Contents of the section:
History of thermal analysis and ICTAC and CALCON societies

THERMAL SCIENCE AND ANALYSIS:
TERMS CONNOTATION, HISTORY, DEVELOPMENT, AND THE ROLE OF PERSONALITIES
Jaroslav Šesták

HISTORICAL ROOTS AND DEVELOPMENT OF THERMAL ANALYSIS AND CALORIMETRY,
Jaroslav Šesták, Pavel Hubík, Jiří J Mareš
Book chapter

SOME HISTORICAL ASPECTS OF THERMAL ANALYSIS:
ORIGINS OF TERMANAL, CalCon AND ICTA
Jaroslav Šesták
TERMANAL 2005 - published in Bratislava

FROM CALORIC TO STATHMOGRAPH AND POLAROGRAPHY
Jaroslav Šesták, Jiří J Mareš

CZECHOSLOVAK FOOTPRINTS IN THE DEVELOPMENT OF METHODS OF THERMOMETRY, CALORIMETRY AND THERMAL ANALYSIS
Pavel Holba, Jaroslav Šesták
Ceramics – Silikáty (Prague) 56 (2) 159-167 (2012)
Thermal science and analysis
Terms connotation, history, development, and the role of personalities

J. Šesták

Abstract History of thermoscopy and thermometry is reviewed showing the role of temperature degrees including the forgotten logarithmic scale. The importance of natural laws of energy, motion, least action, and thermal efficiency is discussed. The meaning of idiomatic terms—thermal physics, thermodynamics, thermostatics, thermotics, and thermal analysis—is specified and revealed within two parallel developed branches of thermal science. Itemized 105 references with titles.

Keywords Thermometry · Thermodynamics · Thermostatics · Thermotics · Thermal physics · Natural laws · Temperature scales · H.Suga · T.Ozawa

Introduction

A plentiful literature about thermal science [1–5] and its precedent thermometry [6–11], as well as historic thermal analysis [12–21], is available through various sources easy accessible even from internet. Therefore, we do not want to repeat available figures, but prefer mentioning some hidden aspects responsive to the record of accessible citations, while not claiming completeness. All history records reach back to the early concept of hotness [22] as the scientific principle on which temperature measurement is based and evolved as a part of the development of thermal science.

Thermoscope, thermometer, thermometry, and temperature scales

The ancient Greek discerned the expansion of air by heat long time ago. The earliest writings concerned that the phenomena were the Works of Philo of Byzantium and Heron of Alexandria (II Century B.C.). The Greeks made simple thermometers in the first century BC, but there was no way to quantify heat with hot and cold still following the Aristotelian tradition of being treated as fundamental qualities of the universe. The ideas of Aristotle were adopted by Galen (A.D. 130–200), who was the first describing the heat and cold by a number about fifteen hundred years ago. And, the word temperature originated from “temper,” after Galen determined the “complexion” of a person by the proportion in which four human “qualities” were tempered [6–8]. It is known that by the 16th Century, knowledge of the “weatherglass” (the other common name for thermoscope) became widely spread among educated people either due to the new edition of Heron’s papers or upon the accessibility of excerpts of Arabian alchemistic manuscripts.

One of the first modern-times considerations on active principles (heat and cold) acting on a passive matter can be found in the treatise published in 1563 by Italian Bernardino Telesio (1509–1588) and perceived by Francesco Patricio (1529–1597) and Giordano Bruno (1548–1600). The first air thermoscope appeared in 1594 through Galileo Galilei (1564–1542), but the Englishman Robert Fludd (1574–1651) was also regarded as one independent inventor around 1617. Yet, another originator was
indicated Cornelis J. Drebbel (1572–1633) who made a
two-bulbed J-shaped thermometer between 1598 and 1622.
In 1626, the factual word “thermometer” was initially used
to describe thermoscope equipped with a scale marked with
eight degrees by Jean Leurechon (1591–1670) in his book [23]. Shortly after, the world-known Czech educator Jan
Amos Comenius (1592–1670) inserted reflections on the
role of heat and cold in nature into his book work [24] and
then, in 1659, published another worth noting book [25] on
the nature of heat and cold. In 1665, Christian Huygens
(1629–1695) had a brilliant idea to use the melting and
boiling points of water as a standard gauge.

The first quantitative thermal law expressing the depend-
ce of temperature of a cooling body (expressed in 8
degrees) on the time was published in 1701 by Isaac Newton
(1643–1727). Such a forgotten attempt to put high temper-
atures on a mathematical scale 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 \(\theta\) was the temperature in units of the above scale and \(x\) represented the logarithmic temperature [26–28].

One of the earliest challenges at calibration and stan-
dardization between thermometers was attempted in 1663 by
the members of Royal Society in London, who agreed to use
one of several thermometers made by Robert Hooke
(1635–1703) as the standard so that the reading of others
could be adjusted to it. Non-Euclidean mathematician
Johann H. Lambert (1728–1777) revealed in his less familiar
book “Pyrometria” as many as nineteen temperature scales.
Differential air thermometer was invented, almost simulta-
nceously, by John Leslie (1766–1832) of Edinburgh and by
Benjamin Thompson, Count Rumford (1753–1814) and
consequently James Clerk Maxwell (1831–1879) recognized
that for thermometry (to be a logically closed system) it is
necessary to add a concept of thermal equilibrium.

Daniel G. Fahrenheit (1686–1736) proposed in 1724 a
temperature scale of 100 degrees from 0 °F (at the tem-
perature of mixture of ammonium chloride, water, and ice)
and 100 °F at the human body temperature and invented
the first mercury thermometer. A year later, Joseph-Nicolas
Delesié (1688–1768) introduced an exotic scale with
240 degrees, which was later (1738) modified and adjusted
to 150°D corresponding to the melting point of water and
to 0°D at boiling point of water (240°D = 60 °C), and this
scale was being used in Russia for the whole hundred
years. The story of different scales, from Fahrenheit and
Celsius degrees to the now-forgotten Rankine, Römer,
Delesié, Réaumur, Lime, or Amontons scales, and the
history of the gradual scientific then popular understanding
of the concept of temperature are familiar and thus not
herewith reiterated [18–22, 26].

Worth of a special attention would be 1848 Thomson’s
approach based on thermal efficiency \(\eta\) (originated [29, 30]
by Nicolas Leonard Sadi Carnot (1796–1832)) introducing
thus a logarithmic temperature scale, \(\theta\), in the form of
\[
d\theta \approx dT/T. \]
After integration, it follows that
\[
\theta = \text{const}_1 \ln T + \text{const}_2,
\]
where both constants can be determined using
the traditionally fixed points of the melting and boiling of
water. This more natural scale, however, would dramatically
change the customary concept of thermodynamics [26, 28]
easing the interpretation of the third law of thermodynamics
replacing the traditional zero temperature by infinity (\(T = -\infty\)). However, the conventional degree of freedom,
\[
\sim 1/2 kT,
\]
would revolutionize to embarrassing proportion-
ality, \(T \sim \exp((\theta - \text{const}_2)/\text{const}_1)\), etc. On the other hand,
the simple interpretation of heat conduction and the cus-
tomary evaluation of efficiency for steam engines necessitate
the temperature to behave like the potential of a heated fluid
and the traditional linear scale, equivalent to the contempo-
rary Kelvin’s international scale, manage to survive as the
most opportune one. There can be seen various attempts
introducing so far inconvenient thermodynamics concepts
based, for example on the Carnot use of caloric [31, 32].

**Thermal physics, thermodynamics, thermotics,
and thermal analysis**

Early attempts to create a common scientific language can
be associated with the early work by Comenius emerging
from his effort to portray heat [25]. However, equally
important was his challenge to articulate his own idea of
universal language [33] and its relation to the encyclopedic
knowledge concept of the “pansophia” having a profound
influence on the discussion on an exploitation of such a
universal language in England. Inquisitively it resulted to
his invitation offered by John Winthrop (1588–1649) a
governor of Massachusetts to become a rector of a new
US university founded by preacher John Harvard. Later,
the Comenius younger follower Gottfried W. Leibnitz
(1648–1716) used his idea of “lingua catholica” in an
attempt to formulate mathematical, scientific, and meta-
physical concepts more effective. He introduced “charac-
teristica universali” hopeful to create a language usable
within the framework of a universal logical calculation
[34, 35] or “calculus ratiocinator” convincingly affected
by Rene Descartes (1596–1650) through his correspond-
ence with Comenius [21]. Descartes [36] became
responsible for the formulation of conservation law applied
to the amount of movement (momentum-mv) later cor-
corrected by Leibnitz as “vis viva” (mv²). On the other hand,
it is worth mentioning that the law of conservation was
foreseen by another Czech mastermind Jan Marcus Marci (1595–1667) [37].

Another significant impact to generalized understanding of nature was brought by Pierre de Fermat (1601–1655) when introducing the principle of least time [38]: “the Nature acts via the easiest and the most accessible method reached within the shortest time.” A century later it was resumed by Pierre-Louis M. de Maupertuis (1698–1759) who in 1744 envisaged the least action premise noting [39]: “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 \( (m) \) with their velocity \( (v) \) and the distance travelled \( (l) \), which interestingly correlates with the Planck constant \( h (=mv\ell) \). It recently became the basis to explain the inborn self-periodicity of many natural processes [40–42]. These fundamental laws of motion became equally crucial as the Carnot temperature limits for the thermal efficiency of heat engines [20, 29, 31, 32].

The decisive experimental studies, thanks to which temperature became a clearly measurable physical quantity, contributed the formation of a contemporary discipline language. In the 1840s, a thermodynamic discourse was worked up by Henri Victor Regnault (1810–1878) whose attitude, however, turned out long after Joseph Black (1728–1799) [15, 17, 26, 43] distinguishing between the specific heat (heat capacity) and the latent heat [19, 30]. Curiously, his less known correspondence [21] with James Watt (1736–1819) who invented steam engine in 1776 remained unmentioned. Consequently, Pierre Simon de Laplace (1749–1827) and Antoine Lavoisier (1743–1794) performed in 1786 their first calorimetric measurements [25, 44–50]. Yet, after the detailed results of 1842 Regnault’s dilatometric and heat capacity measurements, and together with 1824 theorem of Carnot [29, 32] and its 1834 interpretation by Benoit-Paule E. Clapeyron (1799–1864) it provided the basis for the 1848 introducing of absolute temperature scale by William Thomson (baron Kelvin of Larges) (1824–1907) and for the factual inception of thermodynamic “language” [15, 51–53] as a new science, not forgetting the work of Josiah Willard Gibbs (1839–1903) [15, 21, 51]. Literally, this new science would be optimally associative with the term “thermostatics” by way of thermally equilibrated states and developed through the Carnot, Clapeyron, Clausius, and/or Gibbs work as a branch of “dissipationless work” understanding of the science of heat [2, 26].

Complementary approach involving the concept of “workless dissipation” comprise, however, temperature gradients (existing everywhere and in thermostatic concepts often neglected due to necessary simplifications) which was developed in the course of studies by Newton, Fourier, Stokes and/or Onsager framing thus the new field of “true” thermodynamics involving irreversible processes [1–3, 54]. Most remarkable personalities became Joseph Baptiste Fourier (1768–1830) while publishing the laws of heat transfer 1822 [55] and Lars Onsager (1903–1976) [56] while depicting the equations of irreversible processes (later rooting the field of extended thermodynamics [57, 58]).

So far, the enduring term of thermodynamics subsists the energetic concepts [59–63] of temperature and heat based upon the Greek word “therme” (= heat); however, it is worth noting that it also involves a Greek concoction for the motive power of heat, i.e., thermodynamics actually means “heat-engine science.” It is concerned with heat and its relation to other forms of energy and work defining macroscopic variables which describe average properties of material bodies, and explains how they are related and by which laws they change with equilibrating [59–71]. There are many grandfathers such as a UK professor Edward Armand Guggenheim (1901–1970) [3, 69].

Yet, more general terms “‘thermal science” or “science of heat” [2] sustain for a shared study of thermodynamics, fluid mechanics, heat transfer, thermal investigation, combustion, and thermokinetics while more restricted terms “thermodynamics” [44, 72–74] involve the combined study of thermodynamics, statistical mechanics, and kinetic theories providing thus an umbrella subject which is typically designed to provide a general introduction to each of core heat-related subjects.

