classical domains of modern physics are, however, not architectonically compatible as the

electromagnetic zero-point field (EZPF) does not appear to produce the expected classical gravitational effects. We may expect that the frequency ω_c correspond to the size of the particle and its inability to respond to oscillations of the zero-point field with wavelengths of arbitrary smallness. Provided that ω_c is large enough (or wavelength small enough), the *Lorentz* invariance of EZPF spectrum will not be measurably affected and can be related to the *Planck* limiting frequency $\omega_p = (c^5/\hbar g)$ [s⁻¹], where c and g are the speed of light and gravitational constant, respectively. It may draw in a relation describing the density, ρ_v , and pressure, p_v , of vacuum by means of a kind of force per unit mass, Λ (often regarded as the cosmologic constant) i.e., $\rho_v = \Lambda c^2 / (8 \pi g) = -p_v/c^2$, which is a property of a fluid behaving in all physical respects as a zero-point field.

Casimir made even an unsuccessful attempt to derive the fine-structure constant by constructing an electron model based on the assumption that an electron is a sphere of uniform charge density, with total charge equal to electron charge, e , whose radius is determined by the balance between the attractive *Casimir* force (holding the electron together) and the Coulomb repulsion (tending the electron to expand). The effect of moving boundaries received attention in view of an observer in a uniformly accelerating frame who would conclude that the frame (with the acceleration a), was in a thermal bath of temperature $T = \hbar a / (2\pi c k)$, where k is the standard *Boltzmann* constant. In fact, the acceleration promotes zero-point fluctuations to thermal fluctuations. Similarly, if the plates of the *Casimir* experiment are accelerated away from each other, photons can be generated in the gap [111].

There is a kind of dichotomy arguing either that the EZPF does not gravitate or it does but it is cancelled by another field of a negative energy density. The *Casimir* effect is commonly derived on the basis of wave-mechanical arguments, wherein two parallel plates exclude modes with wavelengths larger than the plate separation,

producing a decrease in energy between the plates compared to their external environment, or equivalently a force of attraction between the plates. This reasoning is actually generic, applying not only to electromagnetism but also to other wave phenomena such as gravity, inertia⁷. It was attempted to measure it experimentally, but due to the difficulty of the perfect alignment of plane plates, or a plane and a sphere, the predicted biquadratic dependence of the *Casimir* force was found to an accuracy of about 5%.

The physics of the EZPF is based on known laws and is mathematically fairly straightforward, so that a practical application should be deliverable in a relatively short future. If the EZPF is real, in principle it does provide a new source of energy that has potential applications to technology, and particularly spacecraft propulsion. One cannot but agree with other opinion that conventional spacecrafts limited to velocities $v \ll c$ are impractical for exploring outer space beyond our solar system. If the EZPF exists, then it presents an untapped source of energy; and in conjunction with modern quantum field theory wherein virtual particles can come into and go out of existence below the limits set by *Heisenberg's* uncertainty principle, the opportunity exists in principle for new forms of travel.

c) Hypothetical Bartoli's engine working with zero-point electromagnetic radiation

The analysis of functional properties of a heat engine driven under variably curious circumstances is an old assignment of various scientists and inventors. Conveniently, a pair of systems at different temperatures is a classic environment for a heat engine, which produces available work during the relaxation to a common equilibrium. It is generally believed that a direct interaction between the two systems will always decrease the amount of obtainable work due to the inevitable energy dissipation. Changing the initial and final states, a direct coupling introduces a change in both work and dissipa-

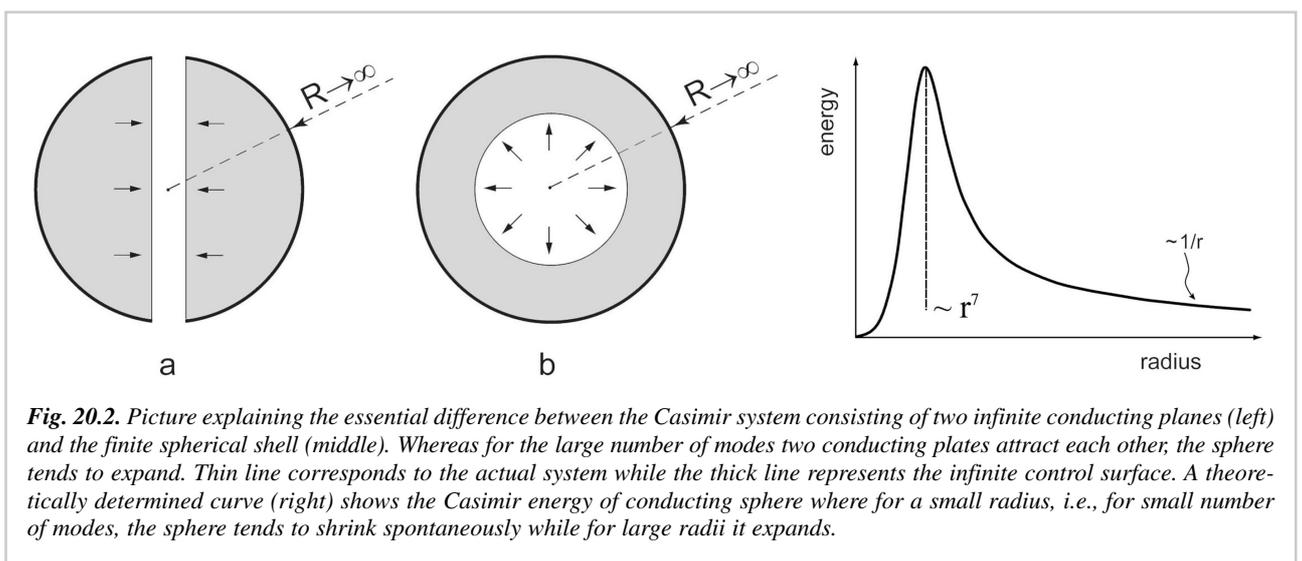


Fig. 20.2. Picture explaining the essential difference between the *Casimir* system consisting of two infinite conducting planes (left) and the finite spherical shell (middle). Whereas for the large number of modes two conducting plates attract each other, the sphere tends to expand. Thin line corresponds to the actual system while the thick line represents the infinite control surface. A theoretically determined curve (right) shows the *Casimir* energy of conducting sphere where for a small radius, i.e., for small number of modes, the sphere tends to shrink spontaneously while for large radii it expands.

tion. In some time window, however, work can be gained due to the direct coupling (which thus factually enhances the work) while dissipation become relevant only for much longer times. The amount of extracted work may increase at the cost of a change of the final state of bath [112]. If interactions and fluctuation exist among various subsystems of isolated localizations where self-organization may occur, the entropy may not hold as additive quantity as shown for plasma or non-linear interactions [113].

This became important, for example, in studying the local thermodynamic efficiency [114] of Brownian-motion based motors and related models. Brownian heat engine uses local temperature gradients in asymmetric, periodic potentials to move particles against external forces using quantum wave properties of particles. The efficiency is limited by irreversible heat flow carried by particles that make contact with different heat baths. Practically, it can be achieved by a suitably chosen width and position of an energy filter tuned along the Fermi occupation functions so that electrons are transferred elastically through the energy filter between two otherwise thermally isolated, identical, 2-dimensional electron reservoirs (e.g. tunneling via quantum dots) [115]. With the advent of improved methods of making nano-structures, such as micro-fabrication technology, it has turned out to be also possible to explore forces arising from quantum fluctuations in greater detail. For example, the cantilever became available, which is a silicon micro-machined device (often known as MEMS: micro-electro-mechanical system) [116] or a harmonic oscillator with a *Casimir* interaction has been modeled but not yet built [117]. Another case of an unusual heat engine⁸ is the possibility to cyclically process a particle of type-I superconductor in H-T space so that all heat extracted from the high temperature heat reservoir can be converted to work [118].

Heat engine powered by electromagnetic radiation is another auspicious candidate for the future energy exploitation particularly when we look at the somehow ‘peculiar’ relation between quantum mechanics and laws of thermodynamics. Historically, there are several varieties of heat engines designed to carry out reversible cycles with the electromagnetic radiation as a working medium, but not all of them are usable in a rather delicate case where the zero-point radiation (ZPR) becomes truly involved. *Mareš et al.* [119] proposed a modification of the original *Bartoli’s* heat engine discussed above. In their adaptation, a lot of details of the original design were omitted, taking advantage especially of its spherical symmetry and of the concept of fully reflecting shell. They started with the analysis of the kernel component of this particular modification of *Bartoli’s* engine – the fully reflecting spherical shell bathed in ZPR. This highly idealized device is supposed to be made of a very thin sheet of perfectly conducting material of negligible specific heat that can be deformed without any effort. It represents rather a mathematical continuous boundary absolutely

reflecting the electromagnetic radiation regardless of its frequency and providing thus an adiabatic insulation of the cavity. At the zero temperature such a spherical shell of radius r contains a certain portion of ZPR, which is compatible with its boundary conditions and which inevitably remains enclosed within. Owing to the perfect reflectivity of the cavity walls, the enclosed radiation can neither be absorbed nor escape. In other words it is trapped there “for ever”, i.e., kept inside the cavity with no possibility to communicate with the external world. Assuming that the radius, r , is macroscopically large enough, the electromagnetic spectrum excited by the ZPR within and outside the sphere has to resemble its normal mode spectrum. It is represented just by the solutions of *Maxwell’s* equations for which the tangential component of electric and normal component of magnetic vector at

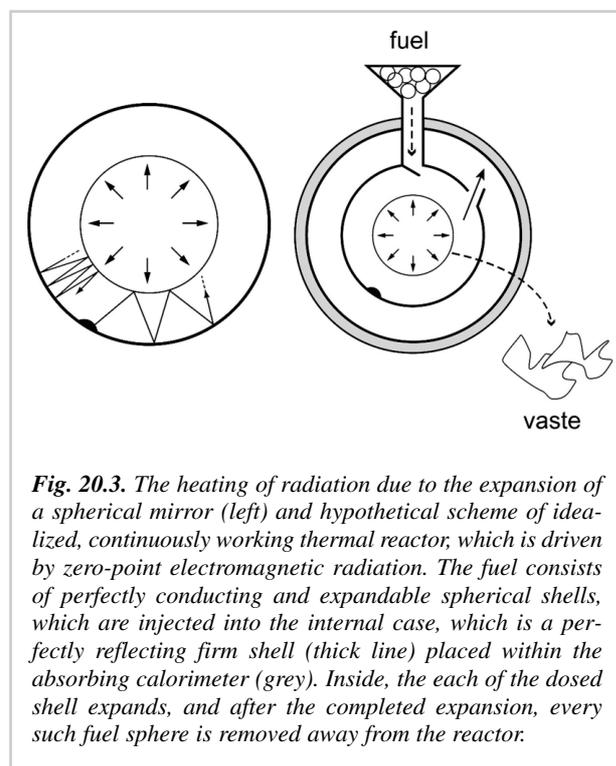


Fig. 20.3. The heating of radiation due to the expansion of a spherical mirror (left) and hypothetical scheme of idealized, continuously working thermal reactor, which is driven by zero-point electromagnetic radiation. The fuel consists of perfectly conducting and expandable spherical shells, which are injected into the internal case, which is a perfectly reflecting firm shell (thick line) placed within the absorbing calorimeter (grey). Inside, the each of the dosed shell expands, and after the completed expansion, every such fuel sphere is removed away from the reactor.

the wall vanish and for a conducting sphere it is given by a superposition of orthogonal spherical harmonics (i.e., the lowest eigenfrequency $\omega_0 = 2.74 c/r$). In the high-frequency limit the normal mode spectral density of the sphere practically merges with the spectral density of ZPR and the difference of the spectral composition inside and outside the shell brings about *Casimir’s* ‘ponderomotive’ effect. Intuitively, the absence of the ZPR spectrum below ω_0 should result into the shrinkage of the shell in close analogy with the popular interpretation of the above-discussed case of attractive force between two conducting parallel planes [120].

The situation, however, is far from trivial and thus the detailed enumeration of modes is necessary. For this procedure, the spherical shell has, in comparison with the arrangement of two parallel planes, some important

advantages; namely that the boundary condition on the shell is single-valued so that there are no extended traveling modes and only standing normal modes are present there. Moreover, the absence of edge effects and the geometrical finiteness of the system further simplify the problem. Another remarkable fact should be mentioned here, namely, that the solutions of *Maxwell* equations with macroscopic boundary conditions remain invariant with respect to conformal mappings in the 4-D space (alternatively called also “spherical wave transformations”). Because any real-space spherical wave transformation can be built up from spherical inversions it can easily be proved (by taking the conducting shell as a sphere of inversion) that there is one-to-one correspondence between normal modes inside and outside the

shut again in order to heat a slightly the soot and the radiation in the annular space between the reflecting shells up to the temperature $T_0 \leq T_C$. Because of *Doppler's* wavelength shift on moving reflector, the following spontaneous expansion of the inner deformable shell will heat the thermal radiation in the annular space up to the temperature T_M . Comparing the equilibrium thermal pressure in the calorimeter with *Casimir's* pressure, it is obvious that by a proper choice of the initial temperature and dimensions of the engine, the condition $T_M > T_C$ can be achieved. It occurs just if the following inequality is fulfilled, $T_C r_M < 0.266 c/k_B$, where r_M is the maximum radius of the inner shell and k_B the *Boltzmann* constant. Opening the window will then transfer a certain amount of heat to the calorimeter, slightly increasing its temperature.

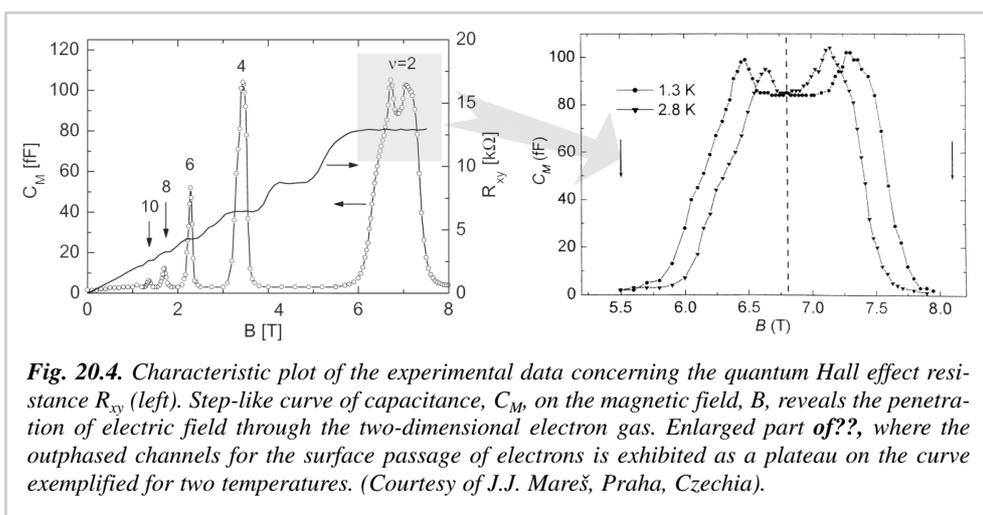


Fig. 20.4. Characteristic plot of the experimental data concerning the quantum Hall effect resistance R_{xy} (left). Step-like curve of capacitance, C_M , on the magnetic field, B , reveals the penetration of electric field through the two-dimensional electron gas. Enlarged part of??, where the outphased channels for the surface passage of electrons is exhibited as a plateau on the curve exemplified for two temperatures. (Courtesy of J.J. Mareš, Praha, Czechia).

shell. In other words, the numbers of normal terminating modes follows the relation for energetic excess⁹, $E = 15 \hbar c / [(2\pi)^3 2 \ln 2] (1/r)$. Its physical content subsists from the conducting sphere bathed in the electromagnetic zero-point radiation, which has a tendency to expand. It means that conducting spherical shell placed solely in physical vacuum performs a macroscopic quantum system of well defined geometrical extent revealing the tendency to expand spontaneously at the expense of practically inexhaustible non-localized energy of ZPR.

The above-mentioned team-work initiated by *Mareš* [116] described modification of *Bartoli's* engine, as shown in Fig. 3, which consists of firm fully reflecting spherical shell. The arrangement is completed by a small, absolutely black particle (“soot”), which is inserted into a large spherical black-body adiabatic calorimeter on its inside wall. The inner space of this firm shell can be temporarily connected with the calorimeter through a window in its wall. Then a smaller reflecting and deformable sphere (the properties of which were described above) is placed at the center of the firm shell. It is assumed that the whole system is perfectly evacuated, initial temperature of the calorimeter is T_C and the rest of the engine is at absolute zero temperature. Let the window in the wall of the firm sphere be now opened for a while and

Letting aside the indisputable possibility of extraction of work and/or heat from the vacuum, the process just described may be treated in several ways. First, if we assume the inner shell is a finite system with an intrinsic quantum property to expand, the process will be “spontaneous”. We have to do with the case where “the heat passes spontaneously from a colder body to the hotter one”, which is in clear contradiction

with the second law of thermodynamics in the original *Clausius's* wording. Such a straightforward argument is rather naive (however, not too rare in the literature) and does not stand the confrontation even with a more advanced *Clausius's* formulation of the second law of thermodynamics claiming: “a passage of heat from a colder to a hotter body cannot take place without compensation”. The “compensation” here means a change within the system, which eventually has in consequence the “natural” heat transport from a higher to a lower temperature. At first glance, it is very tempting to judge that the “compensation” is realized here by the expansion of the inner shell followed by the heat flow from the hotter soot to the colder calorimeter. However, the inner shell itself is considered to behave like a usual mechanical conservative thermodynamically closed system, which was provided at the moment of its creation with some initial potential energy and then became a part of the system. In this case, one can conclude that there is nothing strange and that no violation of the second law takes place.

However, an important question persists there, namely, whether the effects of purely quantum origin, such as *Casimir's* forces, are in this way taken into account correctly. In our opinion, it cannot be the case, because, as mentioned above, every manifestation of the ZPR implies

quantum behavior of the responding structure, which is sensitively depending on the local geometry of the structure under investigation and is inevitably accompanied by the processes in the whole Universe as well. In other words, any system able to see the ZPR is quantum ‘*per se*’ and opens (in spite of its finiteness) in the sense of thermodynamics. In this situation, it is impossible to interpret the “compensation” locally, in the frame of a closed system, and it must be shown further on – due to its quantum nature (‘entanglement’, see later) – that the system is extended throughout the whole Universe and is thus ultimately open. In such a case, it is evident that the local application of the second law of thermodynamics is non-eligible and its as-supposed violation may be only fictive.

d) Quantum impact on the study of low dimensional systems

It should be stressed out that the experimental quantum physics [121,122] is essentially the low temperature physics (< 4 K) because for the separate observation of quantum effects it is necessary to effectively suppress thermal background characterized by the thermal energy ($k_B T$).

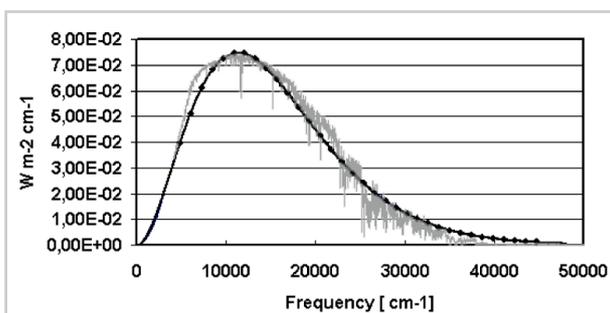


Fig. 20.5. Spectral flux at one astronomical unit (1 AU) compared with the ideal black body radiation at $T = 6780$ K.

This field gets factually out of the reach of thermal science in its traditional sense, which is, indeed, worth of emphasis. In the center of interest are here quantum formations of low dimensions (2-D wells or 1-D dots), whose characteristic size (<nanometers) is comparable with the dimension of an electron wave packet and whose outgrowth is the exclusive behavior of the electronic subsystem in terms of quantum mechanics. In the quantum wells, shaped by the so-called ‘ δ -layers’ (ultra thin layers doped on atomic scale), the anomalous negative magnetoresistance was observed, as caused by quantum interference of partial electron waves, as well as the unusual thermal dependence of electric conductance as a possible result of the zero electromagnetic fluctuations in vacuum.

Soon after the discovery of the quantum *Hall* effect¹⁰, attempts to evaluate the electron density of states by measuring magnetocapacitance between the two-dimensional electron gas and the metallic gate in the ordinary *Hall* bar structures have appeared [123]. The observed oscillation, the minima of which were positioned just at the quantum

Hall plateaus, were interpreted using the universal relationship between the thermodynamic electron density states, $D_T = (dn/dE_F)$, and the quantum capacitance K_Q of unit area, i.e., $K_Q = e^2 D_T$, where e is the electron charge, n the carrier sheet concentration in the two-dimensional channel and E_F is the *Fermi* energy. This model, however, is not quite generally recognized for the explanation of the oscillations observed because the longitudinal conductivity vanishes at the quantum *Hall* plateaus where E_F coincides with the localized states.

Mareš et al [124] introduced an essentially improved penetration technique free of previously disturbing imperfections and capable of more absolute measurements of density extended states in two-dimensional structures and distinguishing between bulk and edge states. Such a typical result of quantum effect measurement, see Fig. 4, can be observed exclusively at low temperatures only where two dimensional electron gas is confined to two dimensions only by the walls of the quantum well usually realized by flat boundaries between different semiconductors, e.g., heterojunction between GaAs and GaAlAs with various stoichiometry. The quantum *Hall* effect is observed in the two-dimensional electron gas, where the electric current, I , is flowing along the quantum well via two-dimensional electron gas and where the perpendicular magnetic field is simultaneously applied. It leads to the appearance, on the edges of the sample, of a measurable voltage (*Hall* voltage, V_H) which is a consequence of the *Lorentz* force. However, the dependence of *Hall* voltage on the magnetic field is in this case not simple, but has the above mentioned characteristic steps (quantum *Hall* plateaus) corresponding to the crossing of the discrete quantum of the magnetically induced energy levels (called *Landau* levels) by *Fermi* level of the system. The transversal resistance, R_{xy} is than equal to V_H/I . The remarkable feature of quantum *Hall* effect is the values of R_{xy} , which corresponds to the plateaus of the experimental curves. According to our present knowledge it is exactly given by the integer multiples of the universal constants, h/e^2 , showing again the prominence of the basic quantities of our Universe.

It should be noticed that this result is not a consequence of the special structure of the electronic density of states of quantum well, but it is rather due to its *topology*. This fact can be illustrated by the comparison with the magnetocapacitance measurements, which can directly provide us with density of states of such systems. Namely, the capacitance measured through the grounded two-dimensional gap, C_M , is practically inversely proportional to the density of states. At the magnetic field, corresponding to the quantum *Hall* effect plateaus, this quantity reveals evidently interesting fine structure, whose composition is in the course of further interpretation similar to the understanding of transitions in superconducting (vortex formation) or superfluid states (quantum swirls in He). It can be linked to the degree of separation from the *Fermi* level, so that the fine structure can possess two distinct states [125], characterized either by the ubiqui-

tous flow of superficial electrons or by their self-organized single multi-conducting line, which joins every point in the patch as a one-dimensional quantum-wire patchcord (similar to the *Peano-Hilbert* 1-D infinite curve which live in the 2-D plane, cf. Chapter 13).

e) Quantum information processing

Besides the energy enquiries pointing down towards the yet fully unexploited world of quantum mechanics there is another associated neighborhood of the emerging field of quantum information processing and technology (QIPT) [126,127]. Following extrapolation of the exponentially decaying number of electrons per an elementary

Most information manipulation is done digitally, so data is processed in the form of bits. The two states of a conventional data bit take many forms such as magnetic orientation, voltage, light pulses etc. At any time, a bit is always in one state: written in suggestive quantum notation, it shows $|0\rangle$ and $|1\rangle$, hence the name, although bits get flipped as data is processed or memory rewritten. However, the quantum analogue of a conventional bit, so-called ‘qubit’, has a rather more freedom. It can “sit” somewhere in a two-dimensional Hilbert space. We can picture it as the surface of a sphere with a general form $|\psi\rangle = \cos\alpha |0\rangle + \exp i\phi \sin\alpha |1\rangle$ parameterized by two angles. Factually, the conventional bit has only the choice of the two poles while a qubit can live any-

where on the surface of the sphere. States such as (1) are superposition states, they have amplitudes for and thus carry information about the states $|0\rangle$ and $|1\rangle$ at the same time. Similarly, the register (collector) of N qubits can have exponentially many (2^N) amplitudes, whereas the analogous conventional data register can hold one of these states at any given time. Clearly, if it is possible to operate, or compute, simultaneously with all the amplitudes of a quantum register, there is the possibility of massively parallel computation based on quantum superposition.