There is yet another a more unfamiliar term “thermotics” (akin the term “mathematics”) staying also behind the generalized science of heat (and also based on its Greek origin), apparently used as early as in 1837 [75]. In 1967, American physical chemist Ralph Tykodi (1925) made an attempt to revive thermotics [76, 77] as an idiom which, he said, should be equal in usage to 1946 version of “energetics” provided by the Danish physical chemist Johannes Nicolaus Bronsted (1879–1947) [59, 60]. In this view, thermotics subsist a thermal science comprised of three sub-branches: “thermo-statics” pertaining to the ordinary classical equilibrium aspects of heat, “thermo-dynamics” relevant to those aspects for which time variation is important, and “thermo-staedics” concerning the aspects that are temporally steady or stationary. The focus of latter term may be seen more suitable to envelop the field of “thermal analysis” [1, 14–21, 26, 78] the true meaning of which was never appropriately located within the spheres of thermal sciences [2, 26, 30].

The entire term thermal analysis was coined by Gustav Heinrich J.A. Tamman, (1861–1938) [79, 80], further accredited in [12, 13] and then particularized in our previous papers [2, 14, 17–19]. Seemingly the inherent thermoanalytical theory is historically based [12, 81] on equilibrated (i.e., thermostatic) states often omitting the non-equilibrium (flux) character of its measurements, which seems be a most crucial source of inaccuracy in the existing theoretic evaluation of DTA (= differential thermal analysis) [2, 13] where thermal gradients are habitually not incorporated in the evaluation (with few exceptions [82–85]).
A tribute paid to Japanese personalities: Hiroshi Suga and Takeo Ozawa

The field of thermal analysis became a starting point for expanded cooperative studies under the umbrella of the International Confederation (ICTA/ICTAC) [86, 87] which benefits from its over 40 years running established under the profitable impact of many foremost personalities [88] such as the distinguished celebrities of Hiroshi Suga (1930) and Takeo Ozawa (1932–2012) with whom the author has the honor to publish joint studies [89–91] being also the guarantee of the 1996 foundation of the School of Energy Science at the Kyoto University. Both of these Japanese famous persons are accountable for the augmentation of thermoanalytical societies as well as the development of the theory of processes carried out under non-isothermal conditions. Though the work of Ozawa (e.g., [92–99]) received a wider recognition (H-index = 81, total citation record = 38,580 with 2,316 feedback for his best cited paper) because attentive to a more fashionable subject of thermoanalytical kinetics, the work of Suga (H-index = 40, total citation record = 5,582 with 316 feedback for his best cited paper) enveloped a more fundamental subject of generalized behavior and characterization of noncrystalline solids (e.g., [91, 100–105]). Their worldwide impact has positively affected the international cooperation, which is well illustrated by the group photos (above Figs. 1 and 2).

We all are very grateful for their fruitful guidance and affable dissemination of knowledge.

Acknowledgements. The results were developed within the CEN-TEM project, reg. no. CZ.1.05/2.1.00/03.0088 that is co-funded from the ERDF within the OP RDI program of the Ministry of Education, Youth and Sports. The author feels also indebted to his scientific friends, coworkers, and uppermost thermodynamists Pavel Holba (Pilsen), György Liptay (Budapest), Jiří Mareš (Prague), Jiří Malek (Praha), Nobuyoshi Koga (Hiroshima), late German K. Moiseev (Jekaterinburg), Ingo Müller (Berlin), late Tooru Atake (Tokyo), late Ivo Proks (Bratislava), Vladimir Satava (Prague), Peter Šimon (Bratislava), late Bernhard Wunderlich (Knoxville), Harumi Yokokawa (Tsukuba), and Shmuel Yariv (Jerusalem). The author, however, was disappointed that this tribute lecture was suspended by the conference secretary (Riko Ozao) out from the Commemorate Special Session (crediting the conference honorary chairmen) to general session only.

References

Development and the role of personalities

23. Leurechon J. La Recreation Mathematique; 1628.
42. Proks I, Comenius and Black as progenitors of thermal analysis. Thermochim Acta. 1985;92:3–12.
77. Tykodi RJ. Correspondence: thermodynamics-thermotics as the name of the game. Ind Eng Chem. 2011;60(22).
21 Historical roots and development of thermal analysis and calorimetry

Jaroslav Šesták¹, Pavel Hubík², Jiří J. Mareš²

¹New Technology Research Centre, University of West Bohemia, Univerzitní 8, CZ-30614 Plzeň, Czech Republic
²Institute of Physics ASCR, v.v.i., Cukrovarnická 10, 162 00 Praha 6, Czech Republic
e-mail: sestak@fzu.cz

21.1 Historical aspects of thermal studies, origins of caloric

Apparently, the first person which used a thought experiment of continuous heating and cooling of an illustrative body was curiously the Czech thinker and Bohemian educator [1], latter refugee Johann Amos Comenius (Jan Amos Komenský, 1592-1670) when trying to envisage the properties of substances. In his “Physicae Synopsis”, which he finished in 1629 and published first in Leipzig in 1633, he showed the importance of hotness and coldness in all natural processes. Heat (or better fire) is considered as the cause of all motions of things. The expansion of substances and the increasing the space they occupy is caused by their dilution with heat. By the influence of cold the substance gains in density and shrinks: the condensation of vapor to liquid water is given as an example. Comenius also determined, though very inaccurately, the volume increase in the gas phase caused by the evaporation of a unit volume of liquid water. In Amsterdam in 1659 he published a focal but rather unfamiliar treatise on the principles of heat and cold [2], which was probably inspired by the works of the Italian philosopher Bernardino Telesius. The third chapter of this Comenius’ book was devoted to the description of the influence of temperature changes on the properties of substances. The aim and principles of thermal analysis were literally given in the first paragraph of this chapter: citing the English translation [3-5]: "In order to observe clearly the effects of heat and cold, we must take a visible object and observe its changes occurring during its heating and subsequent cooling so that the effects of heat and cold become apparent to our senses." In the following 19 paragraphs of this chapter Comenius gave a rather systematic description (and also a partially correct interpretation) of the effects of continuous heating and cooling of water and air, and also stressed the reversibility of processes such as, for example, evaporation and condensation, etc., anticipating somehow the concept of latent heat. Comenius concludes this chapter as follows: "All shows therefore that both heat and cold are a motion, which had to be proved." In the following chapter Comenius described
and almost correctly explained the function of a thermoscope (‘vitrum caldarium’) and introduced his own qualitative scale with three degrees of heat above and three degrees of cold below the ambient temperature launching thus a concept of “caloric”.

Nonetheless, it is difficult to trace [1,3-6] and thus hard to say if it was possible (though likely) to disseminate the Comenius idea of caloric from Amsterdam (when he mostly lived and also died) to Scotland where a century later a new substance, or better a matter of fire, likewise called caloric (or caloricum), was thoroughly introduced by Joseph Black (1728-1799) [7] and his student Irvine. Unfortunately, Black published almost nothing in his own lifetime [5,8] and his attitude was mostly reconstructed from contemporary comments and essays published after his death.

Caloric [1,7,9-11] was originally seen as an imponderable element with its own properties. It was assumed, e.g., that caloric creeps between the constituent parts of a substance causing its expansion. Black also supposed that heat (caloric) was absorbed by a body during melting or vaporization, simply because at the melting or boiling points sudden changes took place in the ability of the body to accumulate heat (~1761). In this connection, he introduced the term ‘latent heat’ which meant the absorption of heat as the consequence of the change of state. Irvine accounted that the relative quantities of heat contained in equal weights of different substances at any given temperature (i.e., their ‘absolute heats’) were proportional to their ‘capacities’ at that temperature and it is worth noting that the term ‘capacity’ was used by both Black and later also Irvine to indicate specific heats [7,9-11].

Black’s elegant explanation of latent heat to the young James Watts (1736-1819) became the source of the invention of the businesslike steam engine as well as the inspiration for the first research in theory related to the novel domain of thermochemistry, which searched for general laws that linked heat, with changes of state. In 1822, Jean-Baptiste Joseph Fourier (1768-1830) published an influential book on the analytical theory of heat [12], in which he developed methods for integration of partial differential equations, describing diffusion of the heat substance. Based on the yet inconsistent law of conservation of caloric, Siméon D. Poisson (1823) derived a correct and experimentally verifiable equation describing the relationship between the pressure and volume of an ideal gas undergoing adiabatic changes. Benjamin Thompson (Count Rumford, 1753-1814) presented qualitative arguments for such a fluid theory of heat with which he succeeded to evaluate the mechanical equivalent of heat [11,13]. This theory, however, was not accepted until the later approval by Julius Robert Mayer (1814-1878) and, in particular, by James Prescott Joule (1818-1889), who also applied Rumford’s theory to the transformation of electrical work.

In the year 1826 Nicolas Clement (1779-1842) [11] coined the unit of heat as amount of caloric, necessary for heating 1 g of liquid water by one degree centigrade. Though the expected temperature changes due to “thickened caloric” did not experimentally occur (cf. measurements in “Torricelli’s vacuum” over mercury by Gay-Lussac) and in spite of that Thompson (1798) showed that the heat
could be produced by friction \textit{ad infinitum}, the caloric theory survived many defeats and its mathematical scheme is in fact applied for the description of heat flow until today. The above customary unit was called ‘calorie’ (cal) or ‘small calorie’, whereas a ‘large calorie’ corresponded to the later ‘kilocalorie’ (kcal). The word “calorie” was more widely introduced into the vocabulary of academic physicists and chemists by Favre and Silbermann [14] in 1852. The expression of one kilocalorie as 427 kilogram-meters was given by Mayer in the year 1845.

We should add that caloric differed from the foregoing concept of phlogiston because, beside else, it could be measured with an apparatus called a calorimeter; however, it is not clear who was the first using such an instrument. If we follow the studies of Brush [8], Mackenzie [15] and Thenard [16] they assigned it to Wilcke. It, however, contradicts to the opinion presented in the study by McKie and Heathcote [17] who consider it just a legend and assume that the priority of familiarity of ice calorimeter belongs to Laplace who was most likely the acknowledged inventor and first true user of this instrument (likely as early as in 1782). In fact, Lavoisier and Laplace entitled the first chapter of their famous “Mémoire sur la Chaleur” (Paris 1783) as “Presentation of a new means for measuring heat” (without referring Black because of his poor paper evidence). Report of Black’s employment of the calorimeter seems to appear firstly almost a century later in the Jamin’s Course of Physics [1].

21.2 Underlying features of thermal physics interpreted within the caloric theory

In the light of work of senior Lazare Carnot (1753-1823) on mechanical engines [11], Sadi Carnot (1796-1832) co-opted his ideas of equilibrium, infinitesimal changes and imaginatively replicated them for caloric (in the illustrative the case of water fall from a higher level to a lower one in a water mill). He was thinking about writing a book about the properties of heat engines applying caloric hypothesis generally accepted in that time within broad scientific circles [18-20]. Instead, he wrote a slim book of mere 118 pages, published in 200 copies only, which he entitled as the “Reflections on the motive power of fire and on machines fitted to develop that power” (1824) [21], which was based on his earlier outline dealing with the derivation of an equation suitable for the calculation of motive power performed by a water steam [11]. He discussed comprehensively under what conditions it is possible to obtain useful work (“motive power”) from a heat reservoir and how it is possible to realize a reversible process accompanied with heat transfer. Sadi also explained that a reversibly working heat engine furnished with two different working agents had to have the same efficiency related to the temperature difference, only. Among other notable achievements [14,22-27] there was the determination of the difference between the specific heats of gases measured at constant pressure and volume. He found that the difference was the same
for all gases, anticipating thus the Mayer’s relation for ideal gas: $c_p - c_v = R$. Sadi also introduced the “Carnot’s function” the inverse of which was later (1850) identified by Rudolph Clausius (1822-1888) [28], within the classical thermodynamics, with the absolute temperature $T$. Finally, Sadi adjusted, on the basis of rather poor experimental data that for the production of 2.7 mechanical units of “motive power” it was necessary to destroy one caloric unit of heat, which was in a fair correspondence with the later mechanical equivalent of heat: (4.1 J/cal). It is worth noting that already when writing his book he started to doubt the validity of caloric theory [11,27] because several of experimental facts seemed to him almost inexplicable. Similarly to his father, Sadi’s work remained unnoticed by contemporary physicists and permanently unjustly criticized for his principle of the conservation of caloric, which is, however, quite correct for any cyclic reversible thermal process.

Adhering to the way of Carnot’s intuitive thinking [26,27], the small amount of work done $dL$ (motive power in Carnot’s terms) is performed by caloric $\zeta$ literally falling over an infinitesimal temperature difference $dT$ [11,16,26], $dL = \zeta F(T) dT$. The function $F(T)$ here is the Carnot’s function, which has to be determined experimentally, certainly, with respect to the operative definitions of quantities $\zeta$ and $T$. Carnot assumed that caloric is not consumed (produced) by performing work but only loses (gains) its temperature (by $dT$). Therefore, the caloric has there an extensive character of some special substance while the intensive quantity of temperature plays the role of its (thermal) potential; the thermal energy may be thus defined as the product $\zeta \times T$, in parallel with other potentials such pressure (choric potential) for volume, gravitational potential for mass and electrostatic potential for charge.

Taking into account that caloric is conserved during reversible operations, the quantity $\zeta$ must be independent of temperature and, consequently, Carnot’s function $F(T)$ has to be also constant. Putting the function equal identically 1 the unit of caloric fully compatible with the SI system is defined. Such a unit (Callendar [23]), can be appropriately called “Carnot” (abbreviated as “Cn” or “Ct”). One “Ct” unit is then such a quantity of caloric, which is during a reversible process capable of producing 1 J of work per 1 K temperature fall. Simultaneously, if such a system of units is used [26,27], the relation $dL = \zeta dT$ retains.

The caloric theory can be extended for irreversible processes by adding an idea of wasted (dissipated) motive power which reappears in the form of newly created caloric [26]. Analyzing Joule’s paddle-wheel experiment from view of both this extended caloric theory and classical thermodynamics, it can be shown that the relation between caloric and heat in the form $d\zeta = J dQ/ T$ takes place, which, at first glance, resembles the famous formula for entropy, certainly if we measure the heat in energy units. This correspondence between entropy and caloric, may serve as a very effective heuristic tool for finding the properties of caloric by exploitation the results known hitherto from classical thermodynamics. From this point of view it is clear that the caloric theory is not at any odds with experimental facts, which are only anew explained ([26]). The factor $J$ historically determined by
Joule \( (J \approx 4.185 \text{ J/cal}) \) should have been rather related with the establishment of a particular system of units then with a general proof of the equivalence between heat and energy.

One of the central questions of the Carnot’s theory of heat engines is the evaluation of engine efficiency. The amount of caloric \( \varsigma \) which is entering the completely reversible and continuously working heat engine at temperature \( T_1 \) and leaving it at temperature \( T_2 \) will produce a motive power of amount \( L \). Carnot’s efficiency \( \eta_c \) defined as a ratio \( L/\varsigma \) is then given by a plain temperature drop \( \Delta T = (T_1-T_2) \) (as measured in the ideal gas temperature scale). Transforming the incoming caloric into thermal energy \( T_1\varsigma \), we obtain immediately Kelvin’s dimensionless efficiency \( \eta_K \) of the ideal reversible heat engine, \( \eta_K = \{1 - (T_2/T_1)\} \), which is well-known from textbooks of thermodynamics \([3,29]\).

However, \( \eta_K \) is of little significance for the practical evaluation of the performance of real heat engines, which are optimized not with respect to their efficiency but rather with respect to their available output power. As a convenient model for such a case it may be taken an ideal heat engine impeded by a thermal resistance \([26]\). The effect of thermal resistance can be understood within the caloric theory in such a way that the original quantity of caloric \( \varsigma \), taken from the boiler kept at temperature \( T_1 \), increases, by passing across a thermal resistance, to the new quantity equal to \( \varsigma + \Delta \varsigma \), entering then the ideal heat engine at temperature \( T<T_1 \), and leaving it temperature \( T_2 \). If we relate the quantities \( L \) and \( \varsigma \) to an arbitrary time unit (we conveniently use for this purpose a superscript \( u \)), it follows \( Lu^u = \lambda(T_1-T)(T-T_2)/T \), where for the evaluation of temperature drop across the thermal resistance we can apply the Fourier law \([12]\) \( \dot{\varsigma} = T_1 - T \), where \( \lambda \) is a constant representing the inverse of thermal resistance. The condition for the optimum of the output power with respect to temperature \( T \) then reads \( dL^u/dT = 0 \), from which we obtain \( T = \sqrt{T_1T_2} \) \([26]\). Consequently, the Carnot’s true efficiency of such a system with optimized output power is thus given by a formula, \( \eta_c = T_1 \{1 - \sqrt{T_2/T_1}\} \). Such a root square dependence, which is the direct consequence of linearity of Fourier’s law, is also obviously repeated for the above mentioned dimensionless Kelvin’s efficiency, \( \eta_K \). Because of enormous effort of engineers to optimize the real output power of concrete heat engines, the above formula describes the actual efficiencies quite well as interestingly shown for authentic industrial cases by Curzon and Ahlborn \([30]\).

21.3 Early scientific and societal parentage of thermal analysis

Standard reference books \([16,19,21,29,31]\) are rather coy about the history of thermometry and thermal analysis being the subject of specified papers and book chapters \([1,4-11,15,32-35]\), which goes back to historic times of Isaac Newton \((1642–1727)\) who published his temperature scale in 1701 the significance of which lies both in its range of temperature and in its instrumentation presenting
also the famous Newton's Law of Cooling [36]. First cornerstone of the theory of warmth propagation was provided by J.-B. J. Fourier who initiated the investigation of Fourier series and their application to problems of heat transfer [12]. The very roots of thermal analysis appear in the 19th century where temperature became an observable and experimentally decisive quantity, which thus turned into an experimentally monitorable parameter associated with a consequent underpinning of the field of thermodynamics [29,34,35]. The first characterization of thermometric measurements is identified in Uppsala in 1829 through the earliest documented experiment which nearly meets current criteria. It was Fredrik Rudberg (1800-1839) [15,22] who recorded the inverse cooling-rate data for lead, tin, zinc and various alloys which were placed in a smaller vessel surrounded by a large double-walled iron vessel where the spaces between its two walls, as well as the top lid, were filled with snow to ensure that the inner walls were always kept at zero temperature. Once the experimental condition 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.

One of important impacts came with the discovery of thermoelectric effect [37] by Thomas J. Seebeck (1770-1831) occurring in a circuit made from two dissimilar metals and the consequent development of a device called thermocouple [37,38], suitable as a more accurate temperature-measuring tool, in which gas volume or pressure changes were replaced by a change of electric voltage (Augustin G.A. Charpy (1865-1945) [39]). Henry L. Le Chatelier (1850-1936) [38] was the first who deduced that varying thermocouple output could result from contamination of one wire by diffusion from the other one or 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 thermometry was finally vindicated, which rapidly got a wider use. Floris Osmond (1849-1912) [15,40] investigated the heating and cooling behavior of iron with a goal to elucidate the effects of carbon so that he factually introduced thermometric measurements to then most important field: metallurgy [40].

In 1891, Sir William C. Roberts-Austen (1843-1902) [41] was accredited to construct a device to give a continuous record of the output from thermocouple and he termed it as ‘thermoelectric pyrometer’ (see Fig. 21.1) and in 1899, Stanfield published heating curves for gold and almost stumbled upon the nowadays idea of differential thermal analysis (DTA) when maintaining the thermocouple ‘cold’ junction at a constant elevated temperature measuring thus the entire differences between two high temperatures. Such an innovative system of measuring the temperature difference between the sample and a suitable reference material placed side-by-side in the same thermal environment, in fact initiated the consequent development of DTA instruments.
In 1909 there was elaborated another reliable procedure of preserving the high-temperature state of samples down to laboratory temperature, in-fact freezing-in the high-temperature equilibrium as a suitably ‘quenched’ state for further investigation [34]. It helped in the consistent construction of phase diagrams when used in combination with other complementary analytical procedures, such as the early structural microanalysis (introduced by Max von Laue (1879-1960) and sir William L. Bragg (1890-1971) when they detected the X-rays diffraction on crystals) along with the traditional metallographic observations. Another important step
toward the modern solid state physics was induction of the notion of diffusion by Adolf E. Fick (1829-1901) and its improved understanding by Ernest Kirkendall (1914-2005) as well as the introduction of the concept of disorder by Jakob I. Frenkel (1894-1952) [45] and models of glasses by Tammann [46].

By 1908, knowledge of the heating or cooling curves, along with their rate derivatives and inverse curves were sufficient enough to warrant a first review and more detailed theoretical inspection given by George K. Burgess (1874-1932) [47]. 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. Already in 1895, Charpy described in detail the construction of wire-wound, electrical-resistance based, tube furnaces that virtually revolutionized heating and temperature regulation [39]. 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.

However, the first automatic control was published by Carl Friedrich in 1912, which used a resistance box with a specially shaped, clock-driven stepped camplate 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 lowered the ambiguity in melting point determination from about >2 C down to ~0.5 C. Rates of about 20 K/min were fairly common during the early period later decreased to about quarter. Early in 1908, it was Burgess [47] who considered the significance of various experimental curves in detail concluding 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, nonetheless, little experimental details so that White [48] was first to show more theoretically the desirability of smaller samples providing a more 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. It is obvious that DTA was initially more a qualitative empirical technique, though the experimentalists were generally aware of its quantitative potentialities. The early quantitative studies were treated semiempirically and based more on instinctive reasoning. Andrews (1925) was first to use Newton’s law while Berg gave the early bases of DTA theory [49,50], which was independently simplified by Speil. In 1939 Norton published his classical paper on differential thermal techniques where he made rather excessive claims for their value both in the identification and quantitative analysis exemplifying clay mixtures [51]. Vold (1948) [52] and Smyth (1951) [53] proposed a more advanced DTA theory, but the first detailed theories and applicability fashions, free from restrictions, became
accessible by followers in fifties [3,50,54-58], e.g., Keer, Kulp, Evans, Blumberg, Erikson, Soule, Boersma, Borchard, Damriels, Deeg, Nagasawa, Tsuzuki, Barshad, Strum, Lukaszewski, etc.

In general, the thermoanalytical methods gained theoretical description early sixties [59-61]. The resulting thermal effects, explicitly temperature disparity ($\Delta T$), can be analyzed at four different but gradually escalating levels [3,34,62,63]: fingerprinting (identity), quality, quantity (peak areas) and kinetics (peak shape) which were extensively applied to assessments of phase diagrams, transition temperatures, and chemical reactions, as well as to the qualitative analysis of metals, oxides, salts, ceramics, glasses, minerals, soils, and foods. Because of its easy accessibility DTA was used to study behavior of the constrain states of glasses [64-68], inherent processes conventionally viewed as a diagram of temperature (T) versus enthalpy (H) [66], which derivative resembles the entire DTA curve (informative for the analysis of glassforming processes [34]).

21.4 Theoretical basis, quantitative thermometric and calorimetric measurements

In the beginning, DTA could not be classified as a calorimetric method since no heat was measured quantitatively [59-62]. Only the temperature was determined with the precision of the thermocouple. The quantitative heat effects were traditionally measured by calorimetry. Beside the above quoted ice-calorimeter pioneered by Laplace the early instrumentation for the determination of heat capacity was based on the classical adiabatic calorimeter and designed by Walther H. Nernst (1864-1941) [69,70] for low temperature measurements [71] (in Germany 1911). Its original experimental arrangement involved the introduction of helium gas as a thermally conducting medium by which the specimen would rapidly reach the temperature required for the next measurement.

Although the measurements of heat changes is common to all calorimeters, they differ in how heat exchanges are actually detected, how the temperature changes during the process of making a measurement are determined, how the changes that cause heat effects to occur are initiated, what materials of construction are used, what temperature and pressure ranges of operation are employed, and so on. If the heat, $Q$, is liberated in the sample, a part of this heat accumulates in the calorimetric sample-block system and causes a quantifiable 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 the Tian equation [72].

The calorimetry classification came independently from various sources, e.g. [3,73-75]. The principal characteristics of a calorimeter are the calorimeter capacity, effective thermal conductivity, and the inherent heat flux, occurring at the in-
interface between the sample-block, B, and the 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 \( d(T_B - T_J) \rightarrow 0 \), adiabatic \( (T_B = T_J) \), isothermal \( (T_B = T_J = \text{const.}) \) and isobroolic \( (T_B - T_J) \rightarrow 0 \). The most common version of the instrument is the diathermal arrangement 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 enough 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 internally attached source (often called ‘microheater’). The energy changes are then determined from the energy supplied to the source. For low values of heat, the heat loss can be decreased to minimum by a suitable instrumental set-ups and this version is called as adiathermal calorimeter. An 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.

Eliminating the thermal gradients between the block and the jacket by using an electronic regulation requires, however, sophisticated circuits and more complex set-ups. 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 reservoir in which the calorimetric block is contained, the instrument are often termed transformation calorimeter. Quasi-isothermal calorimeters are, in turn, instruments with thermal compensation provided by electric microheating and heat removal is accomplished by forced flow of a fluid, or by the well-established conduction through a system of thermocouple wires or even supplemented by Peltier cooling effect. The method in which the heat is transferred through a thermocouple system is often called Tian-Calvet calorimetry. A specific group is formed by isoperibolic calorimeters, which essentially operate adiabatically with an isothermal jacket.