Our standard practice shows that we can read ordinary information (book) without noticeably changing it, which is not so simply for quantum information. If a qubit in the state (1) is measured to determine its bit value, it will always give the answer 0 or 1. This is a truly random and irreversible process with respective probabilities of $\cos^2\alpha$ and $\sin^2\alpha$, and afterwards the qubit is left in the corresponding bit state $|0\rangle$ or $|1\rangle$. It thus would be impossible to read, copy

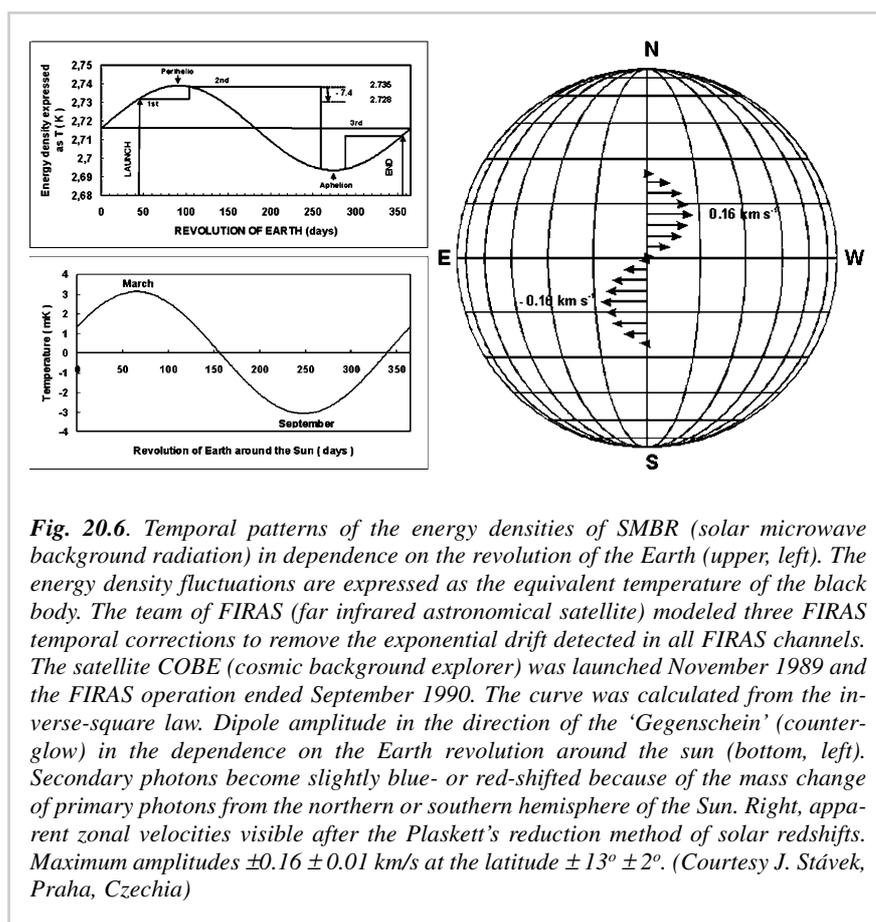


Fig. 20.6. Temporal patterns of the energy densities of SMBR (solar microwave background radiation) in dependence on the revolution of the Earth (upper, left). The energy density fluctuations are expressed as the equivalent temperature of the black body. The team of FIRAS (far infrared astronomical satellite) modeled three FIRAS temporal corrections to remove the exponential drift detected in all FIRAS channels. The satellite COBE (cosmic background explorer) was launched November 1989 and the FIRAS operation ended September 1990. The curve was calculated from the inverse-square law. Dipole amplitude in the direction of the ‘Gegenschein’ (counter-glow) in the dependence on the Earth revolution around the sun (bottom, left). Secondary photons become slightly blue- or red-shifted because of the mass change of primary photons from the northern or southern hemisphere of the Sun. Right, apparent zonal velocities visible after the Plaskett’s reduction method of solar redshifts. Maximum amplitudes $\pm 0.16 \pm 0.01$ km/s at the latitude $\pm 13^\circ \pm 2^\circ$. (Courtesy J. Stávek, Praha, Czechia)

device on a chip it ought to get to one electron per device somewhere around the year 2020. It is clearly too naïve and oversimplifying but, at least, gives us a hint. Eventually, we will get to scales where quantum phenomena rule, whether we like it or not. If we are unable to control these effects, then data bits in memory or processors will suffer errors from quantum fluctuations and device may get malfunctioning. The quantum research has already shown that the potential exists to do much more and instead of playing a support role to make better conventional devices, quantum mechanics could take the center stage in new technology that stores, processes, and communicates information according to its own laws.

or clone, unknown quantum information without leaving evidence of the intrusion. There are many types of usable qubit exits: such as two adjacent energy eigenstates of atoms or ions separated by microwave, vacuum or single photon state of a mode in small optical or superconducting microwave cavities, orthogonal linear or circular polarization of a traveling photon or a weak light pulse, energy eigenstates of a spin in magnetic field or of an electron (or ‘exciton’) in a quantum dot or two charge states of a tiny superconducting island – the practical realization being defined by the application. A resulting multi-qubit processor would enable massively parallel quantum computing, i.e., interference between all the

amplitudes, and such a device could, yet theoretically, be arranged to provide solutions to certain tasks that we will never be able to perform with even the most sophisticated conventional super-computers.

The irreversibility of quantum measurements enables, in addition, two correspondents, say Alice, A, and Bob, B, to communicate with a guaranteed security using photon qubits and public communication. Related quantum cryptography is secure against eavesdroppers, even if they have their own quantum technology. Two qubits, A and B, can exist in a state like $|\psi\rangle_{AB} = 2^{-1/2}(|0\rangle_A |1\rangle_B + |0\rangle_B |1\rangle_A)$, which cannot be factored, so neither qubit has a state of its own, independent of its partner so that all the quantum states of a multi-qubit register contain entanglement. It follows that there is no reason for the two qubits to be in the same register or indeed physical location, and in such cases, distributed entanglement provides for a revolutionary form of communication, so-called quantum teleportation. It may bring remarkable consequences when compared with conventional communication: entangled states can be used as a resource for teleporting quantum states [128,129], destructing them in one place and rebuilding them in another location¹¹.

f) Solar microwave background radiation

Many researchers discussed the somehow curious mechanism of so-called “tired light” and tried to use it to explain the as-received experimental observations in the effort to survey numerous red-shift data that could not be classically interpreted by the standard description using the *Doppler* effect of fast retreating cosmic objects [130]. There is another equilibrium gravitational theory predicting that the material in such a universe is distributed in a fractal fashion whilst the red shift necessarily occurs in integer multiples of a basic unit. This model gives a certain pattern of light propagation where the measured magnitudes of peculiar velocities will increase in direct proportion with distance so that the red shift may be a certain indicator of local measurement scale [131].

The unexpected property of *Brownian* particles tending to self-organize themselves into the form of chemical waves could be described by the ‘Principle of the Least Action’ (cf. Chapter 16). It certainly subsidizes our intellectual curiosity to apply this nonconformist approach even for the hypothetical description of photons in view of tiny *Brownian* particles. *Stávek et al* [132] found an interesting coincidence of their diffusion action with the *Planck* constant, which was confirmed even by other physicists [133,134] in a view that the concept of quantum mechanics might be recognizable on the base of classical resources. As shown in Chapter 16 it may be interpreted as a diffusion process.

The solar microwave background radiation (SMBR) can be seen as a relict of decaying photons and can thus be interpreted as secondary photons emanating from solar (primary) photons. The temporal patterns of the SMBR energy density fluctuation can be taken to support the

scenario based on the analogy with *Brownian* particles. Further development of this concept can guide us to discover several unexpected results. It can enable us to calculate the *Hubble-Nernst* (photo-decaying) constant using the known experimental values of the SMBR energy density and the solar irradiance constant. The temporal patterns in the instrumental data of COBE FIRAS (cosmic background explorer far infrared astronomical satellite) sets confirmed the predicted dependence of the SMBR energy density on the distance from the Sun, i.e., alongside the inverse-square law. The *Plaskett’s* red-shift analysis [135] of the solar surface can be factually used to evaluate both the temperature amplitude ($T = 3.1 \pm 0.2$ mK) and the incoming direction ($\alpha = 167^\circ \pm 2^\circ$; $\delta = -1^\circ \pm 3^\circ$) of the observed SMBR dipole. The existence of the solar granulation, super-granulation, giant cells, pores,

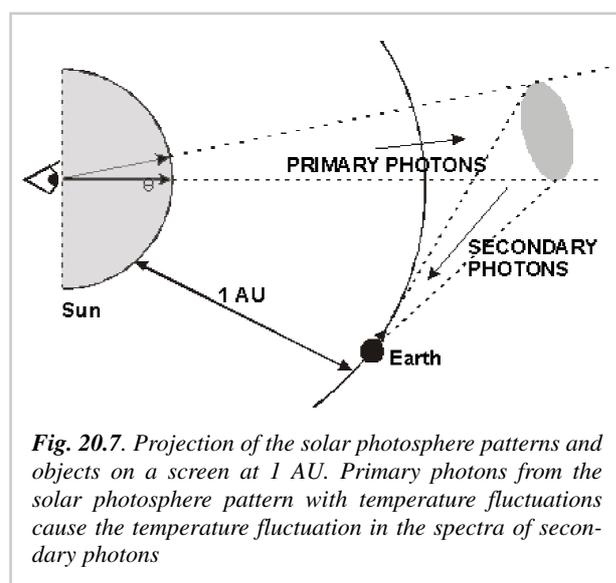


Fig. 20.7. Projection of the solar photosphere patterns and objects on a screen at 1 AU. Primary photons from the solar photosphere pattern with temperature fluctuations cause the temperature fluctuation in the spectra of secondary photons

sunspots and groups of sunspots may thus be explained upon the observed temperature fluctuations of the observed microwave background radiation on the different angular resolution. The limits of these fluctuations can be adjusted from the temperature fluctuations of granules, supergranules and giant cells, and SMBR structure measurements actually performed by satellites COBE FIRAS, DMR (differential microwave radiation) or DIRBE (diffuse infrared background experiment). These (somehow ‘strange’) coincidences lead to the conclusion that the observed microwave background radiation could be considered as a fingerprint of the solar photosphere.

Brownian particles can grow or decay (i.e., dissolve or evaporate) if their surroundings is supersaturated or, opposite, undersaturated by other growth material (photons). *Stávek* and *Ulrich* [136] interpreted the classical growth and dissolution of particles and crystals by *Mandelbrot’s* concept of fractal geometry (cf. Chapter 13). They established the specific growth/dissolution rate G [in $\text{kg kg}^{-1} \text{s}^{-1}$] to be proportional to $\Delta m / (\Delta t m_i) = K L^{D-3}$, where δm represents the mass change of a particle with initial mass m_i (during time δt), K and L are constants

characteristic for the length of particles and D is the fractal dimension of the process ($0 \leq D_R \leq 3$). The analysis of the growth behavior of photons leads to their characteristic fractal dimension D_R equal 3.0. The rate of incorporation is proportional to the mass of those particles. This fractal description of growth and decay processes of Brownian particles with the characteristic fractal dimension, $D = 3$, leads to the model of “tired light” introduced into the astrophysics by *Zwicky* as early as in 1929 [137].

The decay of photons in a time is proportional to the mass of those photons, m , and to the time interval, dt , i.e., to $(m dt)$. Consequently, the change in the mass of photon is given by $dm = -m H dt$, where the constant of proportionality is the *Hubble-Nernst* decay constant of photons, H , with the dimension $[\text{kg kg}^{-1} \text{s}^{-1}]$ as introduced by *Hubble* in 1929 [138]. *Nernst's* name was associated with this process because of his dependable interpretation as the decay rate of photon [139], trying to determine the temperature of CMBR (cosmic microwave background radiation) from the galactic irradiance.

The mode of the reduction of raw spectral data plays a critical role on the final form of the resulting “velocity” patterns¹². Several reduction procedures were proposed for the solar spectral evaluation and *Plaskett* [142] developed a reduction technique that was used at the Oxford Observatory for many years. *Howard* [143] worked out another reduction technique that has been equally employed by many other groups. The comparison of these two techniques reveals dissimilar large-scale velocity fields. *Plaskett's* reduction technique reveals a macro-scaled velocity field with a higher residual zonal velocity in comparison with that by *Howard*. Similarly, *Snodgrass* [144] analyzed the 26-year period at the Mount Wilson observatory and received similar spatial photospheric Doppler patterns as *Plaskett* did, but with significantly lower magnitude of residual zonal velocities. *Plaskett* concluded that the *Faye* formula used in the *Howard* reduction technique could likely smooth the residual velocity patterns. *Plaskett* described the solar velocity patterns as the sum of:

- (i) true rotation and apparent zonal flow,
- (ii) meridional flow and
- (iii) other radial flow and any other wavelength changes.

Such a prolonged research activity of can be summarized as follows: the amplitude of the apparent zonal velocity is $\pm 0,16 \pm 0,01 \text{ km s}^{-1}$ (north red-shifted, south blue-shifted), the latitude of the maximum is $\pm 13^\circ \pm 2^\circ$, which is schematically shown in Fig. 5. These residual velocities in their large-scale velocity field could be traditionally interpreted as some up- and down- streams (with many unusual properties). However, the tired light model of decaying solar photons can offer another interpretation. The “blue-shifted” primary photons radiated from the southern hemisphere have a slightly higher mass in compare with the “red-shifted” primary photons radiated from the northern hemisphere. The universal *Hubble-Nernst* decaying constant would cause the shift in the mass of the emanating secondary photons, i.e., “blue-

shifted” primary photons will emanate “blue-shifted” secondary photons, which is depicted in **Figure 20.s.2a+b**. The solar rotation axis is tilted to the ecliptic plane and therefore the observer in this plane will be exposed alternately to a modified view of primary blue- and red-shifted photons. This mass modification of primary photons can subsequently cause a slight mass change of the secondary photons.

An observer revolving around the Sun should thus detect a dipole in the SMBR with the amplitude $T = \pm 3.1 \pm 0.2 \text{ mK}$, certainly if he will measure the SMBR spectrum in the counterblow (“Gegenschein”) direction from the Sun. The maximum of this amplitude should be detected on the Earth on March 6, with the maximum declination of the Sun being -7.15° . The orientation of this dipole in the equatorial coordinates is estimated to be $\alpha = 167^\circ \pm 2^\circ$; $\delta = -1^\circ \pm 3^\circ$. The dependence of this amplitude on the revolution around the Sun is depicted on the Schema, Fig. 6.

The photospheric layer of the Sun is structured on three spatial scales: the granulation with a typical scale of 10^3 km , the supergranulation on a scale of $3 \cdot 10^4 \text{ km}$, and the giant cells on a scale of $2 \cdot 10^5 \text{ km}$. The high-resolution pictures of the solar photosphere show a pattern of bright and dark markings termed as granulation with the granular size in the range $200\text{--}2000 \text{ km}$. The solar microwave background radiation should copy this similar fine structure and the temperature fluctuations up to about 6 mK . The individual cells have linear dimensions $\sim (1\text{--}4) \cdot 10^4 \text{ km}$ with their lifetimes in the range of hours. The detailed analysis revealed five minutes brightness oscillations with similar spatial characteristics. Although the supergranules are much bigger than granules, they are much harder to see because they are negligibly brighter than their surroundings. The structure of these supergranules is composed from complex bright and dark patterns. The evaluated temperature fluctuations on this spatial scale are at the level of about 1 K . *Howard's* reduction method of solar spectral lines on this spatial scale gives the residual red- and blue-shifts on the level of $\sim 3 \text{ ms}^{-1}$. Therefore, the expected temperature fluctuations of the SMBR should be detected with the amplitude down to $\sim 300 \mu\text{K}$ or less for this angular resolution.

The further possible modification of the observed fluctuations of the SMBR could be caused by other markings in the photosphere. Pores with their size at the scale level of $\sim 10^3 \text{ km}$ could be detected with that angular resolution. Sunspots represent other markings in the photosphere with the linear size in the range $\sim (2.5\text{--}5) \cdot 10^4 \text{ km}$. They are cooler than the rest of the photosphere. Spots tend to form sunspot groups with size range $\sim (5\text{--}15) \cdot 10^4 \text{ km}$. Fingerprints of such big objects with high temperature fluctuations should be easily visible provided that the instrument will be focused in the proper direction. It should detect some residual energy density and temperature fluctuations after the removal of the monopole and dipole energy densities and temperatures. It is predicted

that the fluctuations are closely related to flux fluctuations of primary photons, but it would be difficult to predict the amplitudes of these fluctuations because of the complexity of photon diffusion fields. Future experimen-

tal research is needed to contribute this subject as well as to uphold the other yet uncommon areas under contemporary discussion, which we ventured to expose in this concluding chapter.

¹ At the same time, *Maxwell* also enlightened *Kepler's* observation that the comet stream is tailed away from the sun upon the pressure of the rays falling from the sun. In 1924, the Russian scientist and rocket theoretician *Ciolkovskii* first realized that the pressure of sunrays could be used for propelling a cosmic vehicle furnished by suitable radiation-reflecting sail in the moment when it is lanced out to the cosmic space. As early as in the year 1970 the effects of sunrays were utilized to successfully orient the Mercurial probe 'Mariner'. The recent calculations provided by NASA revealed the estimate that a cosmic sail-ship could be accelerated to the speed five times faster than that achievable by conventional rocket drive. If such a sailor would be launched in the year 2010, it would meet early cosmic probe 'Voyager' in the year 2018, i.e., within eight years it would exceed the distance that 'Voyager' needed forty years to pass. Currently there are several successful (and also unsuccessful) missions, which employed such a sunrays drive for its acceleration, for example, the UNESCO spacecraft 'Star of Tolerance' with the projected sail area of 1600 m² or the proposed sailing vessel 'Cosmos' by the American Planetary Society. Such assignments, however, are still under the scientific disputation whether an absolute reflection of solar photons on the finished mirror would follow the laws of thermodynamics (requesting upon the gain of mechanical energy a change of temperature through the change of the photon wavelength).

² *Bartoli* imagined a perfectly evacuated system consisting of four concentric shells (A, B, C and D). The outermost, A, and the center, D, shells were firm black (fully absorbent) bodies while the intermediary two shells, B and C, were contractible (and upon the need also removable) with a perfectly reflecting surfaces on both sides. The spaces between two outer, A-B, and inner shells, C-D, were thermally isolated while the outermost and central shells, A-D, were in thermal equilibrium. It required following operations: at a given moment the destruction of the second outer shall, B, produces radiation of heat in the entire space between A and C. Later, when the shell A reached thermal equilibrium, the shell B is re-created and the shell C destroyed. Thereupon the shell B is contracted as far as its radius becomes equal to that of C. On repetition by cyclic operations, a definite quantity of heat is taken from A and transferred to D. Such transfer allows, however, an unconstrained assumption that the temperature of D can be higher than that of A. It makes possible to even assume an opposite, anti-gradient heat transfer, which may factually contradict the principles of the second law.

³ A system is defined as being at absolute zero when no heat flow, Q, can occur out of the system during any reversible isothermal process performed on the system. Consequently, for the classical electromagnetic zero-point radiation process, only the nonzero spectrum is suitable for establishing an equilibrium state with the electric dipole oscillators at a temperature of absolute zero. This requirement (Q=0 and T=0) must also satisfy the third law of thermodynamics, i.e., the ratio of Q/T should also approach zero in the limit of T→0, which places a further restriction on the spectrum of incident radiation. Therefore, if a statistical equilibrium configuration is at all possible for a system of classical charged particles, then at a temperature of absolute zero must exist a zero-point classical electromagnetic radiation as well as a zero-point oscillating motion for the charges. Of course, zero-point field and motion are normally associated with quantum-mechanical systems and are alien to the traditional ideas of classical thermal physics. However, a qualitative way of understanding why zero-point fields and motion exist, should be a natural part of thermodynamic behavior of classically charged systems of particles, i.e., they *cannot* exist in a static, stable equilibrium. Hence, if an equilibrium situation for charged particles is at all possible, then the charges must be following a fluctuating, oscillatory path in space. The oscillating charges produce fluctuating electromagnetic fields, which in turn act upon these charges. Thus, any possible equilibrium situation must involve the presence of electromagnetic radiation, as well as an oscillatory motion for the charges, even at a temperature of absolute zero. All motion of charges would then possess a stochastic character. These qualitative ideas correspond moreover to what we observe in nature when at the zero absolute temperature molecular activity does not cease but has a *zero-point* motion.

⁴ The spectrum is divergent (i.e., $\int d\omega u_{000} \rightarrow \infty$) and must have a cut-off point, the suitable limit of which is the *Compton* frequency of electron, $\omega_c = mc^2/\hbar$. The predicted electromagnetic quantum vacuum density is enormous, about 10¹¹⁴ J/m³ or, in terms of mass, 10⁹¹ kg/m³ if the Planck length of 10⁻³⁵ is used to provide the necessary cut-off. For an infinitely flat Universe, it would imply an outward zero-point pressure that would rip the Universe apart. Nevertheless, astronomical data indicate that any such cosmological constant must be mere 4 eV/mm³, or 10²⁵ g/m³, so that the discrepancy between this theory and observation is as great as 120 orders of magnitude. It is arguably the greatest quantitative discrepancy ever observed in the history of science [G.J. Jordan, H. Fearn, P.W. Milonni "Some theoretical significance and implications of Casimir Effects" *Europ. J. Phys.* (2004, in print)]. However, a more realistic energetic content of vacuum can be derived to conform to the integral $\int d\omega u_{000} \rightarrow (\hbar/8\pi^2c^3) \omega_c^4$, which is assumed to amount to ~10²² J/m³. Curiously, even such a quantifiable 'handful amount of vacuum' would literally change about hundreds of million of tons of the ice to steam – not too bad in the future of energy perspectives and prognostication?!

⁵ *Mareš et al.* showed that a frequency shift of a beam reflected from the inner side of a moving mirror (on, e.g., piston) is given by a proportionality, $\omega_1 = K \omega_0$, where frequencies indexed 1 and 0 stand for original and reflected values (Doppler's factor depending on the velocity ratio v/c). Subsequent to N reflections, the multiplying constant gets its power exponent, K^N [J.J. Mareš, V.

Špička, J. Krištofík, P. Hubík „Filling of a cavity with zero-point electromagnetic radiation“, *Entropy* 6 (2004) 216]. To evaluate the limiting behavior of such a process some approximations are obviously needed, which may lead to possibility of certain generalization of the above formula 1. The best way seems to be an effective renormalization, as every reasonable cut-off parameter has to have a character of a constitutive quantity. Therefore, *Mareš* suggested that the equation 1 can be read as $u_{\omega} = \omega^3 f(\omega/\omega_0)$, where f represents a universal (dimensionless) function. By taking into consideration that the limiting behavior of thermal radiation is bounded by Ehrenfest's limiting conditions, such a function may be proposed to hold: $(\hbar\omega/2\pi^2c^3\omega_0)/(\exp\{(\omega/\omega_0)-1\})$. Though not known yet, this proposal may bring a formal advantage of a convergent integral when taken over the infinite range of frequencies.