Even in the 1950s, it was a doubtful prediction that classical DTA and adiabatic calorimetry would merge, producing a differential scanning calorimeter (DSC). The name DSC was first mentioned by O’Neil [78] for a differential calorimeter that possessed continuous power compensation (close-to-complete) between sample and reference. This development came about because the key concern of calorimetry is the reduction of, and certainly also correction for, heat losses and/or gains due to inadvertent temperature distribution in the surroundings of the calorimeter. The heat to be measured can never be perfectly insulated; even in a true adiabatic calorimeter certain heat-loss corrections have to be made and resulting adiabatic deviation must then be corrected through extensive calibration experi-
ments. In order to cancel the heat losses between two symmetric calorimeters were used (e.g., twin calorimetry – one cell with the sample and the other identical, but empty or filled with a reference material), however presented control problems were not easy to handle [3].

True DSC is monitoring the difference between the counterweighing 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. This technique was originally introduced by Eyraund in fifties [84]. Such an experimental regime bears a quite different measuring principle when comparing with DTA because the temperature difference is not used for the observation itself but is exclusively employed for the regulation only. Certainly, it is the way for accomplishing the most precise measurements of heat capacity (close to adiabatic calorimetry) but technically restricted, to the temperature range up to about 700 °C, where heat radiation become decisive making consequently the regulation and particularly compensation complicated.

Three major types of DSCs emerged that all are classified as scanning [79], isoperibolic twin-calorimeters. One type makes use of approximate power compensation between two separately heated calorimeters, and the other two merely rely on heat exchange of two calorimeters placed symmetrically inside a single heater, but differing in the positions of the controlling thermometers. Even the majority commercial DTA instruments can be classified as a double non-stationary resembling calorimeter in which the thermal behaviors of sample are compared with a correspondingly mounted, inert reference [3]. It implies control of heat flux from surroundings and heat itself is 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 mediated by massless phonons so that the inherent flux does not exhibit inertia as is the case for the flow of electrons. The thermal inertia of apparatus (as observed in DTA experiments) is thus caused by heating a real body and is affected by the entire properties of materials, which structure the sample under study.

The decisive theoretical analysis of a quantitative DTA was based on the calculation of heat flux balances introduced by Factor and Hanks [80], detailed in 1975 by Grey [81], which premises were completed in 1982 by the consistent theory made up by Holba and Šesták [3,82,83]. It was embedded within a ‘caloric-like’ framework centred on macroscopic heat flows encountered between large bodies (DTA cells, thermostats). Present DTA/DSC instruments marched to high sophistication, computerization and miniaturization, see, e.g., Fig. 21.1

All the equations derived to the description of theoretical basis of DTA/DSC methods can be summarized within the following schema [3,34], which uses a general summation of inherent terms (each being responsible for the subsequent distinct function): Enthalpy + Heating + Inertia + Transient = Measured Quantity. It implies that the respective effects of enthalpy change, heating rate and heat transfer are reflected in the value of the measured quantity for all set-ups of the
thermal methods commonly exercised. Worth noting is the *inertia term*, which is a particularity for DTA (as well as for heat-flux DSC) expressing a specific correction due to the sample mass thermal inertia owing to the inherent heat capacity of real materials. It can be visualized as the sample hindrance against immediate ‘pouring’ heat into its heat capacity ‘reservoir’ and it is apparent similarity to the definite time-period necessary for filling a bottle by liquid. Keep in mind, that the consequential compensation DSC calorimetry is of a different nature because it evaluates, instead of temperature difference ($\Delta T \Rightarrow 0$), compensating heat fluxes and thus the heat inertia term is absent $[3,34,82]$. The practice and basis of DSC has been treated numerously $[85,86]$.

In order to meet an experimental pre-requisition of the transient term (involving the instrumental constant characteristic of a particular DTA apparatus), the routine procedure of calibration is indispensable for a quantitative use of DTA. It is commonly guaranteed by a practice of an adequate incorporation of defined amounts of enthalpy changes by means of the selected test compounds (which widespread standardization, however, failed so that no ICTAC recommendation was issued). Nevertheless, in the laboratory scale, certain compounds (and their tabulated data) can be employed, but the results are questionable due to the various levels of the tabulated data accuracy. Thus it seems be recommendable to use the sets of solid solutions because they are likely to exhibit comparable degree of uncertainty (such as $\text{Na}_2\text{CO}_3\cdot\text{CaCO}_3$ or $\text{BaCO}_3\cdot\text{SrCO}_3$ or various sesquioxides mixtures like manganese spinels) $[3]$. However, the use of the Joule heat effect from a resistance element on passage of electric charge is a preferable method for achieving a more ‘absolute’ calorimetric calibration. It certainly requires special set-ups of the measuring head enabling the attachment of the micro-heater either on the crucible surface (similarly to DSC) and/or by direct immersing it into the mass of (often powdered) sample. By combination of both experimental methods (i.e., substance’s enthalpies and electric pulses) rather beneficial results $[87]$ may be obtained, particularly, when a pre-selected amount of Joule heat is electronically adjustable (e.g., simple selection of input voltage and current pairs) $[3,34]$. It was only a pity that no commercial producer, neither an ICTAC committee, have ever became active in their wider application.

### 21.5 Modulated temperature, exploration of constrained and nano-crystalline states, perspectives

Yet another type of thermal measurement that had an early beginning, but initially did not see wide application, is the *alternating current* (AC) calorimetry) $[79,88]$. Advantage of this type of measurement lies in the application of a modulation to the sample temperature, followed by an analysis of responses. By eliminating any signal that does not correspond to the chosen operating frequency, many of the heat-loss effects can be abolished. Furthermore, it may be possible to probe rever-
sibility and potential frequency-dependence of changes of the studied sample. The heat capacity $C_s$ of the sample can be determined from the ratio of the heat-flow response of the sample, represented by its amplitude $A_{HF}$, to the product of the amplitude of the sinusoidal sample-temperature modulation $A_T$ and the modulation frequency $\omega=2\pi/p$ (p being the period). The next advancement in calorimetry occurred in 1992 with the amalgamation of DSC and temperature modulation to the temperature-modulated DSC (TMDSC) [79,89-91]. In this quasi-isothermal operation, sample temperature $T_S$ oscillates about the underlying temperature $T_0$ (constant/increasing) similarly as in an AC calorimeter (which bears an analogy modulus of a familiar isothermal dynamic mechanical analysis - DMA). The ensuing phase lag, $\epsilon$, is taken relative to a reference oscillation, $T_S = T_0 + A_T \sin(\omega t - \epsilon)$, and by deconvolution of the two signals; an average signal, practically identical to the standard DSC output and a reversing signal, related to the AC calorimetry. There, however, are additional factors necessary for consideration because of the peculiarity of twin calorimeter configuration, such as there is no thermal conductance between the sample and reference calorimeters, zero temperature gradients from the temperature sensors to the sample and the reference pans, and, also, zero temperature gradients within the contents of the pans. In other words, an infinite thermal conductance between temperature sensors and the corresponding calorimeters should be assumed. In summary, three directions of calorimetry were, thus, combined in the 20th century, which dramatically changed the capabilities of thermal analysis of materials [79]: The high precision of adiabatic calorimetry, the speed of operation and small sample size of DSC, and the possibility to measure frequency dependence of thermal behavior in AC calorimetry.

Another reason for both the modulation mode and the high-resolution of temperature derivatives is the fight against ‘noise’ in the heat flow signal in temperature swinging modifications. Instead of applying a standard way of eliminating such noise (and other unwanted signal fluctuations) by a more appropriate tuning of an instrument, or by intermediary measurements of the signal in a preselected distinct window, the fluctuations can be forcefully incorporated in a controlled and regulated way of oscillation. Thus the temperature oscillations (often sinusoidal) are located to superimpose over the heating curve and thus incorporated in the entire experimentation (temperature-modulated DTA/DSC) [89]. This was, in fact, preceded by the method of so-called periodic thermal analysis introduced by Proks as early as in 1969 [92], which aimed at removing the kinetic problem of ‘undercooling’ by cycling temperature. 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.

Another way of a more clear-cut investigation was introduction of microanalysis methods using very small samples and millisecond time scales [93,94]. It involved another peculiarity of truthful temperature measurements of nano-scale crystalline samples [95] in the particle micro range with radius $r$. The measurement becomes size affected due to increasing role of the surface energy usually
described by an universal equation: \( T_f/T_c \equiv (1 - C/r)^p \) where \( \infty \) portrays standard state and C and p are empirical constants (\( \approx 0.15 \text{ nm} < C < 0.45 \text{ nm} \) and \( p = 1 \) or \( \frac{1}{2} \)) [96-98].

Measurement in such extreme conditions brings extra difficulties such as measuring micro-porosity [99], quenching [94] and associated phenomena of the sample constrained states [64-68], variability of polymeric macromolecules [100,101] together with non-equilibrating side effect or competition between the properties of the sample bulk and its entire surface [97] exposed to the contact with the cell holder [34]. Increasing instrumental sophistication and sensitivity provided possibility to look at the sample micro-locally [93,101-103] giving a better chance to search more thoroughly toward the significance of baselines, which contains additional but hidden information on material structure and properties (in-homogeneities, local non-stoichiometry, interfaces between order-disorder zones [104]). Popular computer built-in smoothing of the noised experimental traces (chiefly baselines) can, however, become counterproductive.

In the future, we may expect certain refining trends possible returning to the original single-sample set-ups with recording mere heating/cooling curves. However, it will happen at the level of fully computerized thermal evidence involving self-evaluation of ‘calibration’ behavior of the sample thermal inertia and its subtraction from the entire thermal record in order to proliferate thermal effects possibly computing the DTA-like records. In addition, it may even incorporate the application of an arbitrary temperature variation enabling the use of self-heating course by simple placing the sample into the preheated thermostat and consequent computer evaluation of standardized effects or hitherto making possible to introduce fast temperature changes by shifting the sample within the temperature gradient of a furnace [3,34], etc.. Worth noting are special trends [105] particularly based on the modified thermophysical procedure of the rate controlled scope of thermal analysis (RCTA) [106] and/or on the diffusion structural diagnostics as a result of suitably labeled samples [107].

Upcoming prospect of thermal analysis scheme may go down to the quantum world [108] as well as may extend to the global dimension [109] touching even the remote aspects of temperature relativity [110], which, however, would become a special dimension of traditional understanding yet to come.

### 21.6 Some issues of socially shared activity, thermoanalytical and calorimetric journals and societies

The historical development and practical use of DTA in the middle European territory of former Czechoslovakia [33] was linked with the names Otto Kallauner (1886-1972) and Joseph Matějka (1892-1960) who introduced thermal analysis as the novel technique during the period of the so called “rational analysis” of ceramic raw materials [111] replacing the process of decomposition of clay minerals.
by digestion with sulphuric acid, which factually played in that time the role of the contemporary X-ray diffraction. They were strongly affected by the work of H. LeChatelier [38] and their visits at the Royal Technical University of Wroclaw (K. Friedrich, B. Wohlin) where the thermal behavior of soils (bauxite) was investigated during heating and related thermal instrumentation was elaborated. Calorimetric proficiency was consequently gained from Polish Wojciech Świętosławski (1881-1968). Much credit for further development of modern thermal analysis was attributed with Rudolf Bárt a (1897-1985) who stimulated thermal analysis activity at his coworkers (Vladimir Šátava, Svante Procházka or Ivo Proks) and his students (Jaroslav Šesták) at the Institute of Chemical Technology (domestic abbreviation VŠChT) in Prague.

In this aspect a special notice should be paid to the lengthy efforts, long journey and fruitful service of International Confederation of Thermal Analysis (ICTA and Calorimetry – ICTAC, instituted later in the year 1992 and facilitated by G. Della Gatta) as an important forerunner and developer in the field of thermal analysis, cf. Fig. 22.2. It has an important preceding history [6,112,113] connected with the former Czechoslovakia and thermoanalytical meetings organized by Prof. R. Bárt a just mentioning the earliest 1st Conference on DTA, (Prague 1956), the 2nd (Prague 1958) and the 3rd Conference on Thermography (Prague 1961) and the 4th Conference on DTA (Bratislava 1966). Robert C. Mackenzie (1920-2000) from Scotland was an invited guest at the 1961 meeting and upon the previous communication with Russian L.G. Berg and US P.D. Garn as well as Hungarian L. Erdey an idea for the creation an international society was cultivated aiming to enable easier contacts between national sciences, particularly across the separating ‘iron curtain”, which in that time divided the East and West Europe [6]. The first international conference on thermal analysis was then held in the Northern Polytechnic in London, April 1965 and was organized by British scientists namely B.R. Currell, D.A. Smith, J.P. Redfern, W. Gerrard, C.J. Keattch and D. Dollimore with a help of R.C. Mackenzie, B. Stone and US professors P.D. Garn and W.W. Wendlant, Canadian H.G. McAdie, French M. Harmelin, Hungarian L. Erdey, Japanese T. Sudo, Swedish G. Berggren and Italian G. Lombardi. Some invited speakers from the East Europe were particularly asked to come to bridge then existing tough political control on physical, freedom and civil frontiers strongly restricting the human rights of the Easterners (dominated by Soviet Union until the late 80s), such as F. Paulik (Hungary) and J. Šesták (Czechoslovakia). The consequent ICTA foundation in Aberdeen, September 1965, was thus established by these great progenitors of thermal analysis, Russian Lev G. Berg being the first ICTA presidents (with the councilors J.P. Redfern, R.C. Mackenzie, R. Bárt a, S.K. Bhattacharyya, C. Duval, L. Erdey, T. Sudo, D.J. Swaine, C.B. Murphy, and H.G. McAdie).