- ⁶ Curiously there is even a contemplation of an inquisitive relation to a macroscopic collision that is experienced to happen when two freighter ships pass each other at a closer distance than a certain security separation, which results in their mutual attraction and subsequent crash. Certainly, being more serious, we should only account for the entire micro-world where this somehow curious idea appeared in the year 1948 when *Casimir* and *Polder* [H.G.B. Casimir, D. Polder, *Phys. Rev.* 73 (1948) 360] obtained a term for which the interaction energy varies as r^{-7} for large intermolecular separation, r , depending on the polarizability of molecules. This represents a contribution that was not predicted by the *London's* well-established calculation [F. London, *Zeit. für Physik* 63 (1930) 245] made back in the year 1930, according to which the *van der Waals* unretarded forces arise directly from the *Coulomb* interactions between the molecules undergoing quantum fluctuations ($\sim r^{-3}$). *Casimir* [Proc. Kon. Ned. Akad. Wetenschap 51 (1948) 793] went on to analyze the much simpler, ideal case of two macroscopic, uncharged and perfectly conducting parallel plates, which has since then been widely adopted as a model for the study of these phenomena. However, a typical force thus created is very small, for example, for a plate area of 1 cm² and a separation of 1 μm the force amounts to about 10⁻⁷ [N]. On this scale it, evidently, is not easy to disentangle the Casimir contribution from the force due to charge fluctuation. In 1965 *Marshall* [T.W. Marshall, *Nuevo Cim.* 38(1965)206] studied the balance between the average energy lost through radiative reaction and the average energy gained from the background field for an oscillation in the space between two parallel conducting plates, which reproduced the quantum result for the *Casimir* effect (including a small thermal contribution when $T > 0$). In a similar spirit, *Boyer* [T.H. Boyer, *Phys. Rev.* 174 (1968) 1764] reconstructed *Casimir* results for the energy change by proposing that the force between the plates arises from the zero point field subject to boundary conditions. Further, following the classical work by *Lifshitz* [E.M. Lifshitz, *Zh. Eksper. Teoret. Fiz.* 29 (1955) 94] on dispersion forces between dielectric bodies, *Boyer* calculated the force between the plates by evaluating the electromagnetic stress tensor thus explicitly showing that there is a clear-cut connection. Today there is an impressive list of further theoretical and experimental applications of the basic idea underlying the *Casimir* effect that leave no doubts of its validity.
- ⁷ The origin of inertia is a long-standing problem in physics and the idea that the rest mass of a particle like an electron is purely electromagnetic in origin has a history of more than a century but falls beyond this outlook. However, one can question why electromagnetism is supposed to play such a fundamental role in inertia compared to other known three interactions of physics.
- ⁸ Heat engine process cycles, based on coherent magnetocaloric effect and using a superconductor as the working medium, utilize isothermal and adiabatic phase transition of the superconductor in order to move the magnetic field, H , and temperature, T , coordinates of the superconductor and thereby achieve a closed cyclic path in H - T space. In the isothermal case, the superconductor is in contact with a heat reservoir, as the magnetic field is changed to induce phase transitions, the heat reservoir supplies and adsorbs the latent heat evolved. In the adiabatic case, the superconductor is thermally isolated and the latent heat evolved cools or heats the superconductor itself, via the thermophysical process known as the magnetocaloric effect. Such a heat engine can be run with selected attributes of the isothermal and adiabatic phase transitions even if the working medium is an atypical superconductor, which macroscopically exhibits quantum mechanical aspects. It obeys traditional formulation of the second law of thermodynamics and the efficiency is again less than unity because the quantum mechanical aspects are part of a collective system such that for any process. In this respect, it is worth noting that *Svobodny* and *Kalva* [*Phys. Stat. Sol.* B208 (1998) 187] tried to interpret magnetocaloric effect as a transfer of energy between the so-called ‘quasiparticles’. In the case of the weak magnetoelastic interactions, it is a transfer of energy between ‘magnons’ and thermal ‘phonons’ while for the stronger interactions, the quasiparticles (of quasimagnons and quasiphonons) should be assumed similar to previous magnons and photons (i.e., the second quantization of energy of collective excitations). The magnetocaloric effect is thus understood as a nonlocal and noncoherent transfer of energy between the quasiparticles, i.e., not a traditional flow of heat throughout the sample but the transfer of energy accomplished in the same time in the whole volume of material. It indicates that the energy of one of the phonon-like modes (parallel or perpendicular to the crystallization anisotropy axis) goes to zero by approaching the phase transition. Therefore, it cannot be described by standard procedures applied to heat propagating through the real space, but there is a need for the description of other, more sophisticated type, such as diffusion in the space of wave vectors. It evokes the question (cf. Chapter 4) of a collective equation describing the generalized diffusion-like processes in the wake of idea of the universality of dual, particle-like and wave-like, character of matter. The real-value proportionality constant, occurring in such a universal equation, applies for the case of normal diffusion while its imaginary value leads to the quantum-mechanical equation [Z. *Kalva* and J. *Šesták*, *J. Thermal Anal. Calor.* 76 (2004) 67]. It is along the *Fynmann's* and *Steiner's* idea of searching for “nature's natural numbers” considering such a constant as a hypercomplex number. The long standing task how to interconnect such macroscopic and microscopic course of diffusion encounters already many classical papers: for example *D. Kershaw* “Theory of Hidden Variables” *Phys. Rev.* B136 (1964) 1850 or *E. Nelson* “Derivation of Schrödinger Equation from Newtonian Mechanics” *Phys. Rev.* 150 (1966) 1079. It is touched even by so called ‘dissent literature’ such as *P. Marquard*, *G. Galeczki* “Action and Quantum Mechanics” *Apeiron* 2 (1995) 5 or *J.P. Wesley* “Classical Quantum Theory” *Apeiron* 2 (1995) 27.

- ⁹ There is a striking coincidence with a macroscopic process taking place in our everyday chemical reactor. Any such a heat engine is fed by fuel, which chemical energy (change of structure) is transformed and returned back to the background bath. Any change of structure must bear a consequential exchange of the zero point energy. The smaller the size the greater is the change.
- ¹⁰ *Hall* effect gives the development of a transverse electric field in a current-carrying conductor placed in a magnetic field where the magnetic field is perpendicular to the flow of electric current and the created electric field is thus perpendicular to both. *Fermi* level is the electrochemical potential for purely electronic system at which the *Fermi-Dirac* distribution function of an assembly of electrons is equal to one-half (= *Fermi* energy). *Lorentz* force acts on a charged particle moving in the electric and magnetic fields and equals to the particle's charge times the sum of the electric field and the cross product of the particle's velocity with the magnetic flux density.
- ¹¹ Teleportation is the name given by sci-fi writers to the feat of making an object disintegrate in one place while a perfect replica appears somewhere else, first suggested by *Bennett* in 1985 [Phys. Rev. Lett. 1985, p.70]. Today's theory is based on the famous effect often called '*Einstein-Podolsky-Rosen* correlation' or conveniently 'entanglement' (in the meaning of superposition, embroilment or mix up) known since 1930s [Physical Rev. 47(1935) 777]. In 1993 this intuition was confirmed by showing that a teleportation is possible in principle by destructive observation (a photo-detector measures photon in a destroying manner by its absorption and conversion into electric signal) or by new difficult-to-execute technique known as quantum non-demolition measurements (where a photon in a cavity is probed without absorbing any net energy from it). It is worth noting that teleportation is a fundamentally different process with respect to the classical transfer where the object must be seen and understood and its image (photograph, order chart, digital scan, etc.) transmitted to the receiver who uses the instructions to build the object and even duplicate copies. During teleportation, however, the object can be simply perceived to be first 'destroyed' to fundamental particles and then 'reconstructed' from such particles available somewhere else. To put it plainly, in the quantum teleportation process, physicists take a photon and transfer its properties (such as polarization, i.e., the direction in which its electric field vibrates) to another photon, even if the two photons are at remote locations. The technique works by sending one half of an entangled light beam to both teleporting stations, A and B, while A measures the interaction of this beam with the beam it wants to teleport, the B uses it to make an identical copy of the beam the A wanted to teleport. The original beam, however, is lost in the process. For better illustration, let us imagine that at the sending station, A, the quantum teleporter encodes a photon, P1, with a specific state (e.g. 45 degrees polarization). This travels towards a beam-splitter (half-silvered mirror) while two additional entangled photons are created. The polarization of each photon is in a fuzzy, undetermined state, two photons have yet a precisely defined interrelationship but they must have complementary polarization. Entangled photon, P2, arrives at the beam-splitter at the same time as the message photon, P1. The beam-splitter causes each photon to either continue towards detector, D1, or change the course and travel to detector, D2. In the quarter of all cases the teleporter, A, does not know where the two photon go off into different directions. By this fact, that the two photons are now indistinguishable, the message photon P1 loses its original identity and becomes entangled with P2. Since the message particle P1 must have complementary polarization to the particle P2, then the other entangled particle P3 must now attain the same polarization value as P1. Indeed, the receiver station, B, sees the polarization value of particle P3 at 45 degrees. So far is this scheme intended only for quantum-scale particles and in its actual version been already executed at the University of Innsbruck back in the year 1997. Let us remind that teleportation strictly excludes any multiple copying but for the information translocation still obeys the law of limiting speed of light.
- ¹² The scenario proposed by *Stávek* [140] for decaying primary solar photons enables to evaluate the *Hubble-Nernst* constant and the energy density of the microwave background radiation by using the experimental values of the solar irradiance at the Earth distance 1 AU from its source. The ratio of both energy densities gives the particle concentration of secondary photons in the primary ones as 4 ppm. The total number collisions Z_w of purely chaotic motion of molecules of a perfect gas per unit time per unit area is $Z_w = N c' / 4$, where c' is the mean speed and N is the number density of molecules. The decay of solar primary photons absorbed in a unit volume per unit time and the radiation of the formed CMBR is given by the standard relation including the *Stefan-Boltzmann Law* ($\approx T_{\text{SMBR}}^4$, which characterizes the intensity of the black-body radiation at the temperature), which is proportional to the product ($H t J / (V c')$, where H is the Hubble-Nernst constant, t is time, J/V stands for the solar irradiance absorbed by the blackbody with unit volume and c represents the mean velocity. The relationship describes the decay of primary photons and provides the value of H (if T_{SMBR} is approximated by 2.716 K at 1 AU and J/V by 1368 J/m³) to match the value of $2.395 \cdot 10^{-18} \pm 0.003 \text{ kg kg}^{-1} \text{ s}^{-1}$ (or $73.90 \pm 0.08 \text{ km Mpc}^{-1} \text{ s}^{-1}$ in the velocity units) [140]. The final result of the Hubble Space Telescope (HST) key project to measure the Hubble constant gave the value $H = 72 \pm 8$ (or ± 2.3) $\text{km Mpc}^{-1} \text{ s}^{-1}$ which is a striking concurrence. Upon integrating the relation $dm = -m H dt$ we get $m(t) = m_0 \exp(-H t) = m_0 \exp(-HL/c')$, which incorporates the swiftness constant, c' , describing the velocity of motion of the diffusion field of photons from their source in a distance L ; the resulting red-shift relationship is read in the form $H/(c' L)$. The recent space technology makes it possible to collect precise solar data far from the influence of the Earth's atmosphere, see Fig. 5, which shows the dependence of solar spectral flux at 1 AU on the frequency with dimension cm^{-1} . The maximum solar spectral irradiance $\text{W m}^{-2} \text{ Hz}^{-1} \text{ sr}^{-1}$ comes at the wavelength $\lambda = 880 \text{ nm}$. Many sets of experimental data were collected thanks to the cosmic background explorer (i.e., COBE space mission using the FIRAS, DMR, and DIRBE instruments). The maximum microwave background radiation (again in $\text{W m}^{-2} \text{ Hz}^{-1} \text{ sr}^{-1}$) against the frequency (cm^{-1}) lays at 1.88 mm for $T = 2.716 \text{ K}$ at 1 AU. The coefficient k is defined as $1.88 \cdot 10^{-3} / 880 \cdot 10^{-9} = 2136$ and relates together wavelengths of primary and secondary photons (e.g. the position of FIRAS channels detecting the flux of secondary photons after this transformation gives the wavelength of their primary photons). The points added to Fig. 6 correspond to the frequencies of primary photons. When some primary photons lose a part of their original mass in the form of a secondary photon, they become red-shifted by the value of $4.68 \cdot 10^{-4} = (\lambda_x - \lambda_0) / \lambda_0 = \Delta m / (m_0 - \Delta m) = 1 / \lambda_{\text{SMBR}} (1 / \lambda_0 - 1 / \lambda_{\text{SMBR}})$, where λ_x and m_x describe the decayed primary's photon. The secondary particle concentration calculated from both energy intensities is 4 ppm. The recalculation of this red shift to the velocity units gives the value of

140.4 km s⁻¹. The concept of red-shift quantification was brought to the astrophysics in 1973 and was confirmed by, e.g., *Broadhurst* [141]. As mentioned above *Arp* [130] analyzed all available red-shift data in order to estimate the accuracy of the 72 km/s periodicity. The estimated averaged deviation from the period was only ± 8 km/s (or ± 2 km/s for the most accurate red-shift data) and it seems that the red-shift quantification found for the solar primary photons fits the yet curious concept of *Stávek's* [140] rather well.

¹³Though the subjects in this chapter have rather ulterior connections to the field of classical thermodynamics, these reflections tackle frontiers of quantum and nanoscale (mesoscopic) thermodynamics, which are related to a broader understanding of the generalized concept of thermal science and temperature itself. This chapter, however, may bring certain inquisitiveness among the widely divergent spectrum of possible readers, certainly, awaiting thus a rather antagonistic responsency.

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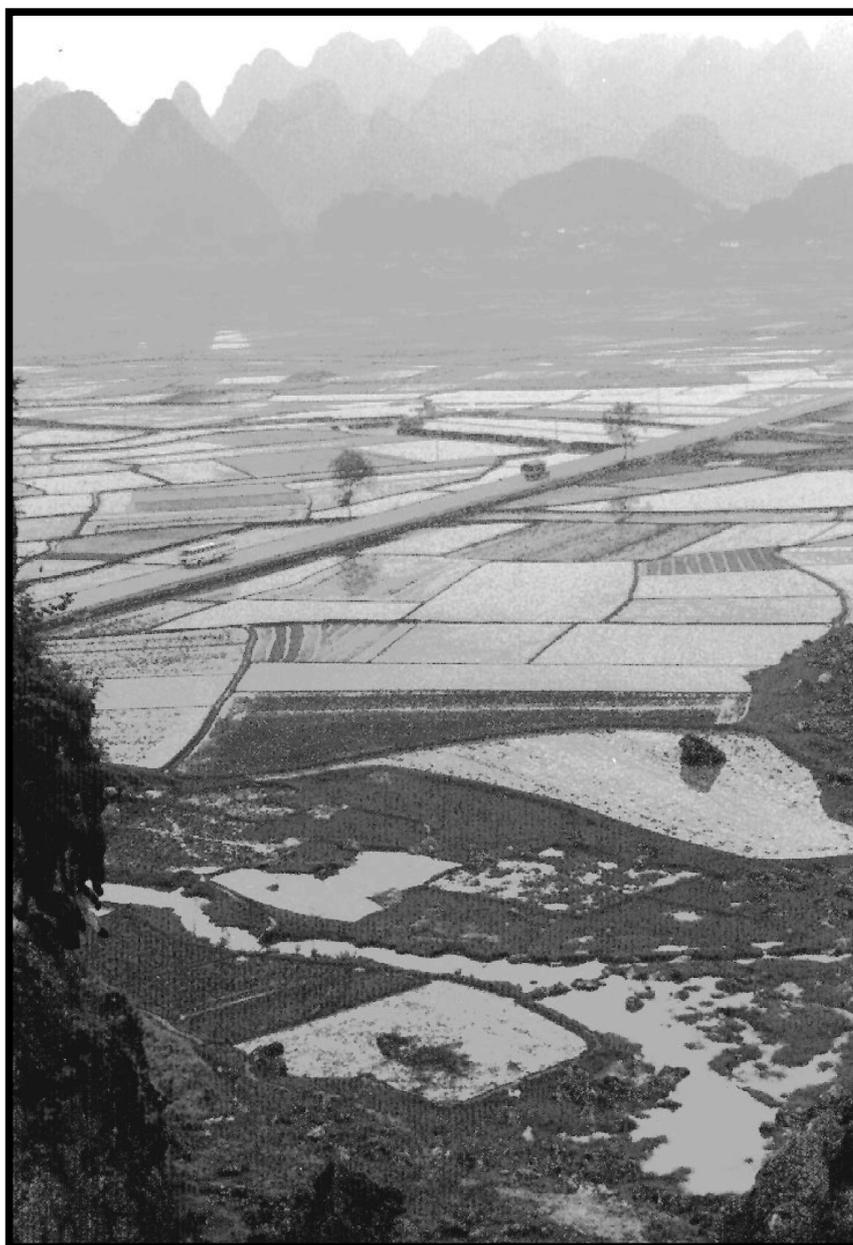
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MOTTO "For we know in part and we prophesy in part...But when that which is perfect has come, then that which is in part will be done away"
[CORINTH. 13:9 & 13:10]



'Guiling' means 'the landscape unequal in the world' looking like traditional Chinese painting with peaked mountains reminiscent of picturesque green sugar loafs placed riverside of the arcane 'Li' and framed by paddy fields – time is allowed to make a breathtaking stop (1987)

Conclusions

I would like to express my appreciation to all those who were spirited enough to reach the end of this rather thick book and encourage those who have read only the introduction and this conclusion to glance through the chapters that lie in-between. These neglected chapters may be worthy of attention – certainly and depending on the readers' taste and reaction, which can be anticipated to vary naturally between a positive and negative opinion, possibly inconsistent in a broader spectrum of this book's subjects. Certainly, all critical assessments are acceptable in the current, rather curious state of our knowledge, extending from the factual spheres of science to pure philosophy and touching the imminent subject of inter-disciplinarity [1], which was actual in the past and would be confidently similar in the future as the adequate signs of an opposite subject evolution.

I plead, however, for tolerance when looking upon all the passages from this book, which, due to their disperse nature, I could not write with equal feeling and powers, and I am not self-righteous enough to be able to have done so. I would just like to quote “*Nobody should assume that what I am saying is true. It is not given to us to know what is true in this sense. But everybody knows that I write this scientific treaty in an implicit unwritten understanding among the scientists that I can be absolutely believed to be what I believe*” [2].

Even in the modern world with its progressive technologies and exceptional theories, a more broadly assumed philosophy, understood as the admiration of the miracle of life, has retained its influential role in the challenge of striving to maintain a sustainable civilization on both the levels of matter and mind. The struggle of Mankind for a better life, while striving to stay alive in the bosom of Mother Nature and pursuing eternal fire/heat, should be understood as a fight for lower disorder and the utmost level of information, and not a mere seeking for sufficient energy. I am sincerely hopeful that there will come, soon or later, some novel scientific discoveries that will possibly arise from curious ideas (such as those sketched-out in the last Chapter 20 dealing with the electromagnetic zero-point field) and which would make the survival of our civilization feasible. If not, we should keep learning how to be congenial with our modest means to our gracious Earth, which has awarded us the land where we can live; a land that was offered to our forefathers and, hopefully, will remain serviceable to our children, too.

Physics, and thermodynamics as one of its natural components, can be considered the heart of natural science and science itself is not a discipline contradictory to and incompatible with artistic and even moral or religious feelings of human beings. Science, as art does, requires imagination and intuition. Our scientific hearts should be tolerant of new scientific motifs, which sometimes are thought bizarre and thus abandoned and delayed by scientific narrowness. As an example the brilliant works of *Gibbs*, *Röntgen*, *Bérousov* or *Feigebaum* can be noticed, which were buried and hidden from common knowledge

for some time in obscure and insignificant annals. At the same time we should suppliantly perceive and respect positive mystic faith of some greatest physicist, such as *Heisenberg*, *Schrödinger*, *Einstein* or *Planck* who in searching the deepest corners of nature became religious. Such an attitude did not contradict their widely respected scientific credit. Moreover, their scientific attempt to achieve better and better understanding of the laws of nature factually matured to a very private approach, which manifested their own internal vision of the Great Architecture of The Universe.

We have learned how to understand thermal features of nature from its macroscopic phenomenology down to its microscopic statistics. Such address also included yet specific class of objects in nanometric region, i.e., nanoclusters, which can be referred to as ‘*mesoscopic*’ shaping thus a new domain of thermodynamics possibly important in gene technology, molecular and quantum engines, nanocrystal growth, nanochip fabrication as well as in the control of oscillatory processes (life). We know that classical thermodynamics in the formulation of *Clausius*, *Kelvin*, *Planck* or *Gibbs* is concerned with processes and the associated second law is clearly not time-reversal invariant because thermodynamics is built upon an edifice of equilibria. We showed, however, that most of real situations are non-equilibrium so that the eminent question of what happens when we look at disequilibrium keeps continues. Thermodynamic literature often uses the term ‘irreversible’ to denote process one may also call irrecoverable, i.e., if the transition from initial to final state cannot be fully undone once the process has taken place. There follows much variety in views on irreversibility and the second law of thermodynamics. On one end, *Planck* maintained that this law expresses the irrecoverability of all processes in nature presented, however, without deeper demonstration. On the other extreme is *Gibbs*, who completely avoided any connection with time. But even for approaches in the middle, the term reversible is used in various meanings: time-reversal invariance, recoverable, and quasi-static. Therefore the question of whether or not the second law of thermodynamics can be violated in a particular situation is not clear yet specially assuming quantum limits [3] (decoherence, dephasing, rectified motion as well as relative openness of all systems due to the background of electromagnetic zero-point field).

A specific place captures the understanding of periodic precipitation of reaction products and oscillatory behavior of certain chemical reactions which description involves the *Planck's* universal constant. There is no consensus yet concerning its legitimacy as various scholars regard it either accidental without any deeper physical meaning or enigmatic, with something very important behind. The most consequential criterion resides as follows: how to decide whether a particular physical problem belongs to the domain of classical or quantum physics, i.e., if the quantity of type of action (relevant to a given physical problem) is comparable with the *Planck's* quantum. It seems plausible that for its approval

Conclusions

it can be adequate to make clear about the condition under which the numerical values of classical diffusion (*Fick*) constant attains that spheres of the quantum (*Fürth*) motion [4]. This convergence can provides certain resulting conditions for acting species, i.e., for ball-like particles (thus simulating molecules), which exhibit no observable persistency when moving through low viscous media. In such a case *Einstein-Smoluchowski* formula [5] is applicable in the form $k_B T / (3\pi\eta a) \gg h / (4\pi M)$. Beside the standard constants (k_B , h , π) we can conveniently substitute for dynamic viscosity that of liquid water, $\eta_{H_2O} = 10^{-3}$ [kg/(ms)], and for temperature its room value, $T_{room} = 300$ [K], which yields the inequality $8.4 \times 10^{15} \gg a/M$, where a [m] is the size and M [kg] is the molecular weight ($\times 1.67 \times 10^{-27}$). Accounting for particular ions and their radii we can find that the most suitable candidates for such ‘quantum’ behavior (Brownian particle) capable of self-organization are sodium, calcium and silver. Certainly similar analyzes is yet due to the special case of the most mobile protons (H^+) possible important in life processes (e.g., thermo- and electro- dynamics of the propagation of nerve signals). Such relevant experiments and theories focused to the boundary range of nano- and macro-scale is another domain of mesoscopic thermodynamics open to fruitful future.

The sciences, databases and information exchange have all expanded tremendously over the past few hundred years. One of the many changes in thoughts and scientific confrontations over this period was the convincing preference of the vibrational theory over the flow caloric theory in thermal physics though the latter persisted until now in various forms of flow equations. However, the novel object of the so-called ‘dark’ energy and/or matter might somehow endure then provisional position of caloric in explaining the problem of antigravity.

Even today the world of physics is somehow divided into the authorized (and by reviewers well accepted) papers and those contributions that are not in favor with the standard contentment of regular journals. They, thus, form an appreciable sphere of refugee (often-labeled dissident) physics well known from the Internet and subject of other (someway-expelled) journals [6].