The progress of thermal analysis was effectively supported by the allied foundation of international journal, which editorial board was recruited from the keynote of both 1965 TA conferences as well as from the renowned participants at the 2 nd ICTA in Worcester (USA 1968). In particular it was Journal of Thermal

The field growth lead, naturally, to continuous series of the US Calorimetry Conferences (CalCon) [115-117], which supposedly evolved from a loosely knit group operating in the 1940s to a recent highly organized assembly working after the 1990s. Worth mentioning are Hugh M. Huffman (1899-1950) and James J. Christensen (1931-1987), whose names were recently used to shield the CalCon Awards presented annually for achievements in calorimetry. There is a number of other respectable cofounders, pointing out D.R. Stull, G. Waddington, G.S. Parks, S. Sunner, F.G. Brickwedde, E.F. Westrum, J.P. McCullough, D.W. Osbome, W.D. Good, P.A.G. O’Hare, P.R. Brown, W.N. Hubbart, R. Hultgren, R.M. Izatt, D.J. Eatough, J. Boerio-Goates, J.B. Ott. It provided a good example how the democracy-respecting society changing their chairmanships every year, which, however, did not find a place in the statutes of later formed ICTA. Consequentially, the Journal of Chemical Thermodynamics began publication in the year 1969 firstly edited by L.M. McGlasham, E.F. Westrum, H.A. Skinner and followed by others. More details about the history and state-of-art of thermal science and the associated field of thermal analysis were published elsewhere [3-6,32-35,112,113,115-117].

A specific domain of thermal analysis worth of attention (but laying beyond this file) is the weight measurement under various thermal regimes, pioneered by Czech Stanislav Škramovský (1901-1983) who coined the term ‘statmograph’ (from Greek stathmos = weight) [1,6,35], which, however, was overcome by the generalized expression ‘thermogravimetry’ as early introduced by French Clément Duval (1902-1976) or Japanese Kotaro Honda (1870-1954) [33-35, 118-121]. Consequently, it yielded a very popular topic of simultaneous weight-to-caloric measurements under so called quasi-isothermal and quasi-isobaric conditions [35,122] making use of the apparatus ‘derivatograph’, see Fig. 21.1, originated in Hungary in late 1950’s [122], see Fig. 21.3. It apparently lunches an extended field of microbalance exploitation and their presentation in regular conferences [123].
Fig. 21.2 Portraits show some influential personalities on the international scene, which are noteworthy for their contributions to the progress of the fields of thermal analysis (TA) and calorimetry including the founders of ICTA/ICTAC (around the inserted emblem), living persons limited to age above 75.

**Upper from left:** Cornelius B. Murphy (1918-1994), USA (TA theory); Robert C. Mackenzie (1920-2000), Scotland (DTA, clay minerals, history); Sir William C. Roberts-Austen (1843-1902), England (thermoelectric pyrometer); Gustav H. J. Tammann (1861-1938), Germany (inventing the term thermal analysis) and Nikolaj S. Kurnakov (1860-1941), Russia (contriving the first usable DTA); **below:** Lev G. Berg (1896-1974), Russia (TA theory); Rudolf Bártu (1897-1985), Czechoslovakia (ceramics, cements); Walther H. Nernst (1864-1941), Germany (originating low-temperature calorimetry); Édouard Calvet (1895-1966), France (heat-flow calorimetry) and Henry L. Le Chatelier (1850-1936), France (devising thermocouple); **yet below:** David J. Dollimore (1927-2000), England (later USA – theory, kinetics); Hugh M. Huffman (1899-1950), USA, founder of CalCon; James J. Christensen (1931-1987), USA (calorimetry); Wojciech Świętosławski (1881-1968), Poland (calorimetry); Čeněk Strouhal (1850-1922), Czechoslovakia (thermics, Strouhal numbers); yet below: Hans-Joachim Seifert (1930-), Germany (phase diagrams); Takeo Ozawa (1932-), Japan (energetic materials, kinetics); Eugene Segal (1933-), Romania (kinetics); Hiroshi Suga (1930-), Japan (calorimetry) and Giuseppe Della Gatta (1935-), Italy (calorimetry); **yet below:** Wesley W. Wendlandt (1920-1997), USA (TA theory, instrumentation); Bernhard Wunderlich (1931-), USA (macromolecules, modulated TA); Paul D. Garn (1920-1999), USA (TA theory, kinetics); Jean-Pierre E. Grolier (1936-), France (calorimetry) and Ole Toft Sørensen (1933-), Denmark (CRTA, non-stoichiometry); **Bottom:** Cyril J. Keattch (1928-1999), England (thermogravimetry); Hans G. Wiedemann (1920-), Switzerland (TG apparatuses, instrumentation); Shmuel Yariv (1934-), Israel (earth minerals); Joseph H. Flynn (1922-), USA (DSC, kinetics) and Patrick K. Gallagher (1931-), USA (inorganic materials).

Fig. 21.3 Recognized pioneers of thermal analysis, of Hungarian origin, who were accountable for the development of instruments (popular East-European TA apparatus “derivatograph”) - Ferenc Paulik (1922-2005), right, and for initiation of fingerprint methodology (multivolume atlas of TA curves by Akademia Kiado) - George Liptay (1931-), left.

Fig. 21.4 The photo from 28th conference of the Japanese Society on Calorimetry and Thermal Analysis (JSCTA) in Tokyo (Waseda University, 1992) shows (from left) M. Taniguchi (Japan), late C.J. Keattch (GB), late R. Otsuka (Japan), S. St. J. Warne (Australia, former ICTA president), H. Suga (Japan), J. Šesták (Czechoslovakia) and H. Tanaka (Japan). The regular JSCTA conferences started in Osaka 1964 under the organization of Prof. S. Seki who became the first president when the JSCTA was officially established in 1973. Since then, the JSCTA journal NETSU SOKUTEI has been published periodically.
References:

22. Strouhal, Č.: Thermika. (Thermics). JČMF, Praha (1908)


111 Kallauner, O., Matějka, J.: Beitrag zu der rationellen Analyse, Sprechsaal 47, 423 (1914); and Matějka, J.: Chemické proměny kaolinitu v žáru” (Chemical changes of kaolinite on firing) Chemické listy 13, 164-166 and 182-185 (1919)

IN:

Glassy, Amorphous and Nano-crystalline Materials

Thermal Physics, Analysis, Structure and Properties
Series: Hot Topics in Thermal Analysis and Calorimetry, Vol. 8
Šesták, Jaroslav; Mareš, Jiří J.; Hubík, Pavel (Eds.)
1st Edition., 2010, Approx. 350 p., Hardcover
Due: October 2, 2010
SOME HISTORICAL ASPECTS OF THERMAL ANALYSIS: ORIGINS OF TERMANAL AND ICTA

Jaroslav Šesták

Institute of Physics, Academy of Sciences
Cukrovarnicka 10, CZ-16253 Prague 6 and
Faculty of Applied Science, West Bohemian University,
Universitní 8, CZ-30614, Pilsen, Czech Republic
sestak@fzu.cz

This brief story of the birth and early growth of the field of thermal analysis has been prepared in order to celebrate the coincidence jubilee of the 140th Anniversary of the Czech-and-Slovak Chemical Society, 50th Anniversary of Czechoslovak and Slovak thermoanalytical conferences and 40th Anniversary of the International Confederation of Thermal Analysis. It includes both the scientific and societal figures about international and national backgrounds.

There is a rather extensive literature dealing with the subject of thermal analysis including its historical aspects, which thorough survey [1–22] is not the aim of this article. Here we would like to concentrate to some objective aspects and personal experience seen and witnessed during the 40 years of the domain growth and maturing when taking into account that thermal analysis (thermometry) is the hierarchically superior as well as joining subject for later separated calorimetry and general non-isothermal studies (particularly in kinetics).

The first person to use a kind of continuous heating and cooling of a sample for investigation of the properties of substances was curiously Czech thinker and Bohemian educator Jan Amos Comenius (1592–1670). In his Physicae Synopsis, which he finished in 1629 and published first in Leipzig in 1633, the importance of hot and cold in all natural processes was frequently stressed. Heat (or better fire) is considered as the cause of all motions of things. The expansion of substances and the increased space they occupy is caused by their dilution with heat. By the influence of cold the substance gains in density and shrinks. The condensation of vapor to liquid water is given as an example. Comenius also determined (although very inaccurately) the volume increase in the gas phase caused by the evaporation of a unit volume of liquid water. In Amsterdam in 1959 he published a treatise investigating the principles of heat and cold [24], which was probably inspired by the works of the Italian philosopher Bernardino Telesius. The third chapter of Comenius’ book was devoted to the description of the influence of temperature changes on the properties of substances. The aim and principles of thermal analysis were literally given in the first paragraph of this chapter: citing the English interpretation “In order to observe clearly the effects of heat and cold, we must take a visible object and observe its changes occurring during its heating and subsequent cooling so that the effects of heat and cold become apparent to our senses”. In the following 19th paragraphs of this chapter Comenius gave a
rather systematic description (and also a partially correct interpretation) of the effects of continuous heating and cooling of water and air, and also stresses the reversibility of processes like, for example, evaporation and condensation, etc., preceding somehow the concept of latent heat. Comenius concludes this chapter as follows: “All shows therefore that both heat and cold are a motion, which had to be proved.” In the following chapter Comenius described and almost correctly explained the function of a thermoscope (‘vitrum caldarium’) but introduced his own qualitative scale with three degrees of heat above and three degrees of cold below with the ambient temperature in the middle.

The modern interpretation of heat was given by Čeněk Strouhal (1850–1922) [24] and its historical aspects were later detailed in [18, 21, 22].

Some historical features of measuring heat and temperature

With little doubts, until the work of Black and Irvine in the middle of 18th Century, the notions of heat and temperature (from temper or temperament first used by Avicenna in the 11th Century) were not yet distinguished in-between. Black’s work, together with that done by Magellan, revealed the quantity that caused a change in temperature (but which was itself not temperature) providing thus 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. The key factor in his theory was the new substance of heat (or ‘matter of fire’), called caloric, which crept in among the constituent parts of a substance and gave it expansibility. Caloric differed from foregoing concept of phlogiston because it could be measured with an apparatus called a calorimeter, which was first designed by Wilcke and later used by Laplace, Lavoisier and others. Nevertheless, caloric was seen as an imponderable element with its own properties. Unfortunately, the great pioneers, Irvine and Black, published almost nothing in their own lifetimes and their attitudes were mostly reconstructed from contemporary comments and essays published after their death. Irvine supposed that heat was absorbed by a body during melting or vaporization, simply because at the melting or boiling points sudden changes took place in the ability of the body to contain heat. Irvine’s account that the relative quantities of heat contained in equal weights of different substances at any given temperature (i.e., their ‘absolute heats’) were proportional to their ‘capacities’ at that temperature and it is worth noting that the term ‘capacity’ was used by both Irvine and Black to indicate specific heats. They also introduced the term ‘latent heat’ which meant the absorption of heat as the consequence of the change of state.

Black’s elegant explanation of latent heat to the young Watts became the source of the invention of the businesslike steam engine as well as the inspiration for the first research in theory related to the novel domain of thermochemistry, which searched for general laws that linked heat, with changes of state. Rumford presented qualitative arguments for such a fluid theory of heat with which he succeeded to evaluate the mechanical equivalent of heat. This theory, however, was not accepted until later approved by Mayer and, in particular, 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. The characterization of one kilocalorie as 427 kilogram-meters was first launched by Mayer in the year 1845. The caloric-like description of heat as a fluid has survived, nevertheless, until today being a convenient tool for easy mathematical depiction of flows.

The roots of modern thermal analysis extends back to the 18th Century, again, because the temperature became better understood as an observable and experimentally decisive quantity, which thus turned into an experimentally 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 [14, 21] recorded inverse cooling-rate data for lead, tin, zinc and various alloys. Although this contribution was recognized even in Russia by Menshutkin it was overlooked in the interim and it is, therefore, worthwhile to give a brief account here.

![Early thermometry showing the time-honored ice calorimeter, which was first intuitively used by Black and in the year 1780 improved by Lavoisier 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. Thermochronical 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. 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).]