Popper [7] emphasized the importance of probability in Nature and its behavioral mechanism, as well as its importance to scientific mentality. Indeed, *Popper* once famously said that “*non-triviality probabilistic conclusions can only be derived (and thus explained) with a help of probabilistic premises*”. In the same irreconcilable way, *Popper* treated any attempts to prove compatibility of the reversible *Newton* equation in mechanics with the concept of entropy increase, the irreversibility of *Boltzmann* equation and phenomena observables in nature, writing “*a clear stand should be made in favor of an ‘open’ universe – one in which the future was in no sense contained in the past or the present, even though they do impose severe restrictions on it*”. He rejected any attempt to derive irreversible thermodynamic and kinetic laws from the reversible equations of classical mechanics. However, even quantum randomness was not good

enough for him as the freedom of will is incompatible with neither determinism nor randomness and, armed with randomness, he said that biology cannot be reduced to the array of physics, chemistry and so on. He recalled the ‘vital force’ (cunning) being a product of life (selection) rather than anything like the ‘essence’ of life saying “*organic structures and problems arise together, i.e., organic structures are theory-incorporating as well as problem-arising structures*”. Consciousness emerges at the highest level of being – having a conception of the world as consisting of:

- (i) things (physical objects),
- (ii) subjective experiences (mental states) and
- (iii) statements in themselves (ideas, images, art), cf. Chapter 3.

Allow me to repeat for the second time that I tried to join so far uncommon spheres of privity within the ordinary domains of science and humanity, using the occasion to portray my broader conception [8] of thermal science which, however, may be seen as a more-and-less objectionable mixture. I recall the approach I have been using within my university lectures aimed to give rise to a shared borderland between the scientifically and philosophically seen features of nature, which were well appreciated by my students. I also cannot omit my sincere thanks for the financial support of humanity grant. I have completed this authorship in my best will and with a view to help the interdisciplinary of knowledge in the primary understanding of the Pythagorean term ‘philosopher’, the one who seeks to uncover the secrets of nature.

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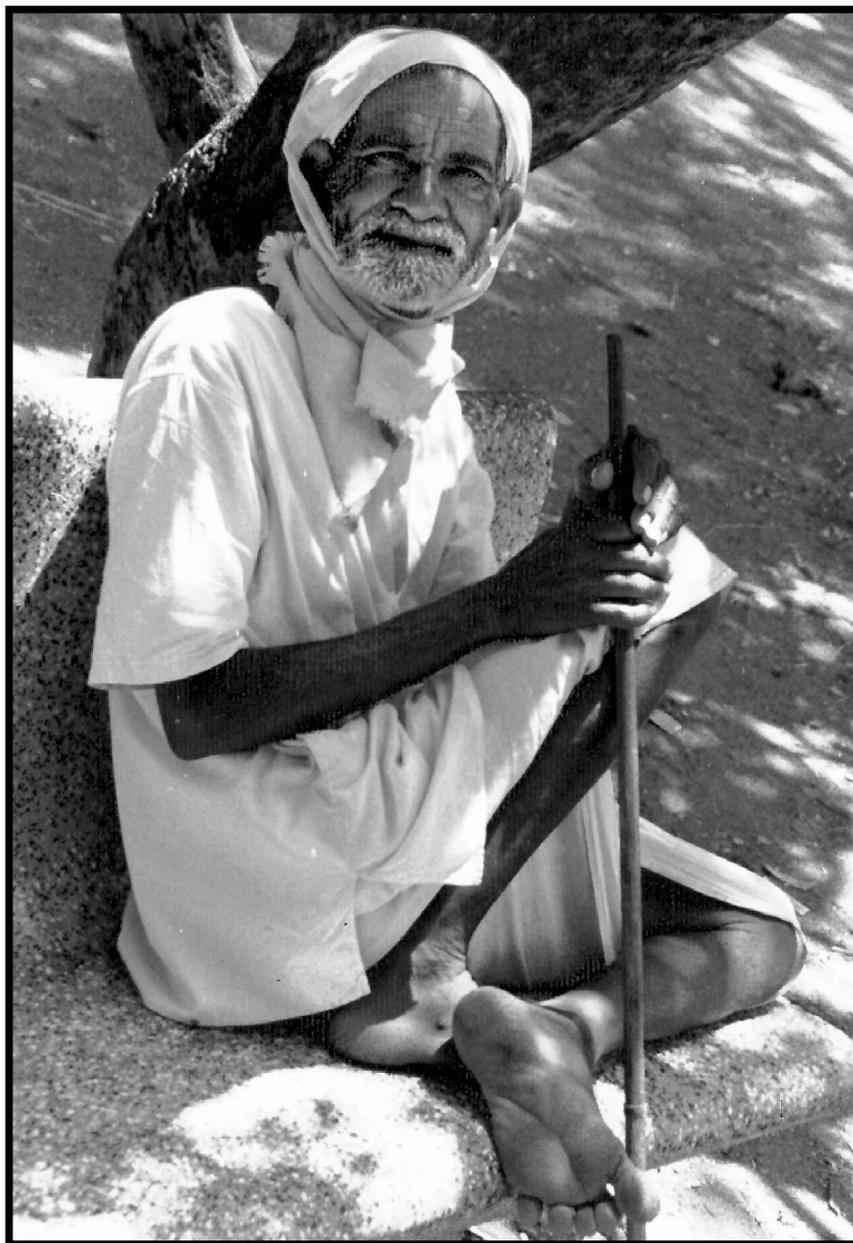
dead and who after this enforced internment found it incongruous to continue his law career under the growing regime full of bursting extrajudiciality and who thus became a devoted thermoanalyst (virtually "litigating samples"), subsequently oppressed again by communistic totalitarianism.

My deepest and most sincere appreciation, however, is paid to my family, particularly my wife *Věra*, who graduated in both the Czech Institute of Chemical Technology in Prague (M.Eng., VŠChT) and the University of Missouri in Rolla (M.S., UMR, USA) and who for a long time has also coauthored my articles (on the growth and utilization of single crystals of various semiconductors) and ceaselessly corrected my transcripts. She truly helped me to complete all my books by her friendly support, patience, enthusiasm and encouragement – kindheartedly tolerant to my ceaseless chaotic nature. Similarly my heartfelt thanks are directed to my children, *Alžběta* (26) and *Pavel* (24), who always provided beneficial critique, helped to keep a pleasant family environment, and also aided my photography attempts – all of whom I have most earnestly dedicated the book.

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INDIVIDUALITIES

Agricola Georgius (Georg Bauer) (1494–1555) Ger. phys. working in Bohemian town Jáchymov, father of mineralogy (devised system of classification of geological specimens), inventor of modern concept of mining ('De re metallica libri XII' 1556)

Agrippa (von Nettesheim) Cornelius Heinrich (1486–1535) Ger. phys., urged return to beliefs, supporter of mystical philosophy (3 spheres – elements, stars, spirit)

Amontons Guillaume A. (1663–1705) Fr. phys., concept of absolute zero thermodynamic temperature at which gas pressure vanishes, constr. of thermometers and barometers

Ampère Marie André (1775–1836) Fr. phys., founder of electrodynamics (Ampère's Law), inventor of galvanometer ('Théorie des phénomènes electro-dynamiques' 1826)

Anaxagoras of Clazomenae (500–428 BC) Gr. phil., existence results from ordering of seeds by infinite mind (concept of atoms), theory of perspectives

Anaximenes of Miléto (588–528 BC) Gr. phil., conceptions of physical rather than moral law governing cosmos

Andrews Thomas (1813–1885) Irish chem., critical temperatures of gases, heat of chem. combustion

Aristarchos of Samos (3rd century BC) Gr. astr., fixed stars and the sun remain immobile while the Earth revolves about the sun, distance problem by trigonometry

Aristotle (384–322 BC) Gr. phil., (author: Categories; On Interpretation; Prior Analytics; Metaphysics; Ethics; etc.), accepted 4-element theory (+ ether), rejected void, propelling force inversely proportional to resistance, introduced variables into logic, held heat to be center of heat and life

Arrhenius Svante August (1859–1927) Swed. chem, formulated theory of electric dissociation later extended to rate of chem. reactions (Arrhenius constant), discovered expression for latent heat as a function of raising boiling point through dissolved nonvolatile components, appreciated light pressure in cosmic physics, studied reaction velocities, viscosities ('Teorien der Chemis' 1900) and even first noting global warming

Avicena (Abu'ali al-Husain ibn Abdallah, Ibn Sina) (980–1037) Pers. physician, author of Canon of Medicine, studied therapeutic measures, used methods of Aristotle, suggested speed of light must finite quantity, rejected metallic transmutations

Avogadro Lorenzo Romano Amedeo Carlo (1776–1856) It. phys., equal volume of gases at (at the same T and P) contain identical number of particles (Avogadro's Law), studied specific heats, expansion

Babbage Charles (1792–1871) Brit. math., referred as the father of computing in recognition of his design of two machines, the difference engine for calculating tables of logarithms by repeated additions performed by trains of gear wheels, and the analytical engine designed to perform a variety of computations using punch cards

Bacon Francis, Lord Verulam (1561–1626), Brit. phil., inventor of inductive method and empiricism, identified nag.

Force gravitation, held heat is motion, showed salt lower melting point of ice

Baekeland Leo Hendrik (1863–1944) Belg. chem., synthetic resin, plastics (bakelite), contributed electro-chemistry ('Some Aspect of Industrial Chemistry' 1914)

Barrow John D. (1652–) Brit. phys., protagonist of cosmology and gravitation theory as well as aspects of the history and philosophy of science, writer of popularizing books

Bartoli Adolfo (1851–1896) It. phys., radiation pressure of light, specific heat of water and its dissociation, heat engine based on light

Becquerel Antoine César (1788–1878) Fr. phys., cofounder of electrochemistry ('Éléments de l'électrochimie' 1843), used platinum and palladium to measure high temperatures

Becher Johann Joachim (1635–1681), Ger. chem. working in medicine, mineralogy, economics, developer of theory that burning substances are losing their anima, i.e., 'phlogiston'

Beilstein Friedrich Konrad (1838–1906) Rus. chem. and professor in Petersburg Univ., research in anal. and org. chemistry ('Handbuch de Organischen Chemie, 1880)

Belousov Boris Pavlich (1893–1970) Rus. pediatr., problems of protein regime, known for unsuccessful persuading unusual oscillatory manners of some chemical reaction

Bénard Henri (1885–1973) Fr. sci., who made his famous discovery on convection rolles during his thesis based on early studies of B. Thompson (see Strutt)

Berg Lev Germanovich (1896–1974) Rus. chem., originator of thermoanalytical instrumentation

Bergman Tobern Olaf (1735–1784) Swed. chem., founder of mineral chemistry, its classification and quantitative determination of composition, developed theory of chem. affinity

Bernoulli Daniel (1700–1782) Swith math., early formulation of principle of energy conservation, pressure as result of particles impact on the container, differential calculus application in theory of probabilities, acoustics ('Hydrodynamica' 1738)

Bernoulli Johann (1667–1748) Swiss math., developer of differential, integral and exponential calculus, law of quantity conservation – mv^2 ('vis viva')

Bertalanffy (von) Ludwig (1901–1972) Austr. born, Can. biol., research in ordaining conception in biology, inventor of general 'organismic' system theory and comparative physiology ('Modern Theories of Development' 1933)

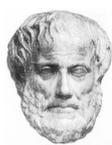
Berthelot Marcelin (1827–1907) Fr. chem., enunciated the principle of maximum work, known for his sharp criticism ('Essai de mécanique chimique fondée sur la thermo-chimie' 1879)

Berzelius Jöns Jacob Baron (1779–1848) Swed. chem., founder of modern chemistry ('Theory of Chemical Proportions' 1814), oxygen as the standard for atomic weights, pioneered gravimetric analysis

Bessel Friedrich Wilhelm (1784–1864), Ger. astron., Bessel's geoid, theory of errors, Bessel's functions



Agricola



Aristotle



Arrhenius



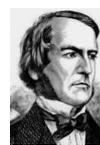
Belousov



Black



Boltzmann



Boole



Boyle

Individualities

Biot Jean Baptiste (1774–1862) Fr. phys., who invented polariscope, fundamental laws of heat, magnetism

Black Joseph (1728–1799), Brit. prof. in Glasgow and Edinburgh, helped lay foundations for quantitative analysis, recognized that heat quantity is different form of heat intensity, concept of specific heats

Boerhaave Herman (1668–1738) Dutch chem., introduced modern concept of chemistry ('Chemical Textbook' 1732)

Bogdanov Alexander Alexandrovich (1873–1928) Rus. phil., who made sophisticated reinterpretation of Mach's empiriocriticism, known for calculating automata, who proposed that all phys., biolog., and human sciences be unified by treating them as systems of relationships ('Tectology: universal organization')

Bohr Niels Henrik David (1885–1962) Danish phys., known for Bohr's model of atomic structure, spectroscopic data to explain internal structure, electrons in the outer-most shall determine chem. properties ('Atomic Theory and the Description of Nature' 1934)

Bolos of Mendes (pseudo-Democritus, circa 200 BC) Gr. nat. sci., probably earliest Greek writer on alchemy ('Psychica at Mystica')

Boltzmann Ludwig Eduard (1844–1906) Austr. phys., cofounder of equipartition theory, kinetic theory of gases leading to theory of statistical dynamics, Stefan-Boltzmann Law of radiation

Boole George (1815–1864) Brit. logician, invented the symbolic processes of algebra as tools of numerical calculation, in which symbols are used to represent logical operations. In his book 'An Investigation of the Laws of Thought' (1854) the mathematical theories of logic and probabilities was proposed as well as the calculus (taking one of only two values 0 and 1–Boolean algebra)

Boyle Robert (1627–1691) Brit. chem., disaffirming the indoctrination of four elements, cofounder of "British Royal Society" and scientific journal "Philosophical Transactions", designed vacuum pump, chemistry of combustion and respiration

Bravais Auguste (1811–1863) Fr. phys., upon observing natural crystals he grouped them into seven crystal systems. A Bravais lattice is called after him, which is an infinite array of discrete points with an arrangement and orientation that appears exactly the same viewed from any point of the array ('Etudes cristalographiques' 1851)

Brouwer Luitzen Egbertus Jan (1881–1966) Dutch. math., founder of modern topology, proved that dimensionality of a Cartesian space is topological invariant, worked in point sets

Brown Robert (1773–1858) Scot. botan., studied plant physiology, known for Brownian movement of microscopic particles

Bruno Giordano (1548–1600) It. phil., drew his cosmology from Copernicus and Lucretius, conceived that Earth revolves around the sun, stars being the center of other planetary systems, burned at stake

Bunsen Robert Wilhelm (1811–1899) cofounder of spectroscopy, investigated variation of melting point with pressure, galvanic battery, new types of labor. equipments (Bunsen burner)

Callen Herbert Bernard (1919–1990) Amer. phys., research on solid-state physics, thermodynamics and statistical mechanics, fluctuation-dissipation theorem

Cantor Georg Ferdinand Ludwig Philip (1845–1918) Ger. math., developed theory of sets, defined real, irrational and transfinite numbers

Carnot Sadi Nicolas Léonard (1796–1832) Fr. phys., founder of thermodynamics (Carnot cycle)

Casimir Hendrik B. G. (1909–1980) Dutch phys., mathematical formalism of quantum-mechanics, hyper-fine structures, thermodynamics, influence of retardation on Van der Waals forces (Casimir forces)

Cavendish Henry (1731–1810) Brit. chem., revealed composition of water, hydrogen, believed that heat is caused by internal motion, anticipated much of the work of the next half century though he published almost nothing, experimentally defined gravitation constant and work on electricity laws

Cayley Arthur (1821–1895) Brit. math., theory of matrices and groups, invariance algebra of matrices, geometry of n-dimensional space,

Celsius Anders (1701–1744), Swed. astr., Earth's ecliptic obliquity, temperature scale

Clapeyron Benoit Pierre Émile (1799–1864) Fr. eng., mathemat. theory of elasticity of solids, found relation between conversion of heat, steam, pressure and volume changes, help construction of locomotives

Clausius Rudolf Julius Emmanuel (1822–1888) Ger. math., reconciled Carnot's theory of heat to equivalence of heat and work (2nd Law of thermodynamics), changes of state (Clausius-Clapeyron equation), contributed theory of electrolysis

Colemann D. Bernard (1930–) Amer. math., researched hydrodynamics of non-classical fluids, theory of wave propagation in materials with memory, co-founder of rational thermodynamics

Comenius (Komenský) Jan Amos (1592–1670) Czech educator and expatriate, known as the 'teacher of nations' who necessitated spontaneity ('Janna Linguarum reserata', 'Orbis Sensualium Pictus' or 'Didactica ragna')

Copernicus Nicolaus (Kopernik Nikolai) (1473–1543) Pol. astron., worked out details of heliostatic theory of solar system, possibly the greatest astronomer since Ptolemy,

Coriolis Gustave Gaspard (1792–1843) Fr. phys., developed theory of relative motion, mechanics, powers and motion, modern definition of kinetic energy ($mv^2/2$)

Čápek Vladimír (1943–2002) Czech phys., studies in quantum transport, quantum limits to the second law of thermodynamics

Dalton John (1766–1844) Brit. chem., founder of atomic theory ("New System of Chemical Philosophy" 1808), deve-



Bravais



Carnot Sadi



Casimir



Clausius



Coleman



Comenius



Debye



Einstein

loped (Dalton's) Law of partial pressures, arranged table of relative atomic weights, chemical stoichiometry in simple numerical ratios by weight

Davy (Sir) Humphrey (1778–1829) Brit. chem., founder of electrochemistry, showed melting of ice pieces by mutual friction below their freezing temperature – heat a form motion, theory of galvanic decomposition, transmission of thermal radiation through vacuum

De Fermat Pierre (1601–1665) Fr. math., devised principle of least time (action) and Fermat's small and big (last) theorem, father of modern theory of numbers, probabilities

De Groot Sybren Ruuds (1916–1990) Dutch phys., research on thermodynamics of irreversible phenomena, relativistic theory of statistic electromagnetic phenomena

Debye Petrus Josephus Wilhelmus (1884–1966) Dutch phys. chem., dipole moments and molecular structure, structure analysis of powdery crystals by means of X-ray diffraction, study of polymers

Democritos (460–370) Gr. phil., known for his cosmological and atomic theories, behavior of atoms is governed by unbreakable natural laws and their aggregates are formed by kind of hook and eye mechanism, investigated structure of human body regarding soul as material, compiled ethical concepts

Denbigh George Kenneth (1911–1989) Brit. phys. chem. protagonists of thermodynamics, first class educator

Descartes René du Perron (Cartesius Renatus) (1596–1650) Fr. math. and physic., known for preservation of motion ($\approx mv$) as an universal principle, studied geometric forms by algebraic means, gave rules of signs, identified matter with extension (nonexistence of voids, 'Principia Philosophiae' 1644), study of meteorology, causality ("cogito ergo sum")

Dewar (sir) James (1842–1923), Brit. chemists, obtained liquid hydrogen, low temperatures (Dewar flask)

Diesel Rudolph Christian Karl (1858–1913) Fr. eng., inventor of diesel engine by ignition through compression

Diokles of Karystos (≈ 400 –350 BC) Gr. phys., idea of pneuma, believed that both sexes contribute to embryo formation

Diviš Prokop (Divish Procopius) (1696–1765) Czech phil. and experim., studied hydrodynamics, electrophysiology and electricity, known as the inventor of lightening rods (1753) proposing their wider use

Du Bois-Reymond Emil Heinrich (1818–1896) Ger. physiol., showed that electric phenomena occur in muscular activity, physiology of muscles, measurable velocity of nerve impulses

Duhem Pierre Maurice Martin (1861–1916) Fr. phys., attempt to construct a general energetic and abstract thermodynamics using axiomatic-deductive approach, theory of elasticity and hydrodynamics ('Le potentiel thermodynamique' 1886)

Dulong Pierre-Louis (1785–1838) Fr. chem., research on refractive indices and specific heats of gases, co-formulated

Dulong-Petit's law, devised empirical formula for the heat values calculation of fuels upon their chem. composition

Einstein Albert (1879–1955) Ger. phys., originator of theories of relativity, laws of motion and rest, simultaneity and interrelation of mass and energy, quantum theory of photoelectric effect, theory of specific heats, Brownian motion, etc. ('Builders of the Universe' 1932), widely characterized elsewhere

Empedokles of Akragas (492–432 BC) Gr. phil., originated classical doctrine on 4 elements, held the Earth to be spherical and planets moving through space, changes could be understood in terms of motion

Epikouros of Samos (342–271) Gr. phil., adopted atomism as mechanistic explanation of universe, pleasure must be life of prudence, honor and justice

Eukleidés of Alexandria (365–300 BC) mathematician, founder of Euclidian geometry

Euler Leonhard (1707–1783) Swiss math., most prolific mathematician, algebraic series, functional notations (Euler numbers), imaginary numbers (i), topology, differential equations, mechanic of fluids, hydrodynamics, oscillations

Fahrenheit Gabriel Daniel (1686–1736) Pol. phys. working in Amsterdam, inventor of alcohol and mercury thermometers dressed with his temperature scale, discovered undercooling of water

Faraday Michael (1791–1867) Brit. phys., one of the greatest experimentalists, explained electromagnetism, introduced concept of magnetic lines, Faraday's laws of electrolysis, unit of electrostatic capacitance named farad

Favre Pierre-Antoine (1813–1880) Fr. chem., known for series of then rather precise calorimetric determinations of heats involved in various chemical reactions

Fechner Gustav Theodor (1801–1887) Ger. phil., pioneering psycho-physics, measuring sensation indirectly in units corresponding to the just noticeable differences between two sensations, cofounder of the famous W-F physiological law ('Elemente der Psychophysik' 1860)

Feigebaum Mitchell Jay (1945–) Amer. phys., famous for discovering the constant 4.6692... for i^{th} bifurcation ($\lim_{i \rightarrow \infty} = d_i/d_{i+1}$) named after him (Feigebaum numbers), his disclosures spanned new field of theoretical and experimental mathematics

Feynman Richard Phillips (1918–1988) Amer. phys., quantum electrodynamics, devised Feynman diagrams as means for accounting possible particle transformations ('Theory of Fundamental Processes' 1961)

Fibonacci Leonardo of Pisa (~ 1170 –1230) It. math., best known for his book of Abacus, putting thus end to old Roman system of numerical notations, his series are now called Fibonacci's

Fick Adolf Eugen (1829–1901) Ger. physiol. who made important discoveries in every branch of psychology, well-known for the Law of diffusion (Ann. Phys. 94(1855)59) named after him



Eukleidés



Euler



Fechner



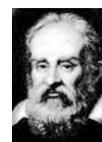
Feigebaum



Feynman



Fourier



Galile



Gamow

Individualities

Fourier Jean Baptiste Joseph (1768–1830) Fr. math., evolved mathematical series known by his name and important in harmonic analysis, providing source of all modern methods in mathematical physics, originated Fourier's theorem on vibratory motions

Frankenheim Moritz Ludwig (1801–1861) Ger. phys., modern structural theory of crystals, introduced cooling curves to study materials (temperature vs. time)

Frankland (Sir) Edward (1825–1899) Brit. chem., organo-metallic compounds, effect of atmospheric pressure on combustion, modern concept of valence, studied flame and luminosity

Friedman Aleksandr Aleksandrovich (1888–1925) Rus. math. and astron., known for nonstationary solution of general theory of relativity, cofounder of dynamic meteorology who anticipated theory of Big Bang

Fürth Reinhold Heinrich (1893–1979), Czech born, Ger. and Brit. physicists, authority in statistical mechanics and Brown movement who gave stochastic approach to quantum mechanics

Galen Klaudios (Galenos of Pergamum) (129-199 AD), Gr. physiol., systemized and unifies Greek anatomic and medical knowledge, possibly a founder of modern science, believed that mind is located in brain

Galilei Galileo (1564–1642) It. astr., showing that velocity of a falling object is proportional to (g t) but not to its weight, invented hydrostatic balance, discovered numerous stars and planets, analyzed projectile motion, gave apparatus for temperature measurements

Gamow George (1904–1968) Rus. born US phys., applied nuclear physics to problems of stellar evolution, proposed theory of origin of chemical elements by successive neutron capture and creation of the universe from a singularity ('Thirty Years that Shock Physics' 1965) and even went to analyze coding for triplet-system of proteins

Gassendi Pierre (Gassendus) (1592–1655) Fr. phil and math., held that atoms differed in size, weight and shape, gaseous pressure is due to collisions, measured velocity of sound

Gauss Karl Friedrich (1777–1855) Ger. math., fundamental theorems of algebra and contribution to modern number theory (Gaussian integers), vectorial representation of complex numbers, method of least squares and observational of errors, unit of magnetic field gauss named in his honor

Gay-Lussac Joseph Louis (1778–1850) Fr. chem., discovered law which states that all gases expand equally for equal increment of temperature, verified law of capillary action, investigated temperature solubility of salts, invented hydrometer, barometer, thermometer

Gibbs Josiah Willard (1839–1903) Amer. phys., father of thermodynamics of heterogeneous substances where he established theoretical basis of physical chemistry (Gibbs phase rule), vector analysis in crystallography, statistical mechanics, even patented railroad brake

Glauber Johann Rudolph (1604–1670) Ger. professor of chemistry in Heidelberg, who invented various synthetic and analytical reactions, gave new philosophy of stills and furnace construction and operation

Gödel Kurt (1906–1978) Czech born US logician who gave proof of completeness of predicate logic and showed that inconsistency cannot be proved in the same system ('Consistency of Continuum Hypothesis' 1940)

Guggenheim Edward Armand (1901–1980) Brit. phys. chem., applications of thermodynamics and statistical mechanics to properties of gases, mixtures, electrolytes

Guldberg Cato Maxmilian (1836–1902), Norw. chem., developed chemical law of mass action, studied chemical equilibrium and reverse reactions

Guthrie Frederick (1833–1886) Brit. phys., studied magnetism, electricity, vibration, cryohydrates ('Elements of Heat' 1868)

Hájek Tadeáš from Hájku (Thaddeus Hagecius) (1526–1600) Czech. astr., alchemist. and personal physician of the Roman Emperor Rudolph II (see Rudolph)

Hamilton (Sir) William Rowan (1805–1865) Irish mathematician introducer of quaternions, alternative formalism for tensor and vector calculation, widely used operation by "Hamiltonian"

Hannay James Ballantyne (1855–1931) introductory experimentation on isothermal mass-change curves

Hausdorff Felix (1868–1942) Jew math. at the Ger. University of Bonn, known for fractal-preceding dimension named after him

Heisenberg Werner Carl (1901–1976) Ger. phys., who worked on atomic structure and founded quantum mechanics, evolved uncertainty principle named after him, suggested that laws of subatomic phenomena be stated in terms of observable properties, involved in the unified field theory ('Das Naturbild der heutigen Physik' 1955)

Helmholtz Hermann Ludwig Ferdinand (1821–1894), Ger. physiol., study on mechanism of eye and ear, theory of music, ('Über die Erhaltung der Kraft' 1847 and 'Handbuch der physiologischen Optik' 1867), credited with explication of conservation laws, elaborated on electrodynamics and indicated electromagnetic theory of light, studied vortex motion in liquids

Helmont (van) Joannes Baptist (1579-1644) Belg. physician, confided in alchemy but rejected 3 principles and fire as element since it has no matter, taught indestructibility of matter, used graduated air thermoscope to measure temperature, thought origin of bodies are water and ferment

Herakleitos of Ephesus (540-480), natural philosopher believing to fire as a central principle, known for his pessimistic view of life

Hermes Trismegistos (Mercurius Termaximus, conceivably the King of Egypt known as Sifaos, ~ 1996 BC, and identified with God Hermes by Greek literature written circa 100-300 AD), legendary person accredited to the foundation of alchemic clandestine books



Gay-Lussac



Gibbs



Heisenberg



Hooke



Joule



Kelvin



Kepler



Kirchhoff

Individualities

Heron of Alexandria (about 1st century) Gr. math., arithmetic solution of quadratic equations, inventor devices operated by steam, fire engine pumps

Hésiodos (about 8–7th century BC) Gr. poet, known for ‘Theogoniá’ essay of myths systematic trying to give the history of world

Hess Henri Germain (1802–1850) Swiss, prof. of chem. in Rus. St. Petersburg Univ., founder of thermochemistry, formulated (Hess’) Law stating that amount of heat evolved is irrespective to intermediary stages

Heyrovský Jaroslav (1890–1967) Czech phys. chem., discoverer of polarography

Hilbert David (1862–1943) Ger. math., investigated theory of numbers and relative fields, developed Hilbert space in work on integral equations

Honda Kótaro (1870–1954) Jap. phys., who pioneered thermogravimetric measurements and who introduced strongest steel and magnet

Hooke Robert (1635–1703) Brit. naturalist, cofounder of vibration theory, who devised an equation describing elasticity that is still used today (“Hooke’s Law”), worked out the correct theory of combustion, assisted Robert Boyle in studying the physics of gases and improved meteorological instruments (barometer)

Hubble Edwin Powell (1889–1953) Amer. astr., initiated the study of the universe beyond our galaxy (‘Observational Approach to Cosmology’ 1937), classified galaxies and discovered that their radial receding velocity is proportional to their distance (Hubble’s Law)

Huygens Christian (1629–1695) invented pendulum, conservation mobility ($\approx mv$)

Charles IV (1316–1378) Rome emperor and famous Bohemian king (1346), supporter of idea of ‘greater Europe’ founder of the first middle European university

Joule James Prescott (1818–1889) Brit. eng. who quantified heat liberated upon the electric passage through resistance, unit joule named after him

Kamerlingh-Onnes Heike (1853–1926) Dutch phys., obtained liquid helium, found superconductivity of mercury, studied magnetic and optical properties at low temperatures

Kauzman Walter (1916–1980) Amer. chemists, studied thermodynamics and statistics, glasses

Kekulé Friedrich August (from Stradonitz) (1829–1896), author of carbon tetravalent chemical bonding, visualized aliphatic chain series and closed-chain structure of benzene

Kelvin, Baron of Larges (Lord Thompson Williams) (1824–1907) Scot. math., did important contribution in most branches of physical science, developed dynamic theory of heat, collaborated in investigating Joule-Thompson effect, propose absolute scale of temperatures, invented various electric measuring devices and even developed improved mariner’s compass still used today

Kepler Johannes (1571–1630) most famous astronomer who laid the foundation of modern astronomy, studied nature of light and introduced concept of rays, made use of logarithm

Kirchhoff Gustave-Robert (1824–1887) Ger. phys., did spectrum analysis, black-body concept, formulated Kirchhoff’s laws of electricity

Kolmogorow Andrej Nikolajevich (1903–1970) Rus. math., known for theory of functions, concept of probability, irrational functions (‘Basic Concepts of Probability’ 1936)

Komenský, see Comenius

Kreidl Norbert Joachim (1904–1994) Czech origin, US phys. and eng., investigated optical properties of glass, its structure and composition

Kurnakov Nikolaj Semenovič (1860–1941) Rus. thermoanalyst, inventor of the drum photographic recording used in thermal analysis

Lagrange Joseph Louis (1736–1813) Fr. math., showed mechanics could be found on the principle of least action, studied perturbations, hydrodynamics, developed calculus of variations, partial differential equations

Landau Lev Davidovich (1908–1968) Rus. phys., developer of thermodynamic theory of second-order transformations, superfluidity, low temperature physics (‘Continuum Mechanics’, ‘Hydrodynamics and Theory of Elasticity’ 1944)

Laplace Pierre Simon (1749–1827) Fr. math., laid foundation of thermochemistry, theory of probability, made much use of potential partial differential equations since named after him, conducted experiments of specific heat and heat of combustion, developed ice calorimeter

LaViolette Paul A. (1948 –) Amer. astrophys., developer of subquantum kinetics and continuous creation model of the universe, and novel approach to microphysics that accounts for forces in a unified manner

Lavoisier Antoine Laurent (1743–1794) Fr. chem., discovered relation between combustion and oxygen, divided substances into elements and compounds, explained respiration, disproved phlogiston, introduced quantitative methods to chemistry

Legendre Adrien Marie (1752–1833) Fr. math., gave important works on elliptic integrals, laws of quadratic reciprocity, created spherical harmonics, known for Legendre transformations used in thermodynamics

LeChatelier Henry-Louis (1850–1936) Fr. metallurg., did chemistry of silicates and cements, physics of flames, thermodynamics, used first the dependence sample vs. environmental temperature, devised optical pyrometer

LeChatelier Luis (1815–1926) Brit. mine eng., tested products with aluminum content, patented steel production, thermometry – use of thermocouples

Leibniz Gottfried Wilhelm (1646–1716) Ger. math., showed the lost of motion after collision as ‘vis viva’ similarly to ‘vis mortua’, introduced modern mathematical notations, postulated theory of monads (building block of universe) and even designed wagon wheels

Lémery Nicolas (1645–1715) Fr. chem., founder of numerous applications of chemistry in medicine, studied theory of volcanoes, authored textbooks on chemistry (‘Cours de chimie’ 1675)



Landau



Laplace



LaViolette



Leibniz



Lewis



Mandelbrot



Maxwell



Mendelejev

Individualities

Lenoir Jean Joseph Etienne (1822–1900) Belg. inventor, invented workable internal combustion engine, electric motor and signal system for railroads, studied galvanoplastic reproduction

Leonardo Da Vinci (1452–1519) It. artists, one of greatest and most versatile geniuses, commencing those moving bodies can transfer motion which in total is unchanged, among other designed gliders, parachute, elevator, steam gun, studied human anatomy, etc.

Leukippos of Miletos (~ 500–440 BC), Gr. phil., cofounder of atomistic theory, bodies are in circular motion move from center, motion is made possible by positioning empty space

Lewis Gilbert Newton (1875–1946) Amer. chem., studied thermodynamics and free energy of substances, valence and structure of molecules ('Anatomy of Science' 1926)

Libavius Andreas (Liebau) (1540–1616), Ger. physic., histor. and alchemist who described dry reactions in assaying metallic ores, detailed aqueous analysis ('Alchemia' 1597 in which second edition 1606 is the section 'De Pyrotechnica')

Liesegang Raphael Eduard (1869–1947) Ger. phys. chem., expert in dye chemistry who worked systematically in periodic precipitations (known for Liesegang rings)

Linnaeus (Carl von Linné) (1707–1778), Swed. botanists known as father of modern synthetic botany, known for reversing the Clausius scale (freezing 100–boiling 0)

LOBACHEVSKI Nikolaj Ivanovich (1793–1856), Rus. math. who gave innovative geometry reflected on the curved surface of sphere

Lomonosov Michail Vasilijevich (1711–1765) Rus. math., founder of Moscow university, introduced comprehensive system of non-Euclidean geometry

Lorentz Hendrik Antoon (1853–1928), Dutch phys., authority in quantum physics, electromagnetism, thermodynamics, radiation, behavior of light, electron theory of matter, hydrodynamics (mostly cited for Lorentz transformation)

Lulla, Lullius Raimundus (1235–1315) physician and alchemist, devised what he considered an infallible method of proving faith and reason, invented mechanical device (ars magna) which combined subjects predicated of propositions thus producing valid conclusions

Mach Ernst (1838–1916) Aust. phil. and phys., known for his discussion of Newton's Principia and critique of conceptual monstrosity of absolute space ('The Science of Mechanics' 1883)

Maimonides (Moses ben Maimon called Rambam) (1135–1204) Sephardic born Jewish physic. and phil., foremost intellectual figure of medieval Judaism, who tried to merge belief with learning and who recovered Aristotle's ideas ('Guide of the Perplexed' or 'Treatises on Logic' 1165)

Mandelbrot Bezat Benoit (1924–) Pol. born Fr. math., based mathematical theories for erratic chance phenomena and self-similarity, fractal dimension

Marcus Marci Jan (from Kronland) (1595–1667) unknown Bohemian scientist, author 'De proportione motu', already noting principles of the light diffraction, studied impact of bouncer balls

Maupertuis Pierre Louis Moreau (1698–1759) Fr. math. known for the principle of least action

Maxwell James Clerk (1831–1879) Brit. phys., validated kinetic theory of gases, applied dynamical equations in generalized Lagrangian form and showed that electromagnetic action travels through space in transverse waves, as does light, symmetrical (Maxwell) equations of continuous nature of electric and magnetic field used today ('Matter and Motion' 1876)

Mayer (von) Julius Robert (1814–1878) Ger. phys., determined quantitatively equivalence of heat and work, studied principle of conservation laws even extended to living and cosmic phenomena

Mayow John (1641–1679) Brit. chem., studied similarity between chem. process of combustion and physiological function of respiration, showed that only part of air is used in combustion

Mendeleyev Dmitrii Ivanovich (1834–1907), Rus. chem., gave periodic classification of elements, discovered periodicity in their chem. and phys. properties, investigated thermal expansion of liquids ('Principles of Chemistry' 1868)

Meyer Johann Friedrich (1705–1765) Ger. chem., known for theory of 'acidum pingui', contestant of Black's theory

Milesians School see *Thales*

Napier John (1550–1617) Scot. math., best known inventor of logarithm, originated Napier's rules of circular parts for solution of spherical triangles and also Napier's bones (antecedent of a logarithmic rule)

Nernst Hermann Walther (1864–1941) Ger. phys., devised theory of electrothermic potentials, developed third law of thermodynamics and use of low temperature calorimetry

Neumann (von) Johann (Jánoš) (1903–1957) Hung. born US math., known for introducing premises of electronic computing devices and theory of games, math. logic and theory of continuous groups, showed math. equivalence of Schrödinger's wave mechanics and Heisenberg's matrix mechanics ('Mathematical Foundation of Quantum Mechanics' 1931)

Newcomen Thomas (1663–1729) Brit. inventor, known for atmospheric steam engine and its application for pumping water from mines

Newton (Sir) Issac (1642–1726) Brit. math. (phys. and unfamiliar alchem.), most famous scientist, founder of mechanics, extensively described elsewhere

Noether Max (1844–1921), Ger. math., theory of algebraic functions, symmetry aspects

Norton Thomas (1437–1514) Brit. alchemist who recognized importance of color, odor and taste as guides in chemical analysis, improved thermal regime of furnaces

Odling William (1829–1921) Engl. chem., did early research on problems of valence and bounding and table of elements ('Outlines of Chemistry' 1869)



Napier



Newton



Onsager



Paracelsus



Penrose



Planck



Poincaré



Prigogine

Individualities

Ohm Georg Simon (1789–1854) Ger. phys., Found (Ohm's) Law relating resistance to voltage and current strength, studied temperature resistance of metals, unit of electrical resistance named after him

Oinopidés of Chia (\approx 500 BC) Gr. math. and astr., supposed discoverer of ecliptic

Onsager Lars (1903–1976) Norw. chem., researched protonic semiconductors, helped theory of dielectrics, reciprocal transport relations in irreversible thermodynamics named after him

Ostwald Friedrich Wilhelm (1853–1932) Ger. chem., founder of modern physical chemistry, research in equilibrium and rates of chem. Reactions, protagonists of 'energetism'

Otto Nikolaus August (1832–1891) inventor of internal combustion engine

Papin Denis (1647–1712) Fr. phys., improved air pump, discovered principle of siphon, demonstrated (and practically used) that at increased/decreased pressure the boiling point is raised/lowered, improved gunpowder and steam engine

Paracelsus Theophrastus Bombastus von Hohenheim (Philippus Aureolus) (1493–1541) Ger. alchem. and phil., postulated internal 'archei' which acted as alchemists within body separating pure from impure, concept resulted in view of local centers of disease as imbalance of humors (liquid) throughout the body

Pascal Blaise (1623–1662) Fr. math., known for Pascal triangles, builder of first mechanically calculating machines as computer precursors, theory of probability and combinatorial analysis, increased knowledge of atmospheric pressure (denied horror vacui), founder of hydrodynamics formulating law which bears his name, pressure applied to fluid is transmitted unidirectionally

Patzier Michal Ignac (1748–1811) Slovak metallurg., author of indirect amalgamating technology and organizer of the first internat. conf. on natural sciences (Skelné Teplice 1786)

Peano Guisepe (1858–1932) It. math., founder of symbolic logic, non-Euclidean geometry, known for construction of space-filling curve named after him (Peano's axioms)

Peltier Jean Charles Athanase (1785–1845) Fr. phys., watchmaker, discovered a thermo-electric reduction of temperature which effect is named after him

Penrose Roger (1931–) Amer. math., suggesting that all calculation about both micro- and macro- worlds should use complex numbers, which would require reformulation of major laws of physics, famous astronomer and physicist who proposed a new model of universe whose building blocks he called 'twistors' (Penrose tilings).

Petit Alexis-Thérèse (1791–1820) Fr. phys., co-developed methods of determining thermal expansion and specific heats of solid bodies

Philolaos of Tarentum (\approx 500 BC) Ger. phil., held the earth is not center of universe but that is stars and planet circle about central fire

Pictet-Turrentin Marc-Auguste (1752–1825), Swiss phys., who attempted to measure velocity of heat

Planck Max Carl Ernst Ludwig (1858–1947) Ger. phys., best know for Planck's constant representing quantum action, blackbody radiation, thermodynamics, physics before his quantum theory is often called classical

Pláton (Plato) (427–347 BC) most famous Ger. phil., well characterized elsewhere, Platonism in science has general meaning of emphasis on a priori abstract mathematical thinking

Poincaré Henri Jules (1854–1912) Fr. math., gave theory of functions, researched differential equations, theory of astronomical orbits, 3-body problem, theory of light, dimension and relativity ('Thermodynamique' 1892, 'Calculs des probabilités' 1896, 'La science et l'hypothèse' 1906)

Poncelet Jean Victor (1788–1867) Fr. math., formulated principle of continuity, termed energy, gave practicable theory of turbines, Poncelet's overfall (meaning device) in hydrology

Popper (sir) Raimund. Karl (1902–1994) Austr. sci. and phil., known for theory of cognition and science (epistemology), defender of open thinking and society ('Logic der Forschung')

Prandtl Ludwig (1875–1953) Ger. phys., founder of modern hydrodynamics and aerodynamics, proved sound barrier, boundary layer on moving surfaces in liquids, Prandtl number named after him

Presl Jan Svatopluk (1791–1849) originator of modern Czech nomenclature in chemistry and botany

Pribram Karl Harry (1919–) Austr. born US psychol., gave systematization of neuropsychological data, founder of TOTE units as an alternative to reflex arcs providing cognitive structure to cognition ('Languages of the Brain' 1971 or 'Brain and Perception' or 'Holonomy and Structure in Figural Processing' 1991).

Priestley Joseph (1733–1804) Brit. chem., phlogistonist, explained some composites of air, history of electricity and light

Prigogine Ilya (1917–2003) Rus. born Belgian phys. chemist, inventor of nonequilibrium thermodynamics, propagator of the theory of chaos ("La nouvelle alliance avec la nature")

Proust Louis Joseph (1754–1826) Fr. chem., established experimentally (Proust's) Law of definite portions, discovered sugar in some vegetables

Ptolemaios Klaudios (\sim 85–165 AD) Egyp. born, Gr. astr. who gave the first plausible explanation of (the Earth-centered) celestial motions, studied trigonometry and stereographic projections, attempted theory of refraction ('Syntaxis megale', 'Almagest' – most influential work in astronomy)

Pythagoras of Samos (582–494 BC) Gr. phil., best known for Pythagorean theorem, credited with discovery of chief musical intervals, attempted to interpret world through numbers having classified numbers into odd and even,



Pythagoras



Regner



Reinizer



Shanonn



Schrödinger



Sierpinski



Šimerka



Škrumovský

stressed deductive method in geometry, presupposed central fire around which celestial bodies circle

Ramsay (Sir) William (1852–1916) Brit. geolog., gave asymptotic continuous record of heating hydroxides, geographical mapping (stratigraphy)

Rankine William John Macquorn (1820–1872) Scot. phys., researched thermodynamic theory of steam, engine performance, water waves

Raoult Francois Marie (1830–1901) Fr. phys., developed (Raoult's) Law for vapor pressure of solvent in solution being proportional to the number ratio of solvent/solute molecules, demonstrated depression of freezing points proportionally to concentration of dissolved substances

Rayleigh see Strutt

Réaumur de Rene-Antoine Ferchault (1683–1757) Fr. chem. and naturalist, invented method of tinning iron and porcelain, his temperature scale reading from 0 to 80, showed impact of heat on insect development

Regnault Henri Victor (1810–1878) Fr. chem., measured specific heats, vapor pressures of mixtures (Regnault's hygrometer), participated in early adjustment of phys. constants and laws

Regner Albert (1905–1970) Czech phys. chem. who gave thermodynamic basis to electrochemical technology, first class educator

Reinizer Friedrich (1857–1927), Czech born discoverer of cholesterol (including its metamorphosis and stoichiometry formulae $C_{27}H_{46}O$) known for introducing the field of liquid crystals (later widespread by *Otto Lehmann*)

Riemann Georg Friedrich Bernhard (1826–1866) Ger. math., introduced idea of finite but unbounded space (Riemann's functions and prime numbers), devised innovative geometry of the saddle-like space, theory of electromagnetic action

Roberts-Austin (Sir) William Chandler (1843–1902) Brit. metal., designed automatic recording pyrometer with Pt-thermocouples for high-temperature study, demonstrated that that diffusion can occur between attached sheets of gold and lead

Rodovsky Bavor jn. from Bavorov (or Hustiřan) (1526–1592), Czech alchemists, author of possibly first book on cookery

Rowland Henry Augustus (1848–1901) Amer. phys., gave mechanical equivalent of heat and of the ohm, studied magnetic action due to electric convection ('Elements of Physics' 1900)

Rudberg Friedrich Emanuel Jakob (1800–1839) Swed. phys., made refraction measurements, inventor of heating and cooling data for investigating alloys

Rudolph II (1552–1612), Rome Emperor and Bohemian King, famous aesthete and upholder of alchemy in Prague

Rumford (see Thompson Benjamin)

Runge Ferdinand Fridlieb (1794–1867) Ger. phil. and chem. who studied processes of dyeing and first noticed creation of fractal structures that anticipated to become the

archetype for artists ('Farbenchemie' Vol. 1, 2 & 3, Berlin 1834–1850)

Searle John R. (1932–) critic of what he terms *strong artificial intelligence*, according to which all there is to having a mind is implementing the right computer program ('Behavioral and Brain Sciences' 1980 and 'The Rediscovery of the Mind' 1992).