The bare equipment thus 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 the maximum achievement of heat transfer. The spaces between two walls of the outer large vessel, as well as the top lid, were filled with snow to ensure that the inner walls were always kept 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, such as Roberts-Austen some 60 years later. The next experiment that falls into the category of thermal analysis was done in 1837 by Frankeheim who described a method of determining cooling curves (temperature vs. time). This method was often called by with his name but later also associated with the so-called Hannay’s time method, when temperature is increased every time (such a plot would resemble what we now call ‘isothermal mass-change curves’). In 1883, Le Chatelier [26] adopted a somehow more fruitful approach immersing the bulb of thermometer within the sample in an oil bath, which maintained a constant temperature difference (usually 20º between the 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. At that time, thermocouples were liable to give varying outputs so that Le Chatelier was first
to attribute an arrest at about red heat in the output of the platinum-iridium alloy to a possible phase transition. He deduced that thermocouple varying output could result from contamination of one wire by diffusion from the other one possibly arising also 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 thermometry was finally vindicated.

The development of thermocouple, as an accurate temperature measuring device, was rapidly followed by 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 factually introduced thermal analysis to then most important field: metallurgy. However, in 1891, Roberts-Austen [26] was known to construct a device to give a continuous record of the output from thermocouple and he termed it as ‘Thermoelectric Pyrometer’.

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 rather insensitive to pick up small thermal effects. This disadvantage was improved by coupling two galvanometers concurrently 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. 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 [2, 5] 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 min.

The term thermal analysis was introduced by Tamman within the years 1903–1905 [27] who demonstrated theoretically the value of cooling curves in phase-equilibrium studies of binary systems. It was helped by this new approach 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 early X-ray diffraction or metallographic observations.

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 [28]. 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 [29]. 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 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 later decreased to about quarter. It was Burgess [28] 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 dived 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 [30]. 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 [5,7] (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 [31]. Vold (1948) [32] and Smyth (1951) [33] proposed a more advanced DTA theory, but the first detailed theories, absent from restrictions, became accessible [4–13] by Keer, Kulp, Evans, Blumberg, Erikson, Soule, Boersma, Deeg, Nagasawa, Tsuzuki, Barshad, etc., in fifties.

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 physical-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 intermediate by mass-less phonons so that the inherent flux does not exhibit inertia, as is the case for the flow of electrons. The thermal inertia of apparatus (as 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 [34], detailed in 1974 by Grey [35], which premises were completed in 1975 by the consistent theory of Holba and Šesták [13, 36]. It was embedded within a ‘caloric-like’ framework based on macroscopic heat flows between large bodies (cells, thermostats). The need of a more quantitative calibration brought about the committed work of ICTAC and the consequently published recommendations providing a set of the suitable calibration compounds. Calorimetric ‘pure’ (i.e. heat inertia absent) became the method of DSC (Differential Scanning Calorimetry), which is monitoring the difference between the compensating heat fluxes while the samples are maintained in the pre-selected temperature program (Eyraud 1954) [37]. This is possible providing two extra micro-heaters are respectively attached to both the sample and the reference in order to maintain their temperature.
difference as minimal as experimentally possible. Such a measuring regime is thus attained only by this alteration of experimental set up where the temperature difference is not used for the measurement itself but is exclusively employed for regulation. It became a favored way for attaining the most precise measurements of heat capacity, which is close to the condition of adiabatic calorimetry. It is technically restricted to the temperature range up to about 700 °C, where heat radiation turns 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 [38]). This was preceded by the method of so-called periodic thermal analysis (Proks 1969 [39]), which was aimed at removing the kinetic problem of undercooling by cycling temperature. Practically the temperature was alternated over its narrow range and the ample 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 and since that
time the experienced and technically sophisticated development has matured the instruments as automations
to reach 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,
addressers on websites, etc., so that it falls beyond the scope of these notes.

**Thermal analysis in the territory of Czech-Slovakia and its impact on ICTA**

The development of standard methods of thermal analysis in the territory of present-day Czech
Republic is linked with the names of O. Kallauner (1886–1972) and J. Matějka (1892–1960) [1] who
enabled that this novel technique came into a common use during the course of a period of so called
“rational analysis” of ceramic raw materials replacing the process of decomposition of clay minerals
by digestion with sulphuric acid which factually played in that time the role of the contemporary X-ray
diffraction. They were strongly affected by the work of H. LeChatelier [25] and their visits at the
Royal Technical University of Wroclaw (K. Friedrich, B. Wohlin) where the thermal behavior of soils
(bauxite) was investigated during heating and related thermal instrumentation was elaborated [40].
After the World War I, Matějka performed a broad investigation of chemical transformations of
kaolinite under heating (5 g in-weight, 30 °C/min, reproducible location of the thermocouple junction
under reproducible sample packing) and observed as the first the water liberation in the range of
500–600 °C associated with the formation of mineral Al₂O₃·2SiO₂ (dissolvable in acids) and its further
exothermic transformation to Al₈Si₃O₁₈ (~dumotierite) at 900 °C and coexistence of SiO₂ with
sillimanite above 1100 °C [41]. This study was later esteemed by R. C. Mackenzie [8] who pioneered
modern thermal evaluation of clays.

The development of thermogravimetry is connected with the name S. Škramovský (1901–1983)
who investigated thermal decomposition of complex oxalates (of Sc, Pb and Bi) which led him in
1932 to his own construction of an apparatus named “stathmograph” (from Greek “stathmos” =
weight) [42] under consequence of the work of Guichard. A weighted sample was placed into the
drying oven on a dish suspended on a long filament passing through a hole in its upper wall (forming
the balance case) to a hook on the left arm of an analytical balance. A mirror was attached to the
middle of the beam reflecting the image of alight slit into a slowly rotating drum lined with
photosensitive paper. The vibration was reduced by an attached glass rod immersed into paraffin oil
and temperature registered automatically by means of a mercury thermometer provided by platinum
contacts distributed along the whole length of capillary. He pioneered his technique for various
applications (pharmacology).

Much credit for the development of TA methods in the former Czechoslovakia after the World War
II must be attributed to R. Bárta (1897–1985) as he stimulated his coworkers (S. Procházka, V. Šatava,
M. Čáp, M. Vašíček) to construct devices for DTA and TG and the application of these measurements
It also led to the development of few samples of commercially produced TG instrument “TEGRA”
[44].

Some original principles and unique techniques were developed and applied by the Czech-Slovak
scientists, such as I. Proks (Periodic TA [39]), J. Brandštetr (Enthalpiometry [45]), J. Komrska
(Photometric TA [46]), A. Bergstein (Dielectric TA [47]), S. Chromý (Photometric TA [48]), V. Šatava
(Hydrothermal TA [49]), V. Balek (Emanation TA [50]) or M. Vaniš (Accelerated TA [51]). Worth
mentioning is the introduction of multi-store (ribbed) crucible for thermogravimetry [52], invention of
new method for kinetic data evaluation [53], kinetic model (fractal) equation often named after the
authors [53] and a first attempt to solve the kinetic problem of oscillatory reactions [54]. Other important reports tackled the classification of calorimetry [55] or the application of theoretical TA (thermodynamics) in construction of phase diagram [56]. The development of the determination of heat capacities at high- and low- temperature ranges is worth mentioning. A high-temperature calorimeter was designed by the M. Roubal [57] allowing determination of heat capacities in the range of 900–1900 K. V. Pekárek initiated the construction of a isoberobolic calorimeter for the determination of hydrogenation heats in catalytic studies and V. Tydlidát designed a calorimeter for investigating the hydration of cement pastes at increased temperatures [58]. Thermochemical analysis was successfully studied by V. Velich [59] using an isoperibolic calorimeter with an already on-lined computer. The important invention was done within the work of the Slovak Institute of Physics in Bratislava where L. Kubičár [60] designed a new twin dynamic high-temperature calorimeter for the measurements of small thermal effect and introduced the pulse method for heat diffusivity measurement.

Thanks to the Bárt’a’s undertakings the informal discussions on thermal analysis was already held just after the World II curiously unaffected by his undermined health after his return from the Nazis concentration camp. The entire series of thermoanalytical conferences were started within the continuous Bárt’a’s activity at the Department of Glass and Ceramics of the Prague Institute of Chemical Technology by fifties despite very sever political situation when many of renowned scientists and professor were expelled from their jobs by the communistic totalitarianism (including Bárt’a). Initial, recently obsolete terminology, (thermography) was gradually replaced by the recognized terms: thermal analysis or DTA and the final adjustment was made by the Slovak thermoanalysts, who started their famous and someway outstanding project of the national (and also international) conferences, abbreviated as TERMANALS, which continue their earnest to exist until today. It was positively effected by the foundation of the Slovak Group on Thermal Analysis 1972 (M. Vaniš, O. Koráb, V. Tomková, Š. Svetík, P. Králik, late A. Sopková, S. Fajnor, E. Smrčková) and the Czech Group on Thermal Analysis 1974 (V. Balek, J. Šesták, K. Habersberger, P. Holba, late J. Rosický, J. Ederová, M. Beránek, M. Nevřina) both acting under the roof of Czech-Slovak Chemical Society.

Very important discussion meetings, which effected the early construction of international cooperation, were curiously held in Prague during fifties. Though kept under surveillance of communistic secret police, Prof. P. D. Garn (1920–1999) and later, for the most part, Dr. R. C. Mackenzie (1920–2000) paid personal visits to see Prof. R. Bárt’a. Especially, during the 3rd Thermography Meeting in Prague, Dr. Mackenzie together with Drs Šatava, Čap, Vašíček, Procházka (curiously including Šesták, who was then a postgraduate student) agreed on the project of an
international organization, which would assist an international exchange and being preliminary of a help for discriminated scientists, who started to languish inside the former (so called) ‘Eastern Block’ (meticulously separated from the other world by an “iron fence”).

Thus a special notice should be paid to the lengthy efforts and services of International Confederation of Thermal Analysis (ICTA) later including Calorimetry (ICTAC) as an important forerunner of the field of thermal analysis. The first international conference on thermal analysis held in the Northern Polytechnic in London, April 1965, consisted of about 400 participants from various countries, where the choice of key lectures offered the first account of thermoanalysts notable in the field progress.

Some illustrative photos from international meetings, where we can recognize some renowned personalities, for example (clockwise from the upper left) the occasions of Termanal’73: late M. Malinovský and G. Lomnbardi; Termanal’76: V. Tomková, late V. Jesenák and V. Šatava; Budapest’75: F. Paulik, D. Schultze and W. Hemminger; Bratislava’85: A. Báček, P. Gallagher, M. Hucl or H. J. Seifert; Japan’91: late C. J. Keatich, late R. Otsuka, S. Warne, H. Suga and H. Mitsuhashi; and Zakopane’87: H. Piekrasky, K. Wieczorek-Ciurowa, B. Pacewska and J. Pysiak.

However, the original intention of ITCA as to enhance and fully open an international cooperation was somehow elapsed and from the first incorporation of the Eastern scientists among the ICTA officers at the turn of sixties (Berg, Bárta, Erdey) no one from the East was further elected into the ICTA Executive, which was partly due to the anxiety for possible vexatiousness imposed by the
Eastern governments and partly due to the executive’s feeling of an unchanged comfort to stay at the office as long as possible. Unfortunately, it later created unspoken feeling of certain ‘lobbyism’ as, explicitly, there was recently elected from the North American region the forth candidate for the ICTA president leaving thus the Easterners to keep waiting in line for more than 30 years. As a very personal note, I am sorry to disclose some unfriendly attitude towards the Eastern community, which appeared even in such an unusual manner today as the early data on ICTA formation were refused to make available to the author when he was writing this article.