Sedziwój Michael (Sendivogius) (1556–1646) Pol. and/or Moravian alchemist who joined service of Rudolph II, known for emphasizing air for life ('Novum Lumen Chymicum' 1614)

Seebeck Thomas Johann (1770–1831) Brit. phys., devised thermocouple, built a polariscope, studied heat radiation, thermomagnetic effect (known as Seebeck's effect)

Shannon Claude Elwood (1916–1980) Amer. math., research on Boolean algebra, cryptography, pioneered information theory, a full statement of which appeared in 'The Mathematical Theory of Communication' (1949)

Scheele Carl Wilhelm (1742–1786) Swed. chem., favored phlogiston theory, demonstrated presence of calcium phosphate in bones, discovered many new substances (oxygen, acids, toxic gases)

Schrödinger Erwin (1887–1961) Austr. phys., research in specific heats of solids, statistical thermodynamics, showed that matrix mechanics can be replaced by wave mechanics, which put new basis to quantum-mechanics, known for Schrödinger wave equation (solution for the stationary state = eigenfunction)

Sierpinski Waclaw (1882–1969) Pol. math. known from the construction known as Sierpinski gasket, researched logical foundation of mathematical and topology ('General Topology' 1952)

Sitter Willem de (1872–1934) Dutch astr. who proposed that the universe is an expanding space-time continuum with motion and no matter ('Astronomical Aspects of Theory of Relativity' 1933)

Sokrates (469–399 BC) Gr. phil., left no writings, devoted life to educating youth

Stahl Georg Ernst (1660–1734) Ger. chem., renamed Becher's 'terra pinguis' as phlogiston, observed acids have different strength, propounded a view of fermentation

Stephenson George (1781–1848) Brit. eng., built locomotive, designed steam locomotive, founder of Brit. railroad system

Stevens Smith Stanley (1906–1973) Amer. psych., experimental psychology where the power law is named after him and used for the measurements and psychological scaling ('Varieties of Temperament' 1942 or 'Experimental Study of Design Objectives' 1947)

Stokes (Sir) George Gabriel (1819–1903) Brit. math., laid foundation of scientific hydrodynamics, theory of fluid motion, Stokes' Law describes motion of small spheres in viscous fluid, established semi-convergent series used with Bessel and Fourier series, studied variation in gravity



Strouhal



Thompson



Trusdell



Turing



Van-der-Waals



Von-Neumann



Watt



Zedeh

Stolcius Daniel (1600–1660) Czech alchemist, author of 'Viridarium chemicum' and cofounder of mystic society 'Fraternitas Roseae Crucis'

Strouhal Čeněk (Vincenc) (1850–1922) Czech phys., first professor of experimental physics to the Czech Technical Univ., known for work in acoustics (Strouhal's eddy pitch) and thermodynamics ('Thermics' Praha 1906)

Strutt (baron Rayleigh) John William (1842–1919) Brit. math., theory of sound, dynamics and resonance of elastic bodies, contributor to optics, acoustics and electricity, hydrodynamics, (Rayleigh number named after him)

Šimerka Václav (1819–1887) Czech priest and math. who introduced valuation in psychology (logarithmic connotation of feelings) providing basis of theory of information

Škramovský Stanislav (1901–1983) Czech phys. chem. and co-inventor of thermogravimetry through his own-designed 'statmograph'

Tammann Gustav Hendrich Johan Appollon (1861–1938) Ger. chem., research in inorganic chemistry ('Lehrbuch der metallkunde' 1914)

Tesla Nikola (1856–1943) Croatia electrician US resident, invented Tesla motor and system of alternating current power transmission

Thales of Miletos (624–548 BC) Gr. math., tried to find naturalistic instead of mythological interoperation of nature, invented logical proof in geometry, determined sun's course, studied static electricity

Theophrastus of Eresos in Lesbos (370–285 BC) Gr. phil., considered as a founder of botany as systematic study, caricatured various human ethical types, studied mineralogy, meteorology, physiology, physics

Thomsen Hans Peter Julius (1826–1909) Danish phys., important thermochemist, who tried to determine the absolute values of chemical forces in order to improve yet vague concept of affinity ('Thermochemische Untersuchungen' 1906)

Thompson Benjamin (Count Rumford) (1753–1814) Brit. phys., disapproved caloric showing heat as motion, tried to calculate equivalents of heat, invented shadow photometer, water compensation calorimeter, even improved fireplaces and chimneys

Thomson William (see Kelvin Baron of Largs)

Torricelli Evangelista (1608–1647) It. math., noted the pressure of air, inventor of mercuri barometer and thermometer, improved telescope and microscope, investigate theory of projectiles

Truesdell Clifford Ambrose (1921–) Amer. phys., known for founding the basis of rational thermodynamics

Turing Alan Mathison (1912–1954) Brit. orig. math., US cryptography decoder, theoretical researcher of complex systems known as 'Turing machine' (a framework for computing any decidable function) and the 'Turing test' (for evaluating whether machines are thinking)

Tyjemkin (Těmkin) Michail Isaakovič (1908–1979) Rus. math. and phys., essential contributions to the thermodynamics of solid state

Tyndall John (1820–1893) Brit. chem., studied diamagnetism, absorption and radiation of heat by gases, demon-

strated dispersion of light beam by suspended particles in colloids (Tyndall's effect)

Van der Waals Johannes Diderik (1837–1923) Dutch phys., research on gaseous and liquid phases, determined so-called perfect and real gases, thermodynamic theory of capillarity, know for Van der Waals forces between dielectric molecules

van't Hoff Jacobus Henricus (1852–1911) Dutch chem., father of phys. chem., relating thermodynamics to chem. reactions, laws regulating chemical equilibrium, melting points, steam pressure, introduced concept of chem. Affinity

Veille Paul (1854–1934) Fr. chem., first to measure the heat of explosion under oxygen pressure, inventor of calorimetric bomb

Vitruvius Pollio Marcus (\approx 100 BC) It. arch., authority on architecture for centuries, studied hydraulics, clocks, mensuration, geometry, mech. eng.

Waage Peter (1833–1900) Norw. chem., developed so called Guildberg-Waage's Law of mass action

Waterston John James (1811–1883) trying to interconnect 'vis viva' with temperature, equipartition theorem

Watt James (1736–1819) Scot. eng., inventor of steam engine and separate condenser and conversion of reciprocating motion to rotary using sun-and-planet gear, improved combustion furnace, unit watt is named in his honor

Weber Ernst Heinrich (1795–1878) Ger. anatom., pre-founder of famous (Weber-Fechner's) physiology Law, made studies of acoustic and wave motion, pioneered studies on nervous impulses

Wiener Norbert (1894–1964) Amer. math., major contributor to the cybernetics movement, even naming it in his 1948 book 'Cybernetics', worked in theory of probability and potential, and of postulates ('Nonlinear Problems in random Theory' 1958). He defined cybernetics as a discipline concerned with the comparative study of control mechanisms in the nervous system and computers, e.g., "Human Use of Human Beings" (1950) and "Cybernetics of the Nervous System" (1965).

Wichterle Otto (1913–1998), Czech chem., inventor of contact hydrogen lenses, organic polymers and plastics (kaprolaktan named silon)

Wilcke Johan Carl (1732–1796) Ger. phys., formulated independently theory of specific heats, studied electric dispersion and Leyden jar and accepted theory of 2 fluids for electricity

Xenophanés of Kolophon (565–470 BC) Gr. phil., solved problem of combinatorial analysis, worked on theory of primary numbers, wrote history on geometry

Zedeh Lofti A. (1921–) Amer. math., introduced fuzzy logic as a tool for modeling human reasoning

Zénón of Elea (490–430) Gr. math., regarded as inventor of dialectic, used paradoxes to illustrate his philosophical arguments

Zhabotinsky Anatol Markovich (1938–) Rus. born, US co-founder and explainer of oscillatory modes of chemical reactions

Zu Chong-Zhi (Cu Ts'ung or Chohung Chi) (430–510) Chinese math., astron. and eng. often cited in literature

Index



- Accommodation function, 206
 Activation energy, 147,196,204,208,210,212,250
 Activity, coefficient, 115
 Adiabatic, 190
 Adiathermal, 190
 Adsorption, 120
 Advancement, 115,207
 – of transformation, 144
 – of process, 135
 Affinity, 115
 Ageing, 284
 Aggregation, 227,257
 Algorithm, 28,44
 Alchemy, 35,66,72,73,76,80
 Allometric plot, 33,55,222
 – growth, 226
 Alloy, 285,298,318,323
 – glassy, 309,320
 – eutectics, 129
 Amorphous, see glassy, 137
 Amount of substance, 126
 Amplifier, 158,176
 Annealing, 308,309
 – flush, 311
 – isothermal, 310
 Antigravity, 55
 Apparatus, 1,158,193,236
 – automation, 158,175
 – constant, 192,195
 – head, 162
 Apparent, 197,205,207,211,234,254
 – kinetic parameters, 204,206,207,208,258
 – mass, 236
 Area, 46,66,206,211,226,229,242
 – of DTA peak, 192,193,194,196
 Arithmetic, 68,78,225,237
 Arrhenius constant, 172,209,212,250
 Artificial intelligence, life, 26,41,44

Index

- Astronomy, 71,76,78
 Athermal behavior, 128
 Atmosphere, 20,27,51,56,63,82
 – control, 162,166
 – defined composition, 164
 – dynamic/static, 166
 – selfgenerated, 165
 Atom, 87,232,236,270
 Atomists, 86
 Attractor, 53,229,242,248
 Automata, 22,27,44,158
 – cellural, 41
 Avarage contribution, 21,109
 Avogadro number, 62
 Back/reverse reaction, 145,210
 Background, 13,51,196,295
 – of process, 135
 – of DTA peak, 194
 Balances, 160
 – thermogravimetry, 166
 – of thermal fluxes, 191
 Bartoli thermal engine, 326,330,335
 Baseline, 193,194
 Batteries, 284
 Belousov-Zhabotinsky reaction, 22,61,214,255,264,268,345
 Bénard rolls/sells, 51,229,264,266
 Bifurcation, 222,230,231,242,252,257
 Big Bang theory, 54,63
 Biocompatibility, 27,308,322
 Biology, 13,57,59,213
 Bit/qubit, 22,28,44,57
 Black, 158
 – box, 158,190
 – holes, 23,37,60
 Boiling point, 89,100,101,202
 Boltzman constant, 20,28,48,213,234,243,289,292,326,330
 Borhard and Daniels evaluation method, 204
 Brain, 38,40,44
 – human, 40,302
 – artificial intelligence, 44
 Branching, 224,256,262
 Brayton cycle, 281
 Break on curve, 163
 Bridging/nonbridging oxygen, 321
 Broadened transition, 91
 Broccoli visage, 223
 Buoyancy, 162
 Butterfly effect, 242
 CaCO₃ decomposition, 165,193,208,250
 Calibration, 190,192,194
 – plot, 195
 Caloric – thermogen, 32,82,84
 Caloric properties, 23
 Calorie, 84
 – conversion units, 92
 Calorimetry, 82,190
 – classification, 190
 – capacity, 83
 – dynamic, 190
 – throw-in, 190
 – Tian equation, 191
 Calvet calorimetry, 192
 Carbon, 28,46,55,285,287,290,295
 Carnot cycle, 20,25,48,86,101,301
 CAS – Chemical Abstract Service, 36
 Casimir forces, 62,326,327,328,330,335
 CaSO₄, 209
 Catalysts, 260,262,267
 Cell model, 191,231
 Chaos, 13
 Chemical,
 – potential,
 – reaction, 115
 Circle, 32,66,222,224
 Civilization, 12,26,33,44,46,50,63
 Citation index, 36
 Clapeyron equation, 126
 Cloud, 58
 Cluster, 38,51,214,228,267
 – growth, 78,121
 – CO₂, 56,81,203
 – atmosphere, 265,283
 – green-house effect, 286
 Coats and Redfern evaluation method, 122
 Cognitive map, 32,36
 – nearness/remoteness, 32
 – warmness, 32,34,91
 Communication, 28,33,41,43
 Comparator, 176
 Compass, 222,226
 – dimesion, 227
 – settings, 222,226
 Compensation heat fluxes, 191
 – kinetics, 213
 Complexion/coding, 234,235,
 Complexity, 44,51,55,59,80
 – criticality, 126
 Components, 126
 – selection, 127
 – conservative/volatile, 126
 – redistribution in solid, 129
 Compressibility, 113
 Computer, 27,28,37,39,40,42,53,63
 – hardware, software, 39
 – language, 44
 – memory, 22,50,77
 – treatment, 36,57,61,107
 – types of, 41
 Concentration, 128,146
 Conduction, 102
 – probe method, 103
 – scanning calorimetry, see DSC 36,190,191,196,202
 – thermal analysis, see DTA, 190,191,193,195,198,200
 Congruency, 128,132

Index

- Constants of Nature, 20
 Constitutive equation, 113,144
 Control, 174
 – of heat transfer, 105
 – reaction, 174
 Convention, 102,106
 Converters, 290
 Cooling, 178
 – control of, 180,181
 – methods of rapid, 180
 – rate of calorimeter, 190
 Cooper pairs, 311
 Coring, 133
 Correlation, 13,39,58,116,119,261,298,311
 – between kinetic data, 206,211,213
 – function, 229
 – length, 264,316
 Corrosion, 309
 Cosmology, 13,53,60,63,67,73
 Criterion of thermodynamic consistency, 124
 Critical, 126
 – concentration, 126
 – dimension, 180
 – nucleus radius, -exponents, 121
 – temperature, 126
 – cooling rate, 180
 – treshold, 222
 – sample thickness, 181
 Crossover effect, 197,228,247
 CRTA – Controlled rate thermal analysis, 174
 Crucible (see sample holder), 160,191
 – multistory, 165
 – thermogravimetry, 166
 Crystal growth, 179,208
 Curie temperature, 309
 Curve, 159
 – characteristic points, 159
 – construction of, 163
 – smoothing, 230
 Curves, 163
 – experimental, 160
 – characterization, 159,163
 CVD – Chemical vapor deposition, 307,323
 Cybernetics, 50
 Cycle, 242
 – periodic heating, 187
 – oscillation modes, 198
 Dark energy, 63
 Data bases, 35
 Data simulation, 116
 Deformation, 165,209
 Degree of conversion,
 – isothermal, 144
 – nonisothermal, 145
 – kinetic, 135,145
 – thermodynamic, 115
 Degree of irreversibility, 136
 Dehydration, 188, 209,210
 Dendritic, 228,250
 – growth, 230,255,256,257
 Derivatography, 166
 Detection, 175
 – temperature, 177
 Diathermal, 190
 Dielectric, 113
 – measurements, 115
 – polarization, 113
 Diesel engine, 49
 Difference, 26,33,40,59,68,86,101,110,116,119,122,192,
 197,204,227,234,250,257,264
 Differential hydrothermal analysis, 202
 Differential method, 160
 Diffuse transitions, 143
 Diffusion, 105
 – coefficient, 104
 – concentration gradient, 207,255,262
 – quantum speed, 270
 Digitalization, 158
 – filters, 158
 Dilatometric measurements, 160
 Dimension, 13,32,49,92
 – fractal, 58,206,207,214,222,226,227,238
 – Hausdorff, 227,238
 – Lissajous, 187,242
 – self-similarity, 214,222,224,226,238,252
 – topological, 225,226,230
 Direct TA, 160
 Disequilibrium, 20,24,86,112,114
 Disordered, 21,48,113
 – system, 123
 Dissipative, 22,51,60,85,91,242,252,254
 Dissolution, 56,72,91
 DNA – Deoxyribonucleic acid, 41
 Doyle evaluation method, 204
 DSC, 160
 – comparison with DTA, 196
 – curve, 193
 – impurity measurement, 202
 – theory, 192
 DTA, 159
 – correct measurements, 194
 – equation of, 191
 – experimental curves, 160
 – kinetic data, 206
 – peak shape, 163
 Ecology, 13,80
 Economics, 26,33,50,90
 Effect, 159
 – TA curves, 163
 Effectiveness, 40
 Efficiency, 25,291
 Ehrenfest classification, 136,142
 Electric, 20,23,25,26,62
 – calibration, 195
 – conductivity, 104,120
 – field, 110,113,115

Index

- Electromagnetic radiation, 326
 Electronegativity, 118
 Elements, 66
 Emanation TA, 316
 Emf – Electromotive force, 177
 Emission, 326
 Empirical kinetics, 206
 Encryption, 332
 Endothermic/exothermic process, 115
 Energy conversion coefficients, 280
 Energy, 20
 - transducer, 280
 - in vacuum, 327
 - internal, 112
 Engine, 20,49,50
 - cosmological, 291
 - thermodynamic, 280
 - efficiency, 282
 Engineering approach to kinetics, 172
 Enthalpy change, 129,176,192,193,195,196,200,201,299
 Enthalpy, 115
 - data simulation, 116
 - temperature plot, 137
 Entropy, 21,25,28,34,48,52,55,85,108
 - principle, 12,62
 - definition, 28,48,123
 - information, 28
 - thermodynamics, 102,112,113,114,122
 Environment, 12,20,27,34,39,51,61,71,114,281,287,291,302,329
 Epitaxy, 323
 Equilibrium, 112,126
 - advancement, 132
 - background, 132,144
 - constant, 115
 - degree of conversion, 135
 - constant, 115
 Ergodic, 229,230
 Error, 192,199,205,213,230,269
 Eutectic, 128
 - point determination, 197
 - diagrams, 128,130
 Evolution, 229,301,304
 Evolved gas detection/analysis, 160,316
 Excess free energy, 127,298
 - binary system, 127
 Expansion, thermal, 113
 Experimental conditions, 159
 - description of, 158
 - kinetic realizability, 163
 - purpose of measurement, 166
 Exponential-integral, 257
 Exponents, 206,211,228
 Feeling, 107
 Feedback loop, 224
 Feedback, 229,231,260
 Feigenbaum constat, 231,260
 - diagram, 252
 Fermi level 148,212,337
 Ferrite, 144
 Ferroelectric transitions, 113
 Fibonacci numbers, 224
 Fick Law, 104,123,164,228
 Fictitious temperature (glass), 136
 Fire, 46,66
 - industrialized power, 47
 - instrumental reagent, 36
 - history, 46
 - flame, 67
 First order transition, 142
 Fitting procedure, 211
 Fluctuation, 13,16,20,24,51,60,68
 Flynn-Ozawa evaluation method, 204
 Force, 12,32,46,48,61,77,81
 - generalized, 20,23,27,54,70
 - strong – weak, 54,62
 - electromagnetic, 57
 Four elements, 70
 Fourier analysis, 49,86,103,105,108
 Fractal, 13,58,150,207,211,222,228,230,255,260
 - dimension, 227,238
 - random/natural, 228
 - nonrandom, 227,233
 Fracton, 228
 Free will, 34,67,68
 Freeman and Carroll evaluation method, 204
 Fuel cells, 27,284
 - molten carbonate, 285
 - solid oxide, 285
 Fuels, 285
 - solid, 287
 - liquid, 287
 - gas, 287
 Functional dependence, 221
 - function $p(x)$ in kinetics, 209
 - logarithmic, 223
 Functionality, 280
 Fundamental equation,
 - of TA, 126
 - of DTA, 191
 - of kinetics, 147,204
 Furnace, 175
 - gradient, 175
 - control, 176
 Fuzzy logic, 40
 Gaia hypothesis, 56
 Games, 302
 - parity rule, 302
 - theory, 303
 Gas constant, 204
 Gasket, 214
 - Sierpinski, 227
 Geometry, 51,53,60,207,222,238,251,254
 - Euclidean, 13,53,56,63,230
 - fractal, 13,27,38,260
 - Lobachevsky/Riemann, 51,260

Index

- Gibbs free energy, 90,113,115,121
 – of mixing, 91
- Ginstling-Brounshtein kinetic equation, 149
- Glass, 46,54,69,75,100,140
 – formation, 128,308
 – forming ability, 138,149,310
 – transition temperature, 136,140
- Golden, 74
 – mean, 224,225
- Grain, boundaries, 121
 – growth, 121,147
- Gravity, 21,23,46,49,55,57,83
 – constant, 20,62
- Harmonic, 209,237,242,255,266
 – measure, 243
 – wave, 242
- Heat capacity, 23,48,84,103,113,116,122
 – evaluation, 117
 – latent, 83
 – of mixing, 128
- Heat, 12,14,20,25,35,47,56,76,84,87,102
 – Calorie, 82
 – compensation flux, 191
 – conduction coefficient, 103,105,107
 – engine, 49,101
 – flux/exchange, 48,101,105,107,108,113
 – of reaction, 115,143
 – puls, 195
 – transfer coefficient, 49,102,103
- Heat, 26,46,66,83,86,91
 – inertia,
 – transfer, 48
- Heating rate, 114
- Heating, 110,114,120
 – linear, 145
 – constant, 145
 – exponential, 145
- Heterogeneous, 121
 – reaction, 129
 – system, 129
- History, 12,20,42,46,50,58,72,90
 – of thermal analysis, 14,169
- Horizon, 32,38,54
- Horowitz and Metzger evaluation method, 204
- Hrubý glass-forming coefficient, 137,196
- Hubble-Nernst constant, 333,334,337
- Human, 13,25,39,43,46,68,80
 – life, 61,71,100
 – future, 25,40
 – mind, 40,53,59,61,63,77
- Hydrogen, 55,82
 – technology, 284
 – absorption, 285
 – bonds, 54
- Hypothesis, 43,48,54,56,66,68,86,326
 – likelihood, 22,40
- Hypothetical, 132
 – points in phase diagram, 133
- ICTA temperature standards, 194,201
- ICTAC (International Confederation for Thermal Analysis and Calorimetry), 15
- Ideal, 298
 – solid-solution, 129,298
 – gas, 90
- Image analysis, 186
- Impurities, 202
- Incommensurability, 110
- Inertia term (DTA), 191,193,195
- Inflationary, 59
 – universe, 59
- Inflection point, 208,212
- Information content, 159
- Information, 12,16,21,22,28,33,34,36,40,47,58,222,227,231,232,234,235,236
- Infrared heating, 183
- Initial state, 123
- Initiator, 225,226,262
- Instability, 22,51,67,90,119,247,256,263
- Integral calculation methods, 211
- Integrated circuits, 176
- Integration, 204
 – of rate constant, 204
- Intelligence, 41,57,70
- Intelligent processing, 306,322
- Intelligent, 306
 – materials, 306
- Intensive quantity, 112
- Interaction parameter, 128,298
- Interactions, 128
 – Coulomb, 327,328,336
 – in vacuum, 326,327,331
- Interface, 13,42,89,105,106,112,119,121
- Internal energy, 112
- International Practical Temperature Scale (E IPT–66), 194
- Internet, 27,37,41,42
- Interpolation, 207
 – of peak baseline, 194
- Interstitial, 316
- Invariant process, 134,144
- ISI – Institute for Scientific Information, 38
- Iso-conversion evaluation method, 204
- Isodiathermal, 190
- Isokinetic temperature, 213
- Isolation, 126,190
 – of TA system, 174
- Isoperibolic, 190
- Isothermal, 190
 – calorimeter, 190
 – degree of conversion, 144
 – kinetics, 204
- Iteration, 223,229,230
 – iterator 229,230,231,252
- Jander parabolic law of growth, 149
- Jefferson monograph, 127
- J-M-A-Y-K kinetic equation, 149
- Joule, 27,49,83,84

- conversion units, 27,92
- Journals, 34
 - impact factor, 38
 - Thermochemica Acta, 35,36
 - Thermal Analysis and Calorimetry, 35,36
- Julia set, 233
- KCE-Kinetic compensation effect, 213,214
- Kelvin, 23,91,102,140
 - equation, 101,119
 - temperature, 34,103
- Kinetic phase diagrams, 13,132
- Kinetic, 135,147,163
 - calculation of data, 211
 - compensation effect, 213
 - equation, 204
 - parameters, 206
- Kissinger evaluation method, 204
- Kneading, 231
- Knowledge, 14,21,32,37,38,43,76
- Koch curve, 226,238
 - island, 226
- Lambda transformation, 143
- Landau theory, 91
- Language, 13,14,22,40
- Laplace formulae, 119
- LAR – Linearization approximation rule, 119
- Laser, 109,182
 - alloying, 183
 - glazing, 184
 - surface melting/quenching, 184
- Latent, 87
 - heat, 54
 - capacity, 54
- Legendre transformations, 124
- Liesegang rings, 267,270
- Life, 21,25,27,49,55,61,66,69,76,105
 - origin, 21,27,28,41
- Light, 21,46,56,61,66
 - speed, 20,54,55,62
- Liquid crystals, 138
- Lissajous figures, 187,242
- Log/log diagram, 33,55,227
- Logarithm, 33,196,204,222,225,226
 - binary, 235
 - history, 237
 - human sensation, 223
- Logic, 22,40,44,52,54
- Logistic equation, 230
- Lorenz attractor, 229,231,264
- Magnetic Curie points, 309,310
- Magnetic, 113,228,336
 - field, 113
 - measurements, 115
 - standards, 177
 - transformation, 126,
- Magnetization, 113
- Magnetocaloric, 336
 - effect, 336
- coefficient, 113
- Mandelbrot, 227,233,238
 - dimension, 227
 - self-similarity, 214,224,238,252
- Mapping, 39
- Martenzitic transformation, 144
- Material, characterization, 47
 - for construction, 306
 - glassiness, 309
 - preparation, 312
 - properties, 306
- Maurpetuis least action principle, 267,272
- Maxwell transformations, 48,91,317,328
- MBE – Molecular beam epitaxy, 307
- Measurable thermodynamic coefficients, 113
- Measurements, 157,161
 - single, 160
 - multipoint, 160
- Measuring, 158
 - head, 161
 - quantity, 160
- Measurables, 114
- Mechanism of reaction, 149
- Mechanoelastic, 113
 - coefficients, 113
 - measurements, 115
 - properties, 312
- Mechanochemical reactions, 188
- Melt, 180
 - spinning, 180
 - extraction, 181
- Melting,
 - surface,
 - point, 200,201
 - laser, 182
- Mendeleev, 88,116
- Mestable, 90,120
 - phase formation, 90,122
 - state, 112
- Metallic glasses, 180,184,308
- Metastability, 132
- Metatectic/Monotectic, 128,130
- MgCO₃, 165
- Microscope, 184,186
- Milling, 188
- Mimetic material, 312
- Mixing, 127,128
- Mn_xFe_{3-x}O₄, 207
- MOCVD – Metalorganic chemical phase epitaxy deposition, 307
- Model, 189,205,207,226,238,255,267
 - mathematical, 204,210,227
 - physico-geometrical, 147,244,251,262
- Molar, 62,91,116,120
 - quantities, 62,126
 - fraction, 119,126
- Molecular, 22,47,51,55,85
 - weight, 118

Index

- Morphology observation, 186
- Motion, 16,20,23,27,48,51,53,59,69,82,85
- Brownian, 92
 - ordered/disordered, 113
 - quantum, 105,110
- Mullin-Sekerka growth theory, 255,256
- Multiparameter process, 134,145
- Mythology, 52,58,70
- $\text{Na}_2\text{O-CaO-SiO}_2$, 184,320,321
- Nano, 50,63,89
- composites, 47,50,62
 - crystalline material, 13,37
- Natural gas, 285
- Navier-Stokes equation, 123
- Nerves, 304,345
- neurons, 27,39,40
 - signal propagation, 270,345
- Newton cooling law, 23,49,101
- mechanics, 23,27,69,86,91,49,53
- Nomenclature, 15,88,90
- Non-crystalline, 13
- Non-equilibrium, 27,72,110,135
- Non-isothermal, 114,145
- conversion, 144
 - integration, 208
 - kinetics, 204
- Non-stationary, 12,105,109,113,122
- calorimeter, 190
- Nuclear power plants, 288
- Nuclear, 13,26,44,54,57,286
- fission, 26
 - fusion, 57
- Nucleation, 13,119
- critical radius, 121
 - negligible, 122
 - causing metastability, 132
 - under tension/polarization, 131
 - homogeneous, 121
 - heterogeneous, 129
- Nucleation-growth equation, 149
- Numbers, 40,44,57,68,74
- irrational, 68
 - complex, 105
- Observables, 113
- Observation, 23,35,69,87,103
- spot, 186
 - average, 159,186
- Ohm Law, 104
- Open system, 126
- Ordering parameter, 143
- Oscillation, 212,242,268
- Otto cycle, 281
- Overlapping, 146,211
- of nuclei, 146
 - of model functions, 206,211
- Oxidation state, 315
- bridging oxygen, 321
 - stoichiometry, 316
- Oxides, 307
- glass, 138,307
 - biomaterials, 318
 - superconductors, 311
 - stability diagram, 128
- Paradoxes, 77
- Partition function, 244
- $\text{PbCl}_2\text{-AgCl}$, 263
- Pendulum, 242
- Percolation, 214,227,309,318
- cluster, 214,227
 - threshold, 309
- PeriodicTA, 171
- Peritectic, 128,133
- Periodical outcome, 105
- Perturbation, 123
- Phase diagram, 127
- determination, 128
 - enthalpy change, 127
 - three-component, 129
 - two-component, 130
- Phase separation, 145
- Phase transition, 142
- first order, second order, 142
 - broadened, 143
- Phase, 12,33,44,56,63,81,90,107,117,119,121
- diagram, 13,128,130
 - equilibrium, 90,119
 - separation, 119
 - transition/transformation, 54,86,91
- Philosophy, 21,52,76,298
- Greek, 68
 - elements, 298
 - Hermetic, 73
- Phlogiston, 82
- Photovoltaic power, 288
- Pigmentation, 261
- Pippenger relation, 143
- Planck constant, 13,20,22,28,59,263,269,271,292,327,333,335,344
- Pollution, 56,281,284,288,290
- thermal, light, 288
 - CO_2 , 289
- Polymers, 306
- Polynomial, 57
- Power laws, 13,23,28,57,122,226
- sensation, 222
- Preexponential factor, 147,204,211
- Pressure, 147,210
- effect on kinetics, 210
 - shift of equilibrium, 130,147
- Process, 13,22,24,41,50,54,68,86,102,121
- invariant/variant, 135
 - types of, 102,114
- Program, 32,37,53
- computer, 28,42,57
 - temperature, 145
- Proteins, 50

Index

- Proximity to equilibrium, 209
- Quantitative DTA, 192
- Quantum, 13,59,60,68,81,85,270
- information,
 - mechanics, 54,59,63,80,91
 - well/dot, 237
- Quasi-isothermal/isobaric, 190,280
- Quasiregular model, 128
- Quenching methods, 180,181
- Rabbit problem, 338
- Radiation, 13,20,24,35,54,56,62,103,191,193,196,237, 239,267,286,289,291,295,326,329,333,335
- Radioactive tracers, 316
- Random, 21,38,40,58,102,207,227,235,239,254,265,268, 271,299,326,332,345
- walk, 214,228,230
- Rapid solidification, 180
- Rate, 145,195,198,205,208
- of chemical reaction, 145
 - of heating/cooling, 145
- Rational, 32,48,60,61
- approximation, 204
 - thermodynamics, 13,91,122
- Reaction, 115,145
- enthalpy, 145
 - isotherm, 115
 - order, 142
- Reactivity, 36,250,319
- Recording, 160
- Reduced temperatures (glass), 138,149
- Regular behaviour, 128
- Regulated, 158
- quantity, 176
 - system, 161
- Regulation, 158
- circuits, 176
 - response, 176
- Reinassance, 80
- Relativity, 53,63
- general, 60
- Relaxation, 136
- Religion, 54,63,344
- Renaissance, 80
- Reserves, 286
- capital energy, 288
 - income energy, 286
- Resistance thermometer, 177
- Resistance, 104,110
- Rotating spiral, 225
- Saddle point, 299
- Sample, 112,158
- temperature, 177,193
- S-B (Šesták and Berggren) kinetic equation, 149,206
- Scaling, 32
- exponents, 228
- Science, 12,37,38,114
- natural, 16,20,32,49,57,58,81
 - history, 72,80
 - humanities, 13
- Second-order transition, 142
- Self-afinity, self-similarity, 222,224,226,230,233,238
- Self-heating/cooling, 190
- Self-organisation, 260,263,267,271
- SEM – Scanning Electron Microscopy, 161,184
- Sensation, 222,237
- Sensor, 162
- time constant of, 161
- Shape, 22,32,50
- of phase diagram, 130
- Shells, 225,261
- Schrödinger equation, 22,105
- Signal, 161
- Simulation, 116
- Single-crystal, 120,179
- growth, 121
 - dissolution, 150
- Singularity, 46,54,60,63
- SMBR-Solar microwave background radiation, 333,337
- Snowflakes, 226,230,251,257
- Society behavior, 298,302
- Solar energy, 287
- Solid solution, 127
- Solidification, 178
- cooling rates, 180
 - metastability, 132
 - front, 256
 - columnar, 256
- Solubility, 75,81,88
- Specific heat, 83,87,102,117
- Spinel, 144
- Spinoidal, 90,145
- Spirals, 225
- Archimedes, 225
 - golden, 225
 - logarithmic, 225
 - construction, 225
- Splat formation, 180
- Spontaneous heat flux, 191
- Stability, 24,34,51,90,112
- Staircase, 229
- State, 112
- Statistics, 24,91,260
- Stimulus, 23,46
- Stirling engine, 280
- Stoichiometry,
- Strange attractor, 53
- Structure, 13,22,38,51,57,61,85
- crystal, 88
 - dendritic, 236
 - self-similar, tree-like, 222,224,226
- Superconductivity, 228,311,313
- Supercooling/overheating, 78,121
- Surface, 13,53,56,63,106,112,118,119,121,194,208,212, 227,246,250,254,262
- area, 46,103,105,119
 - adsorption, 120

Index

- internal, 246
- reaction, 208,214
- roughness, 106,108,230
- tension, 90,119,256
- curvature, 119,208,227,257
- Surrounding, 24,27,67,103,114,123
- Survival strategy, 302
- Susceptibility, 113
 - magnetic, 113
- Symmetry, 39,60,124
- Sympathy, antipathy, 73
- System, 16,22,24,26,27,34,40,48,52,58,61,85,90,108,112,119
 - determination, 112
 - isolation, 126,190
 - theory, 49
- Šatava-McCallum-Tanner evaluation method, 205
- TA methods, 160
- Table of,
 - Clausius-Clapeyron equations, 113
 - thermoelectric voltage, 177
 - DTA calibration substances, 200
 - electronegativities, 118
 - heat capacities, 117
 - fluxes and forces, 253
 - energy sources, 288
- T-C (Transformation-Cooling) diagrams, 149
- Tektology, 49
- Teleportation, 337
- Temperature difference between, 103
 - block and furnace, 191
 - specimens (sells), 191
- Temperature, 14,20,23,25,35,47,55,62,83,100,110,116,122
 - detection, 84,93,103
 - gradients, 104
 - negative, 126,140
 - definition, 32,102,103,113
 - scales, 34,101,102
 - empirical, 101
 - modulated, 187,198
- Test, 191,194,208,235
- Theory of,
 - DSC/DTA, 191
 - phase transition, 142
 - games, 302
- Thermal, 159
 - analysis (definition), 12,90,159
 - conductivity, 103
 - history, 169
 - pretreatment, 160
 - process, 71
 - feeling, 107
 - gradients, 103,190
 - physics, 24,34
- Thermocouple, 177
 - junction, 177
 - emf, 177
- Thermodynamic, 33,48,89,112
 - data sources, 116
 - variables/functions, 112
 - degree of freedom, 90,126
 - potential, 113
 - state/system, 123
 - transition enthalpy changes, 116
 - mesoscopic, 13,338,344
 - second law, 13,24,25,48,51,55,62,92,102,105,109,232,239,253,271,282,326,335,344
- Thermodynamics, 13,24,26,49,89,102,113
 - rational, 123
 - classical, 48,112,86,91,112
 - thermostatics, 51,86,113
- Thermoelectric, 177
 - thermometers, 177
 - voltage, 177
- Thermography, 14,35
- Thermogravimetry, 166
- Thermochemistry, 35,37,69,82,85
- Thermophysical measurement, 158
- Tian equation, 190
- Tired light, 333,337
- Tissue substitution, 318
- Titanium, 322
 - oxide, 322
 - surface treatment, 323
- Topology, 53,68,225
 - dimension, 225,226,230
- Transducers, 22,36
- Transition point, 142
 - critical, 126
- Transition, 142
 - to glassy state, 136,149
 - to chaos, 231,252
- Transition/transformation, 32,48,51,53,62,68,82,84,86,102,112,115,142,149,195,200,209,225,227,251,255
 - anomalous/real, 142
 - Ehrenfest ideal, 136
 - structural, 186,317
 - studied by DSC, 197
- Transport delay, 161
- T-T-T (Time-Transformation-Temperature), 148
- Turbulence, 51,108
- Turbulent poundary level, 108
- Twin-cell, 160,191
- Undercooling, 78,119,121,142,256
 - frozen state, 136
- Universe, 44,52
 - beginning, 20,62
 - closed, open, 62
 - expanding, periodic, 62
- Unstable, 70,90,112
- Vacancy creation, 316
- Vapor power cycle, 282
- Variables, 112
- Variant process, 135
- Vibrations, 50,77,244
 - harmonic, anharmonic, 244,248

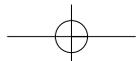
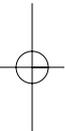
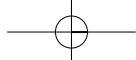
Index

- thermal, 233
- Vis – viva – mortua, 83
- Viscosity, 102,104,136,196,224,245,252,265
- Vitrification (see glass-formation), 136
- Vogel temperature, 136,244
- Warm-cool feeling, 34
- Wave, 192,208,230,237,244,255,262,265,267
 - shape, 192
- Weather, 15,26,56,58,67,108
- Weber-Fechner Law, 222
- Wetting/adhesion angle, 131
- Wind, 283
 - energy,
 - turbines, 283
- Work, 12,23,26,27,36,47,49,83,92,102,123
- Wormholes, 60
- Wulf growth Law, 120
- X-ray diffraction, 36
- $\text{YBa}_2\text{Cu}_3\text{O}_x$, 313
- Young modulus, 310
- Zooming, 32
- ZPR-Zero point radiation, 13,24,62



Layout of the art photos:

- Page 3 – Water going behind the corner, Goose Neck Nat. Mnt., USA 1994
- Page 6 – Passer-by in the Canyonland National Park, USA 1991
- Page 11 – Himalayan teller of tales, Manang, Nepal 1981
- Page 19 – Lighting candles, Prague, Czechia 1989
- Page 29 – Ice axes within Elbrus mountain (5633m), Caucasus, Russia 1977
- Page 31 – Mountaineers at the Uzhbinske plateau (4100m), Russia 1977
- Page 45 – Fighting sunburns, self-portrait in Alps, Austria 1973
- Page 65 – Shaky sculpture, Milles' statue garden near Stockholm, Sweden 1969
- Page 79 – In the afternoon light, Franzensbad, Czechia 2003
- Page 93 – Crossing a mountain pass at 5500m, Himalaya, Nepal 1982
- Page 95 – Frozen scraps of a cow (-30 C), Mongolian plateau 1985
- Page 97 – In front of the Charles Bridge, Prague, Czechia 1975
- Page 99 – Welcome gate to the traditional Chinese garden, Suzhow, China 1985
- Page 111 – Wreckage's below the Brooklyn Bridge, New York 1980
- Page 125 – Vertical patterns of Chicago skyscrapers, USA 1991
- Page 141 – Morning specter of the Charles' bridge statues, Prague 1979
- Page 151 – Resting well, homeless at the Central Park, New York 1991
- Page 155 – Appetite and enviousness, Quetta, Pakistan 1982
- Page 157 – Big eyesight of an afeared child, Bangalore, India 1985
- Page 173 – Read me news aloud, Concepcion, Chile 1992
- Page 189 – Waiting a chance or getting lost, Las Vegas, USA 1991
- Page 203 – Yet traditional world within the Water Gate 'Miyajima', Japan 1996
- Page 215 – Weighing carefully unaware of future, Hanoi, Vietnam 1982
- Page 219 – Crocus and jawbone – beginning and end, Mongolia 1985
- Page 221 – Rain shelter for umbrellas, Taiwan 1992
- Page 241 – Cactus high in the Andes mountains, Chile 1992
- Page 249 – Staying firm for ages, Canyon de Schelly Nat. Mnt., USA 1970
- Page 259 – Secluded beholder of sunset, Brisbane, Australia 1999
- Page 273 – Twilight steaming out at the Yellow Stone Nat. Mt., USA 2001
- Page 277 – Surfer fighting Hawaii combers, Honolulu, USA 2001
- Page 279 – Barber at work, Ganga riverside, Varanasi, India 1982
- Page 297 – Moving child and gloomy woman, Bombay, India 1985
- Page 305 – Cutting coconut for a good drink, Amritsar, India 1982
- Page 325 – Big jump within the outline of Eiffel tower, Paris, France 1990
- Page 339 – Lonely windmill in sun flares, Middle West, USA 1970
- Page 343 – Paddy fields within hummocks, Guiling, China 1987
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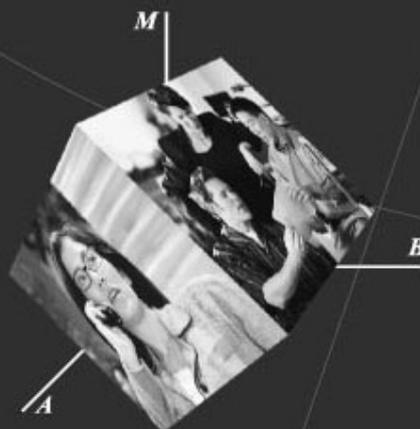
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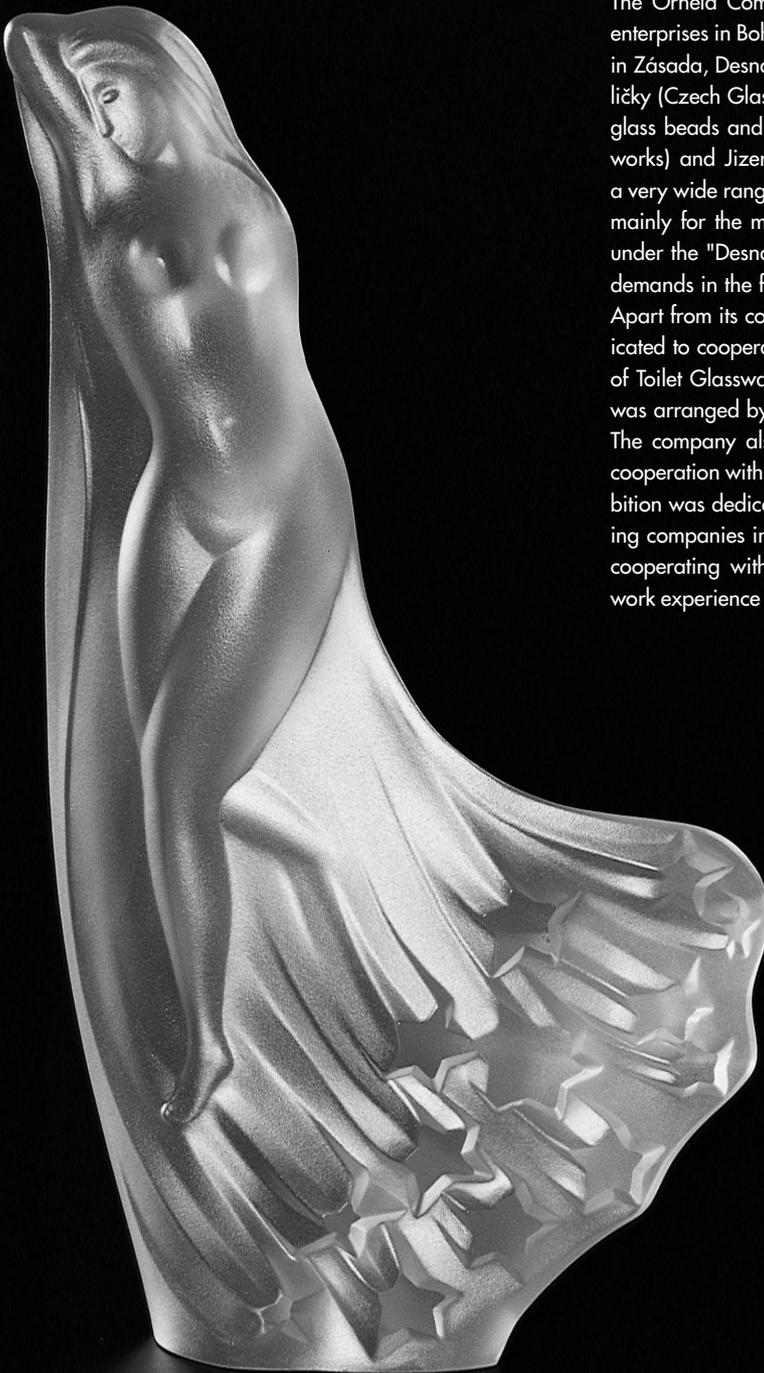
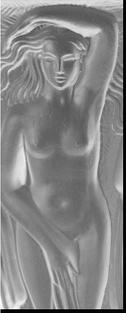
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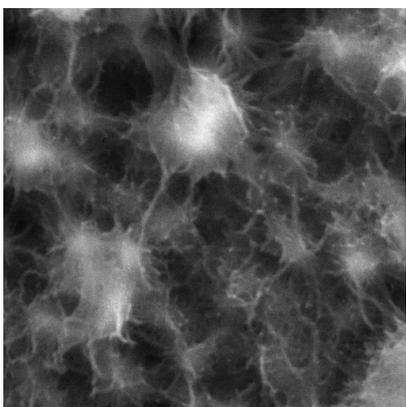
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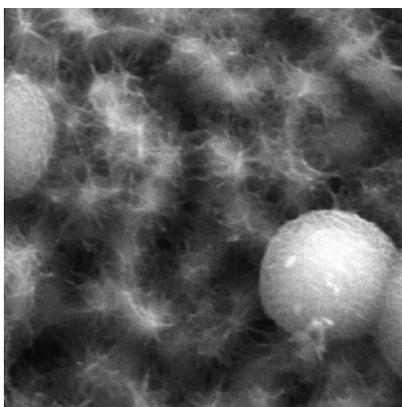


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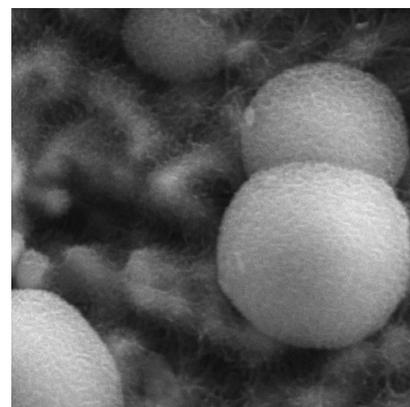
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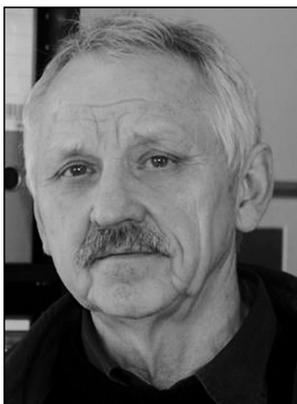


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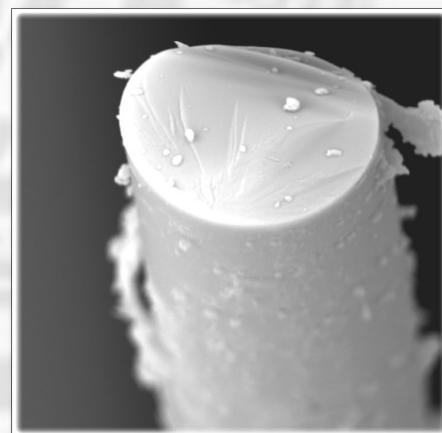
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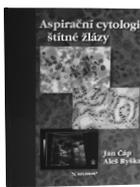
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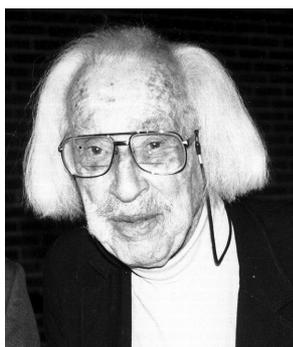




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Norbert J. Kreidl
July 3, 1904, + July 11, 1994

The Slovak Glass Society and Czech Glass Society in cooperation with RONA Lednické Rovne, under the auspices of the International Commission on Glass, organize the Norbert Kreidl Memorial Conference. The conference will be dedicated to the 100th birthday anniversary of Prof. Norbert Kreidl. The venue of the conference was selected with respect to the close personal links of Prof. Norbert Kreidl with Lednické Rovne where he spent part of his fruitful life, as well as the family links with Jozef Schreiber, the founder and original owner of the Rona Company. The conference is dedicated to "Building the Bridges between Glass Science and Glass Technology", the message of Norbert Kreidl to next generations of glass scientists and technologists. The program commemorating the work and life of Prof. Norbert Kreidl will be the inseparable part of the conference.

After receiving doctor's degree in physics from Vienna University 1928, Norbert J. Kreidl became interested in a career in the glass industry, i.e., at J. Schreibers Neffen, at the Moravian-Slovakian border. His life changed dramatically in 1938 when he left with his family Czechoslovakia and joined his former teacher, Prof. W. Weyl in the USA starting to work lifelong for Bausch & Lomb Co. Later after retirement he became professor at the Universities of Rutgers, Missouri (Rolla), New Mexico (Santa Fe), and Arizona (Tucson). Kreidl's international prominence and activities were longstanding and exceptional. He already participated at the 1st Glass Congress of the International Commission on Glass (ICG) in Venice in 1933. He was the president of ICG 1969 to 1972. He always fascinated his students and colleagues by the breadth of his knowledge, his way of thinking in larger contexts and his captivating rhetoric. Previous symposium "Present state and future prospects of glass science and technology" was held in Triesenberg (Liechtenstein 1994) honoring the 90th birthday of Professor Norbert J. Kreidl and was chaired by Wolfram Höland, Volker Rheinberger, Osama El-Bayoumi and Donald Uhlmann. The proceedings were published as a separate issue of *Glastech. Ber. Glass Sci. Technol.* 70C, Frankfurt /M 1997 under the editorial of W. Höland and V. Rheinberger.