One of the topmost achievements of the Czech-Slovak thermoanalysts was the organization of the 8th ICTA in Bratislava, August 19–23, 1985. Factually, it was a brave attempt to prepare and carry out an open international conference in communistic Czechoslovakia where a democratic presentation was yet sanctioned and where a “socialistic preferences” were enforced. In spite the political pressure and under the close watch of secret police the invited plenary lectures were equally aimed also at the Western scientists (R. C. Mackenzie, Scotland and I. Proks, Slovakia; T. Ozawa, Japan; G. Lombardi, Italy Z. G. Szabo, Hungary, E. Gmelin, Germany; V. Jesenak, Slovakia; V. V. Boldyrev, USSR; B. Wunderlich, USA and H. G. Wiedemann, Switzerland – the latter two were the first immigrant scientist from the past East Germany to be invited as honorary guests). It was also for the first time that the scientist from so called ‘hostile capitalistic countries’ were allowed to visit Czechoslovakia (such as S. Yariv from Israel or M. E. Brown from South Africa). Thus it is worth to remember and yet esteem the credibility of the ICTA’8 organizing committee that was bravely acting as follows

M. Hucl, Slovak Technical University, Bratislava, Chairman  
V. Balek, Nuclear Research Institute, Řež, Vice-chairman  
O. Koráb, Slovak Technical University, Bratislava, Secretary  
J. Šestáč, Academy of Sciences, Prague, Scientific Program  
M. Vaniš, Slovak Technical University, Bratislava, Exhibition  
A. Blažek, Institute of Chemical Technology, Prague, Proceedings  
V. Tomková, Slovak Technical University, Bratislava, Executive Secretary  
K. Habersberger, Academy of Sciences, Prague, Conference Affairs  
Š. Svetík, Slovak Technical University, Bratislava, Conference Affairs  
P. Králík, Technical University, Košice, Conference Affairs

The progress of thermal analysis was effectively supported by the allied foundation of international journal, which editorial board was recruited from the key-speaker of both 1965 conferences. In particular it was Thermochimica Acta that appeared in the year 1970 by help of Elsevier and, for a long time, edited by Wesley W. Wendlandt assisted by wide-ranging international board (such as B. R. Currell, T. Ozawa, L. Reich, J. Šestáč, A. P. Gray, R. M. Izatt, M. Harmelin, H. G. McAdie, H. G. Wiedemann, E. M. Barrall, T. R. Ingraham, R. N. Rogers, J. Chiu, H. Dichtl, P. O. Lumme, R. C. Wilhoit, etc.) see enclosed copy of its front-page on the next page.

It was just one year ahead of the foundation of another specialized Journal of Thermal Analysis, which was brought into being by Judit Simon (who has been serving as the editor-in-chief even today) and launched under the supervision Hungarian Academy of Sciences (Académia Kiadó) in Budapest 1969 (L. Erdey, E. Buzagh, F. and J. Paulik brothers, G. Liptay, J. P. Redfern, R. Bárt, L. G. Berg, G. Lombardi, R. C. Mackenzie, C. Duval, P. D. Garn, S. K. Bhattacharyya, A. V. Nikolaev, T. Sudo, D. J. Swaine, C. B. Murphy, J. F. Johanson, etc.) to aid preferably the worthwhile East European science suffering then under the egregious political and economic conditions.
Attentive support of the West Bohemian University (MSMT 4977751303) and Grant Agency of Czech Republic (522/04/0384) is highly appreciated.

TUESDAY, 13th APRIL

MORNING SESSION

Chairman: Dr. J. P. REDFERN

9.20 a.m. Theatre A
Introduction by Dr. W. Gerrard
(Head of the Chemistry Dept., Northern Polytechnic)

9.30 a.m. Theatre A
"Atmospheric Effects in Differential Thermal and Thermogravimetric Analysis."
Prof. P. D. GARN (University of Akron, Ohio)

10.30 a.m. Coffee

11.15 a.m. Theatre A
"Derivatography."
Prof. L. EREDY (Technical University of Budapest)

12.30 p.m. Lunch

AFTERNOON SESSION

2.00 p.m. Theatre A
"General Aspects of Thermal Analysis" (Papers A/1-4)
Chairman: Prof. P. D. GARN

3.30 p.m. Tea

4.00 p.m. Theatre B
"Applications of Thermal Analysis to Inorganic Compounds I" (Papers B/1-4)
Chairman: Prof. W. W. WENDLANDT

Theatre C
"Applications of Thermal Analysis to Polymer Studies" (Papers C/1-4)
Chairman: Mr. D. A. SMITH

Theatre D
"Techniques of Thermal Analysis II" (Papers D/1-4)
Chairman: Dr. B. R. CURRELL

Close—5.30 p.m.

WEDNESDAY, 14th APRIL

MORNING SESSION

Chairman: Dr. R. C. MACKENZIE

9.30 a.m. Theatre A
"The Causes of Error in Thermogravimetry."
Dr. M. HARMELIN (C.N.R.S., Paris)

10.15 a.m. Theatre A
"Miscellaneous Thermal Methods."
Prof. W. W. WENDLANDT (Texas Technological College)

12.30 p.m. Lunch

AFTERNOON SESSION

2.00 p.m. Theatre A
Chairman: Dr. J. P. REDFERN
"Kinetic Studies by Thermogravimetry."
Dr. G. GUICHON (École Polytechnique, Paris)

3.00 p.m. Tea

3.30 p.m. Theatre B
"Applications of Thermal Analysis to Inorganic Compounds II."
(Papers B/5-9)
Chairman: Dr. M. J. FRAZER

Theatre C
"Applications of Thermal Analysis to the Study of Organic Compounds (including Polymers)."
(Papers C/5-9)
Chairman: Mr. D. A. SMITH

Theatre D
"Techniques of Thermal Analysis II."
(Papers D/5-9)
Chairman: Dr. R. C. MACKENZIE

Close—5.30 p.m.

References

42. S. Škramovský, Chemické listy 26, 1932, 521 (in Czech).
44. A. Blažek, Silikáty 1, 1957, 177 (in Czech).
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>President</td>
<td>L. G. Berg (USSR)</td>
<td>C. B. Murphy (USA)</td>
<td>H. R. Oswald (Switzerland)</td>
<td>H. Kambe (Japan)</td>
</tr>
<tr>
<td>Vice-President</td>
<td>—</td>
<td>R. Bárt a (Czechoslovakia)</td>
<td>H. Kambe (Japan)</td>
<td>H.G. McAdie (Canada)</td>
</tr>
<tr>
<td>Secretary</td>
<td>J. P. Redfern (England)</td>
<td>J. A. Hill (USA)</td>
<td>G. Lombardi (Italy)</td>
<td>G. Lombardi (Italy)</td>
</tr>
<tr>
<td>Treasurer</td>
<td>R. C. Mackenzie (Scotland)</td>
<td>R. C. Mackenzie (Scotland)</td>
<td>R. C. Mackenzie (Scotland)</td>
<td>R. C. Mackenzie (Scotland)</td>
</tr>
<tr>
<td>Past-President</td>
<td>—</td>
<td>L. G. Berg (USSR)</td>
<td>C. B. Murphy (USA)</td>
<td>H. R. Oswald (Switzerland)</td>
</tr>
<tr>
<td>Ordinary members</td>
<td>R. Bárt a (Czechoslovakia)</td>
<td>S. K. Bhattacharya (India)</td>
<td>C. Duval (France)</td>
<td>H. Kambe (Japan)</td>
</tr>
<tr>
<td></td>
<td>S. K. Bhattacharya (India)</td>
<td>C. Duval (France)</td>
<td>H. Kambe (Japan)</td>
<td>P. K. Gallagher (USA)</td>
</tr>
<tr>
<td></td>
<td>C. Duval (France)</td>
<td>H. Kambe (Japan)</td>
<td>G. Krien (BRD)</td>
<td>M. Harmelin (France)</td>
</tr>
<tr>
<td></td>
<td>L. Erdey (Hungary)</td>
<td>G. Krien (BRD)</td>
<td>G. Lombardi (Italy)</td>
<td>M. D. Karkhanavala (India)</td>
</tr>
<tr>
<td></td>
<td>T. Sudo (Japan)</td>
<td>D. J. Swaine (Australia)</td>
<td>O. T. Sörensen (Denmark)</td>
<td>H. Lehmann (BRD)</td>
</tr>
<tr>
<td></td>
<td>D. J. Swaine (Australia)</td>
<td>T. L. Webb (South Africa)</td>
<td>S. St. J. Warne (Australia)</td>
<td>F. Paulik (Hungary)</td>
</tr>
<tr>
<td></td>
<td>E. I. Yarembash (USSR)</td>
<td>E. I. Yarembash (USSR)</td>
<td>T. L. Webb (South Africa)</td>
<td>O. T. Sörensen (Denmark)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S. St. J. Warne (Australia)</td>
</tr>
<tr>
<td>Chairmen of Committees</td>
<td></td>
<td>R. Bárt a, Honorary president (Czechoslovakia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standardisation</td>
<td>H. G. McAdie (Canada)</td>
<td>H. G. McAdie (Canada)</td>
<td>H. G. McAdie (Canada)</td>
<td>P. D. Garn (USA)</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>R. C. Mackenzie (Scotland)</td>
<td>R. C. Mackenzie (Scotland)</td>
<td>R. C. Mackenzie (Scotland)</td>
<td>R. C. Mackenzie (Scotland)</td>
</tr>
<tr>
<td>Organising for next Conference</td>
<td>C. B. Murphy (USA)</td>
<td>M. Müller Von Moos (Switzerland)</td>
<td>F. Paulik (Hungary)</td>
<td>S. Seki (Japan)</td>
</tr>
</tbody>
</table>
Historical Prague and its famous Charles University

One of the most important moments in the history of old Bohemia was the foundation of Charles University in Prague, as the first European university north of the Alps, by Emperor Charles the IV. One of its first achievements was the introduction of medieval kinematics, which was brought to Prague by Johannes de Holandria, an Oxfordian from Merton College, who in the year 1368 provided the so-called Merton’s theorem of uniform acceleration to public and detailed this approach during his stay in Prague. Later Czech astronomer Jan Šindel (1375–1456) was studying the planetary motion and his astronomical tables were greatly appreciated by Tycho de Brahe while staying in Prague at the end of the 16th century. Šindel had also a share in designing the advanced astrolabe in the famous Prague’s astronomical clock.

Little renown is Ioannes Marcus Marci (Jan Marek Marků 1595–1667) who probably helped to reveal the fundamental properties of the spectral colors that emerge when light passes through glass prism, was 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 and in the field of spectral dispersion of light he was actually a predecessor of Isac Newton. He wrote for that time very advanced books. e.g. [1], which possibly foreshadowed some laws. Besides the refraction of light he conducted the first-ever systematic study of the impact of bodies, he discovered the difference between elastic and inelastic impacts intuitively moving his thoughts within the reach of the conservation laws. Marci,

Fig. 1 From left: Charles University in Prague (founded by Emperor Charles IV. 1348 and some of their exceptional members and associates, astronomer Kepler Johannes (1571–1630), rector and mathematician Marcus Marci Ioannes (from Kronland, 1595–1667) and famous professor of mathematics and practical geometry Doppler Christian (1803–1853)
however, was strongly convinced that white light was the simplest element (‘quinta essentia’), which, interestingly, was close to the subsequent concept of ‘elementary waves’ propounded about fifty years later by Huyghens in the wave theory of light. There, however, is incomplete information concerning Marci’s educational activities. He was the rector of the famous Charles University and, perhaps, introduced a word 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’ (i.e., learning common crafts such as warfare, navigation, business, agriculture, hunting, medicine or veterinary) but not in ‘artes incertae’ (that was a part of the habitually rejected ‘equivocal arts’ associated with occultism, which traditionally involved alchemy).

Some medivial alchemists and the introduction of caloric

When Rudolph the II (1552–1612) became the Emperor of the Holy Roman Empire and the King of Bohemia, he provided in Prague court a vital support to alchemists, astronomers and physicists. Among the most outstanding scientists were Tycho de Brahe (1546–1601) and Johannes Kepler (1571–1630) whose astronomical observations and calculations were published in the well-known Rudolphine tables. After the death of Tycho de Brahe, Johannes Kepler replaced his position of a royal mathematician in Prague in the year 1601. Using Tycho de Brahe’s data, Kepler determined elliptic orbit of Venus. In his 1609 treatise ‘Astronomia Nova’ Kepler published his two first laws, controlling the motion of planets and according to which the orbit of a planet/comet about the Sun is an ellipse with the Sun’s center of mass at one focus.

Foremost Czech physician and astronomer, Chef Medical Supervisor of the Kingdom of Bohemia at the court of Rudolph the II, was Thaddaeus Hagecius ab Hagek (Tadeáš Hájek z Hájků, 1525–1600) known as an author of several astronomical tractates and books on geodesy, botanics and medicine particularly acknowledged for the first concise book on the beer-making, ‘De cerevisia’ (1585). He essentially helped the flourishing period of alchemy and played a significant role in persuading Rudolph the II to invite Tycho de Brahe to come to Prague.