Norbert Kreidl Memorial Conference



June 23-26, 2004

Trenčín and Lednické Rovne
Slovak Republic

Building the Bridges between Glass Science and Glass Technology

Organized by Slovak Glass Society and Czech Glass Society in cooperation with RONA Lednické Rovne, Alexander Dubček University of Trenčín, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Academy of Sciences of the Czech Republic and Slovak Chamber of Business and Commerce Trenčín, and under the auspices of International Commission of Glass

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Albert Einstein was professor of theoretical physics in Prague in 1911-1912 and read his lectures in the Clementinum and at the Physical Institute. In the same time a new view of space appeared in the Prague cubistic architecture which is unique in the world.

Ernst Mach lived in Prague and contributed to the development of several parts of physics. Christian Doppler discovered and formulated in Prague the physical effect now known as the Doppler principle.



In the first half of the 19th century, Bernhard Bolzano, mathematician and philosopher, advanced significantly fields of logic, variables, limits, continuity and concept of infinity.



Joseph Stepling, a member of the Jesuit Order at St Clement College, represented a new trend in science based on Newton's work. In 1751 he founded the Clementinum observatory which keeps the longest series of meteorological records in the world.



Johannes Marcus Marci of Kronland (1595-1667), professor and rector of the Charles University, investigated e.g. different properties of light (spectral colors, wave nature, diffraction), being a predecessor of Huygens and Newton.



The beginning of science in the Czech territory is related to the founding of the Charles University in 1348, the first university in the Central European region. Prague became the capital of the Holy Roman Empire.



The high level of science in Prague at that time is confirmed by the sophisticated Prague Astronomical Clock at the Old Town Hall. Its mathematical model was developed by professor Jan Sidel. The clock was made by Mikulas of Kadan in 1410.



Rudolph II (1576-1612) invited to Prague many significant scientists, painters, architects and musicians. During his reign Prague became the European centre of science and arts. Tycho Brahe came to Prague in 1599 and began to form a circle of younger co-workers. In 1600 Johannes Kepler arrived.

Civilization, science, physics - Prague milestones



The Prague Castle was founded around 880, Prague became a centre of Czech Lands.

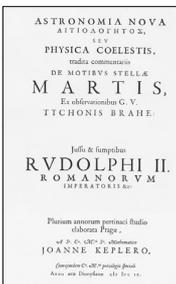


The paper in which Brahe explained his planetary system was published in Prague.

Tycho Brahe is buried in the Church of Our Lady before Tyn at the Old Town Square.



Brahe's high precision astrometric observations of the planets combined luckily with Kepler's theoretical knowledge and resulted in the discovery of law of planetary motion, the most significant and famous scientific result of that time.



Frontiers of Quantum and Mesoscopic Thermodynamics

26-29 July 2004, Prague, Czech Republic

Satellite of the 20th General Conference of the EPS Condensed Matter Division organized by Institute of Physics ASCR and Faculty of Mathematics and Physics of the Charles University, Prague

www.fzu.cz/activities/conferences/fqmt04



Topics:

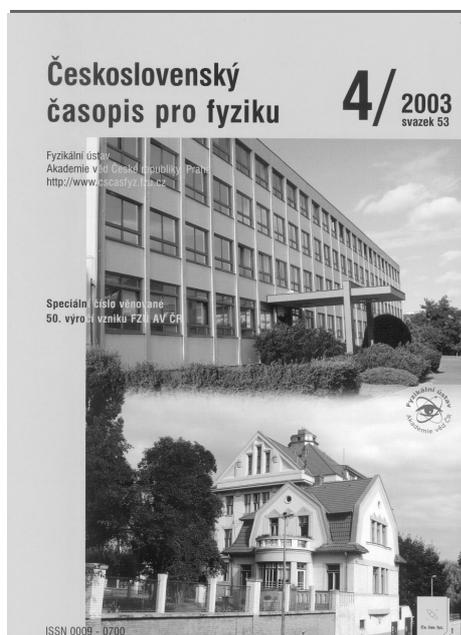
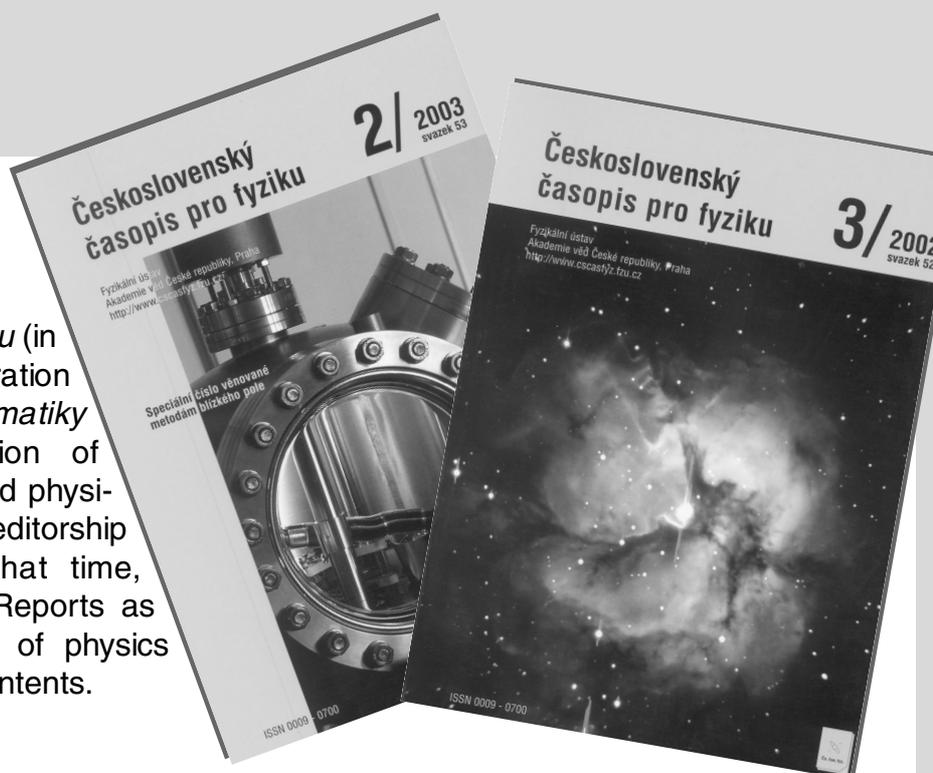
- Quantum, mesoscopic and (partly) classical thermodynamics
- Quantum measurement and decoherence
- Mesoscopic and nanomechanical systems
- Classical and quantum molecular motors and ratchets
- Quantum Brownian motion
- Quantum computing
- Relevant experiments

Confirmed speakers:

- A. Aharony (Tel Aviv)
- B. L. Altshuler (Princeton)
- R. Balian (CEA-Saclay)
- J. Berger (Karmiel)
- T. Brandes (Manchester)
- M. Buttiker (Genova)
- A. O. Caldeira (Campinas)
- P. Hanggi (Augsburg)
- H. Grabert (Freiburg)
- M. Grifoni (Regensburg)
- D. E. Gross (Berlin)
- F. Haake (Dusseldorf)
- H. Linke (Oregon)
- A. J. Leggett (Urbana)
- A. MacKinnon (London)
- J. E. Mooij (Delft) - tentatively
- R. C. O'Connell (Baton Rouge)
- M. O. Scully (Princeton)
- K. Schwab (Maryland)
- T. Seideman (Northwestern Univ.)
- U. Weiss (Stuttgart)
- A. Zeilinger (Vienna) - tentatively
- W. H. Zurek (Los Alamos) - tentatively

History

Československý časopis pro fyziku (in Czech) founded in 1951 by separation of *Časopis pro pěstování matematiky a fyziky*, issued by the Union of Czechoslovak mathematicians and physicists from 1872. Independent editorship was constituted in 1967. At that time, Recent News, Review Articles, Reports as well as papers from the world of physics appeared of the Journal in the contents.



Objectives

Československý časopis pro fyziku is traditionally tribal journal of the Czech - Slovak physical community, whose consistency was not impaired nor separation of republic.

The aim of this journal is not only to inform about new scientific knowledge in physics, but it provides also space for interdisciplinary discussion. It is a journal which addresses to professional physicists, students and the people concerned in other science disciplines. In this journal you can find topical review articles, translations of interesting papers from international journals, interviews and information on Nobel prizes and its laureates. The leading laboratories, not only in Czech and Slovak Republic, are presented and the views on the history of physics complement the rich offer of papers.



Director of the Institute of Physics AV CR
Ing. Karel Jungwirth, DrSc.



Editor in Chief
Doc. RNDr. Zdeněk Chvoj, DrSc.

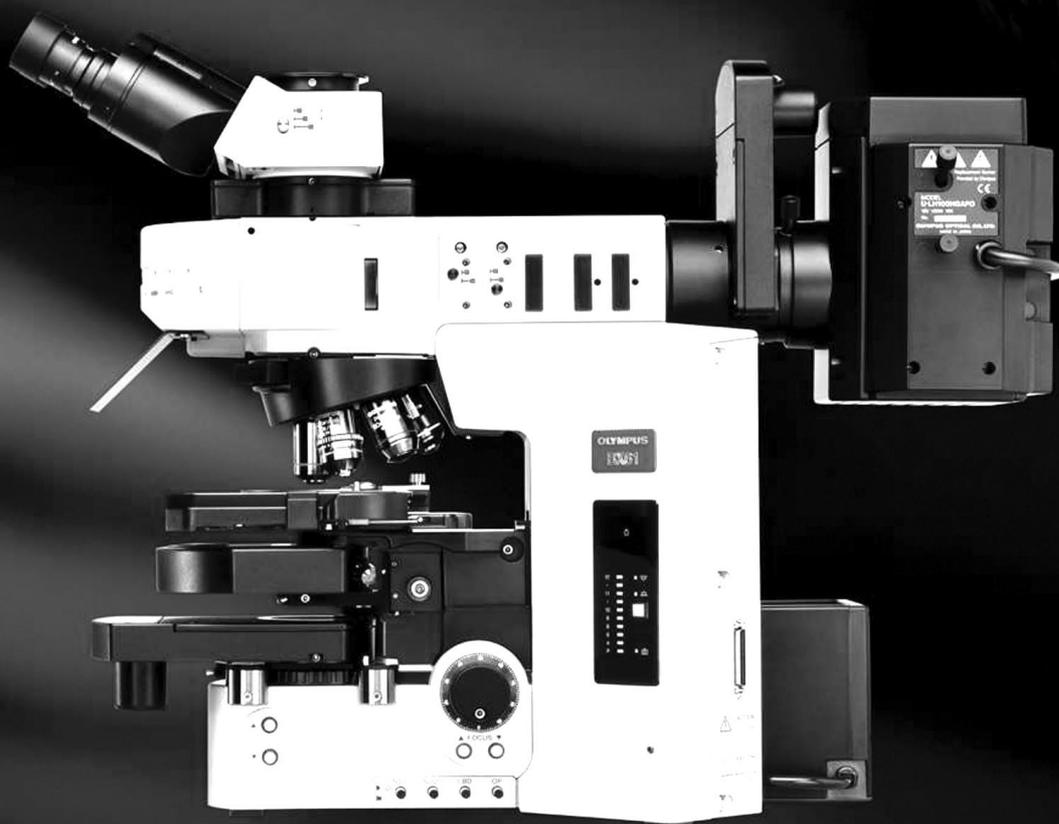


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- Chic, weatherproof metal body
- 6 Preset Creative Scene modes

C-740 Ultra Zoom:

- 3.2 megapixel CCD
- 30x total seamless zoom (10x optical/3x digital)
- 12 shooting modes



C-350 Zoom:

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- 10x total seamless zoom (3x optical/3.4x digital)
- High-quality lens with aspherical glass elements

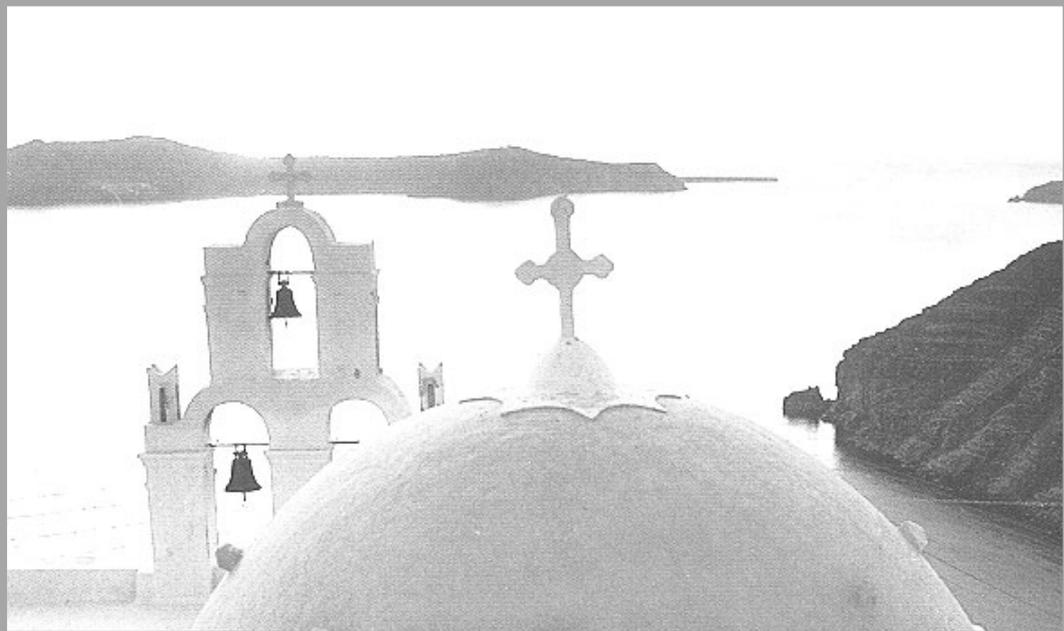


C-150:

- 2 megapixel CCD
- 2.5x digital telephoto zoom
- Four scene program modes



Nature seen by scientist



cameras: Olympus OM2-zoom, IS-200, μ [mju:] II,
Camedia C-2000Z digital zoom and Nikon F 65
with Sigma 28-70/2,8 DF, 70-300 macro/4,5-5,6 DL





Postdoctoral fellow and league basketball player, mountaineer and ski instructor, scientist and occasional window-cleaner, globetrotter and photographer, politician and educator, these are just a selection of Jaroslav Šesták's life's milestones. He originally wanted to study painting, and he kept practicing this hobby for a long time whilst being deeply engaged in science. In the middle of nineteen-seventies he began to involve himself in mountaineering photography (Caucasus, Alps, Himalaya) and he began, under invitation, to give lectures about his travels that were accompanied by color slides. Later on a magazine journal asked him to prepare some photos for publication that were subsequently used to illustrate his scientific books (e.g., "Advanced inorganic materials", Praha 1993). Since that time, Jaroslav Šesták has made twenty photo exhibitions, e.g., in Prague Town Hall Smíchov 1999, in the ECCE TERRA gallery 2000, during the anniversary of the Western Bohemian University, together with the Center for Democracy and Free Enterprise, Plzeň 2001 and in the KLAMOŤKA gallery 2003. As a renowned scientist, he held photo exhibitions at a number of international conferences (Tokyo 1992, Cordoba 1995, Balatonfüred 1998, Copenhagen 2000 or Vancouver 2002).



As the world already appears to be mapped out, Jaroslav decides to paint the world through the new eyes of his photography. His photo shots are not only exotic post-card scenes, they try to exude from them the dramatic nature of living scenes from different corners of the world. He is not satisfied with just the senseless searching of new landscapes to photograph; he tries to capture the beauty that is incensed by his heart, which is as yet unblemished and uncorrupted by the daily rush of an apathetic and spoiled modern society. In typical spirit he has travelled globally, including many conferences, with only a rucksack on his back. During his travels he has passed through places such as The Himalayas, The Chinese Yellow Mountains, The South American Andes and The Western Mountains of Asian Pamir as well as the deserts of The USA, Mongolia, Lapland and Australia, where his home was a sleeping-bag, his means of communication a form of gesticulation and pantomime, and his driving-force his love of nature. (This text is an English translation of a journalistic critique made of Jaroslav's photographs)







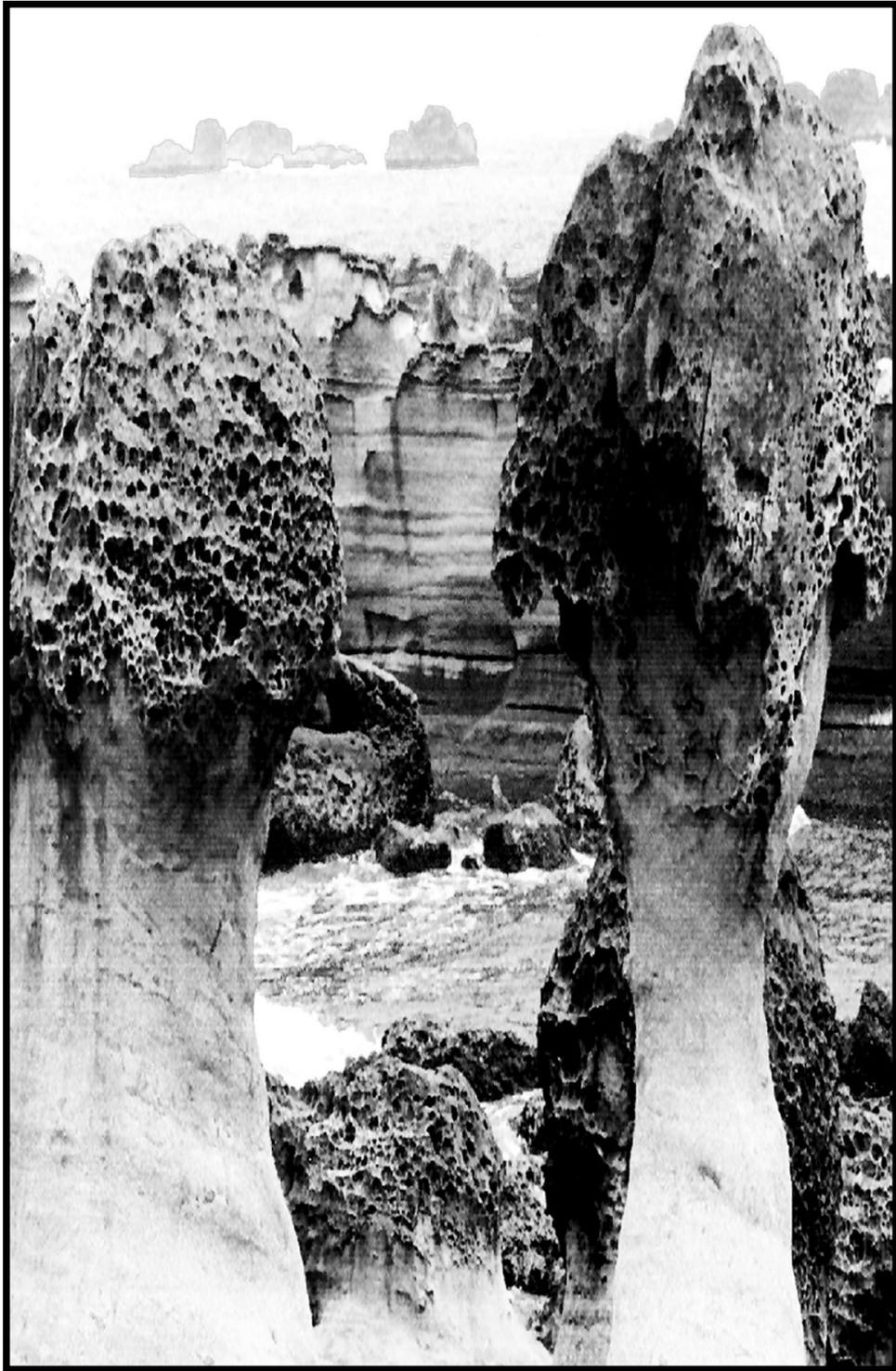






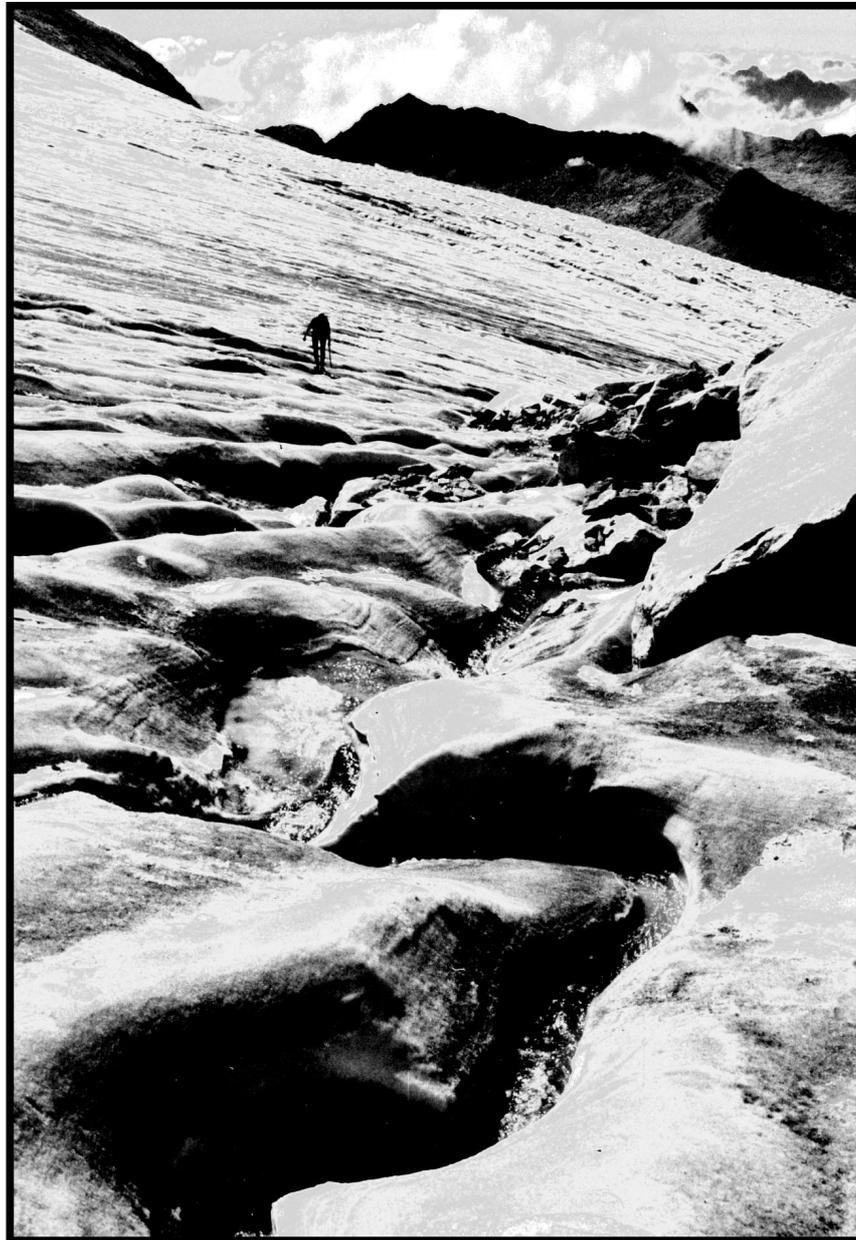




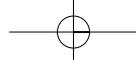


MOTTO: "What is the high place whereunto ye go?"

[EZEKIEL 20:29]



Aloneness of a long-distance runner:
Every man has his own summit that he wishes one day to attain!
(Pic d'Anetto, 3404 m, Pyrenees 1987)



NOTES