Special attention should be paid to the Czech thinker and Bohemian educator, latter refugee Jan Amos Comenius (Komenský 1592–1670). In his Physicae Synopsis, which he finished in 1629 (published first in Leipzig in 1633), he showed the importance of hotness and coldness in all natural processes. Heat (or better fire) is considered as the cause of all motions of things. The expansion of substances and the increasing the space they occupy is caused by their dilution with heat. By the influence of cold the substance gains in density and shrinks: the condensation of vapor to liquid water is given as an example. Comenius also determined, though very inaccurately, the volume increase in the gas phase caused by the evaporation of a unit volume of liquid water. In Amsterdam in 1659 he published a treatise on the principles of heat and cold [2], which was probably inspired by the works of the Italian philosopher Bernardino Telesius. The third chapter of Comenius’ book was devoted to the description of the influence of temperature changes on the properties of substances. The aim and principles of thermal analysis were literally given in the first paragraph of this chapter: citing the English translation [3] ‘In order to observe clearly the effects of heat and cold, we must take a visible object and observe its changes occurring during its heating and subsequent cooling so that the effects of heat and cold become apparent to our senses.’ In the following 19 paragraphs of this chapter Comenius gave a rather systematic description (and also a partially
correct interpretation) of the effects of continuous heating and cooling of water and air, and also stressed the reversibility of processes such as, for example, evaporation and condensation, etc., anticipating somehow the concept of latent heat. Comenius concludes this chapter as follows: ‘All shows therefore that both heat and cold are a motion, which had to be proved.’ In the following chapter Comenius described and almost correctly explained the function of a thermoscope (‘vitrum caldarium’) and introduced his own qualitative scale with three degrees of heat above and three degrees of cold below the ambient temperature.

It is difficult to trace and thus hard to say if it was possible (though likely) to disseminate the idea of caloric from Amsterdam (when Comenius mostly lived and also died) to Scotland where a century later a new substance, or better a matter of fire, likewise called caloric (caloricum), was thoroughly introduced. It was assumed, e.g., that caloric creeps between the constituent parts of a substance causing its melting. Although caloric differed from foregoing concept of phlogiston (because it could be later measured with an apparatus called a calorimeter) it is not clear who was the first using such an instrument. If we follow the studies of Mackenzie and Brush [4, 5] and Thenard [6] they assigned it to Wilecke. It, however, contradicts to the opinion presented in the study by McKie and Heathcode [7] who consider it just a legend and assume that the priority of familiarity of ice calorimeter belongs to Laplace who was most likely the acknowledged inventor and first true user of this instrument (likely as early as in 1782). In fact, Lavosier and Laplace entitled the first chapter of their famous ‘Mémoire sur la Chaleur’ (Paris 1783) as ‘Presentation of a new means for measuring heat’ whereas the report of calorimetric employment by Black seemed to first appear almost a century later in the Jamin’s Course of Physics (Mallet–Bachelier, Paris 1868).

Caloric was seen as an imponderable element with its own properties. Unfortunately, the great propagator, Joseph Black (and his student Irvine), published almost nothing in their own lifetimes [8] and their attitudes were mostly reconstructed from contemporary comments and essays published after their deaths. Black supposed that heat was absorbed by a body during melting or vaporization, simply because at the melting- or boiling-points sudden changes took place in the ability of the body to accumulate heat (~1761). Irvine’s account that the relative quantities of heat contained in equal weights of different substances at any given temperature (i.e., their ‘absolute heats’) were proportional to their ‘capacities’ at that temperature and it is worth noting that the term ‘capacity’ was used by both Black and later also Irvine to indicate specific heats [8]. Black also introduced the term ‘latent heat’ which meant the absorption of heat as the consequence of the change of state.

Black’s elegant explanation of latent heat to the young Watts became the source of the invention of the businesslike steam engine as well as the inspiration for the first research in theory related to the novel domain of thermochemistry, which searched for general laws that linked heat, with changes of state. Rumford presented qualitative arguments for such a fluid theory of heat with which he succeeded to evaluate the mechanical equivalent of heat. This theory, however, was not accepted until the later approval by Mayer and, in particular, by Joule, who also applied Rumford’s theory to the transformation of electrical work. The use of customary units called ‘calories’ was coined by Clément, who was giving in 1824 the following definitions: a ‘small calorie’ allowed to increase by one degree the temperature of 1 g of water, whereas a ‘large calorie’ allowed to melt 1 g of ice. The word ‘calorie’ was then introduced into the vocabulary of academic physicists and chemists (Favre and Silbermann [9]) in 1845. The characterization of one kilocalorie as 427 kilogram-meters was launched by Mayer in the year 1845. The caloric-like description of heat as a fluid has survived, nevertheless, until today being a convenient tool for easy mathematical description of heat flows [3, 10–14]. Recently we tried to refresh the concept of caloric in the view of entropy and its connection to information [15].

Worth noting is the theory of Prokop Diviš (Divisch 1696–1765), which belongs to early pioneering times. Accordingly, ‘Light of the First Day of Creation’ is regarded to be identical with electricity, which is an inherent quality of all things, permeating the whole Universe and manifesting itself by electric and thermal phenomena [16]. Such an idea is, surprisingly, in an apparent agreement with the modern idea of electromagnetic zero-point background radiation [17].

Important role played the Prague Jesuit College of Clementinum and its famous library and observatory (opened in the 1720s) where about 1780 Antonin Strnad (1747–1799) laid the foundation to the oldest known series of systematic metrological observations. Worth noting are physicists and mathematicians Josef Stepling (1716–1778) and Jan Tesánek (1728–1788) who published many original studies and initiated publishing of Prague edition of Newton’s ‘Principia’ supplemented with his own commentaries, in that time best edition reasoned with better mathematical background.

### Renaissance of Prague physics

The first half of the 19th Century mathematical and physical studies in Prague became again on a par with...
the world science. Important role paid some scientists such as František J. Gestner (1756–1832) who is also known as a pioneer of the railway transport in Europe. Excellent achievements are duly associated with the name of Bernard Bolzano (1781–1848) particularly in mathematical logic and analysis and with his friend Christian Doppler (1803–1853) who came to Prague from Vienna in 1829. His famous paper was inspired by astronomical phenomenon: the components of many binary stars differ from each other in color. Though, according to present knowledge, the observed color difference is due to the difference of surface temperatures and not to the difference in radial velocities, the principle itself is correct, being verified, e.g., in acoustics and optics. In 1867 arrived to Prague Ernest Mach (1838–1916) and spent there nearly 30 years. He is known for his discussion of Newton’s Principia and critique of conceptual monstrosity of absolute space in his book ‘The Science of Mechanics’ (1883). Mach encouraged and inspired one of his students (later professor of theoretical physics) Jan Koláček (1851–1913) to study some of his hypothesis later approving that the Mach’s theory correctly describes the dispersion of light, dichroism and circular birefringence. The Mach successor at Prague German University was Ernst Lecher (1856–1926) who is well known for his research on electromagnetic waves (i.e. Lecher wires). Mach also analyzed conceptual basis of calorimetry from more general, almost philosophical, point of views [18]. His influence on the further development of physics was tremendous and he established a mathematically specialized school – a great deal of his attention devoted to optics and acoustics. One of his personal scientific contacts was Czech famous Jan E. Purkyně (1787–1869) internationally known for discoveries in physiology. Another young assistant of Mach was Čeněk Strouhal (1850–1922), later first Czech professor appointed for experimental physics. His studies in acoustic are well known and the Strouhal’s number concerning friction tones (oscillation) is named after him. He wrote and exceptional book on heat called ‘Thermics’ [19].

Czech priest (and, unfortunately, rather unknown mathematician) Václav Šimerka (1819–1887) introduced quantitative evaluation in psychology
(logarithmic connotation of feelings) providing early basis for the theory of information [20]. Czech-born Friedrich Reinitzer (1857–1927) is famous as the discoverer of cholesterol (including its metamorphosis and stoichiometry formulae C_{27}H_{46}O) and is also known for his pioneering work in the field of liquid crystals (latter widespread by O. Lehmann). Bohumil Kučera (1874–1921) examined effect of electrical polarization on surface tension in the interface of two liquids prompting the idea of a new technique later known as the drop-weight method, which provided physical basis for a new, today widely utilized, analytical method called polarography [21] as introduced by Jaroslav Heyrovský (1890–1967), which was awarded by Nobel price in 1959 [22].

An original development of weight measurements is connected with the name Stanislav Škramovský (1901–1983), who, at the Charles University, investigated thermal decomposition of complex oxalates which led him in 1932 to his own construction of an apparatus named ‘stathomograph’ (from Greek ‘stathmos’=mass, weight) [23] that made it possible to measure mass changes. Independently, in the same time Duval used for his way of weight measurements the Latin-based term ‘thermogravimetry’ that later became generally accepted in thermal analysis. As the principle scheme of the stathomograph instrument is not generally known, it is perhaps worth mentioning to describe the arrangement. Škramovský placed a weighted sample into the drying oven on a dish suspended on a long filament passing through a hole in its upper wall (forming the balance case) and hooked to the left arm of an analytical balance. A mirror attached to the beam was reflecting the image of a light slit into a slowly rotating drum lined with photosensitive paper. The unwanted vibration was reduced by an attached glass rod immersed into paraffin oil and temperature was registered automatically by means of a mercury thermometer provided by platinum contacts distributed along the whole length of capillary.

A most prominent personality, which spent fruitful time in Prague was Albert Einstein (1879–1955) [24], a German physicist, 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. (see the book ‘Builders of the Universe’ 1932). In 1911 he obtained his first professorship at theoretical physics at the German University of Prague where he closely cooperated with his friend professor of mathematics, Georg Pick (1859–1942). While in Prague he published 11 papers, most extensive being the survey of the theory of specific heats and very important were studies related with his favorite problem – the interaction of radiation with matter and effort to construct a relativistic theory of gravitation [25].

Worth noting is the so-called Planck-Einstein transformation formula for temperature which reads \( T = T_0 \sqrt{1 - \left(\frac{v}{c}\right)^2} \) [25] and is possibly related to the previous dissertation work by K. von Mosengeil, posthumously published in Ann. Physik 22 (1907) 867. It means that the temperature of a body observed from the system moving with a relative velocity, \( v \), is lower than the temperature in rest system. Basing on this idea in the article published in Ann. Physik 26 (1908) 1, Planck assumed that the First and Second Law of thermodynamics keep their form in all inertial frames. In the year 1953, however, Einstein wrote a letter to M. von Laue in which he doubts the correctness of this formula and rather speculated about a formula used in inverse (temperature as observed in moving system is higher). This statement, which was later proved by H. Ott [26], thus reads as \( T = T_0 \sqrt{1 - \left(\frac{v}{c}\right)^2} \). In both these cases information about the temperature is regarded to be mediated by the coherent electromagnetic radiation. Interestingly, in the case, where temperature is considered to be essentially local property and the thermometer reading is transferred to moving system, e.g., by means of digital coding, the temperature, in the contrast to both above formulae, must be considered as relativistically invariant.

Another distinguished, but unjustly not very appreciated, savant born in Prague was Reinhold Fürth (1893–1979) who devoted his scientific life to the research into the fundamentals of statistical physics [27]. Besides an extensive work concerning Brownian motion and noise phenomena he is also author of stochastic interpretation of quantum mechanics [28]. Accordingly to this theory, the Schrödinger equation is nothing but the classical diffusion equation with complex diffusion constant \( -\hbar^2/2m \). This statement became later a cornerstone of so-called stochastic electrodynamics, which provides an alternative to quantum mechanics [29].

One of the outstanding teachers, who earned great merit for introducing modern theoretical physics and thermodynamics to the curriculum of Charles University, was Frantisek Záviška (1879–1945). One of his textbooks was the first monograph on relativity published in Czech and he is an author of excellent books on thermodynamics [30]. He also concerned waveguides and independently deduced relevant theory early before the microwave technique became important. Other notable physicist was Augustin Žáček (1886–1961) who studied damped electromagnetic oscillations in vacuum electronic systems. His extended studies culminated at 1924 in the discovery of the principle of magnetron, later becoming the basis of radar systems.
The historical development and use of the methods of thermal analysis in the territory of former Czechoslovakia is linked with the names Otto Kallauner (1886–1972) and Jospeh Matějka (1892–1960) who introduced thermal analysis as the novel technique during the period of the so-called ‘rational analysis’ of ceramic raw materials [31]. Much credit for further development of modern thermal analysis is attributed with Rudolph Barta (1897–1985) who stimulated his coworkers (Vladimir Šatava) and his students (Jaroslav Šesták) at the Institute of Chemical Technology in Prague (the latter mentioned names became also initiators of the foundation of the International Confederation for Thermal Analysis in the year 1965 [32]).

Some other details were published elsewhere [31–34].

Acknowledgements

This study was supported by the grant No. A100100639 of the Grant Agency of the Academy of Sciences of Czech Republic and the Institutional FZU research plan No. AVOZ10100521 and the UWB project MSMT No. 4977751303.

References

32. J. Šesták, ‘Some historical aspects of thermal analysis: origin of Termanal and ICTA’ in the proceedings of Termanal 2005, p. 3 (Eds E. Klein, E. Smrčková, P. Šimon).

DOI: 10.1007/s10973-006-8210-1
CZECHOSLOVAK FOOTPRINTS IN THE DEVELOPMENT OF METHODS OF THERMOMETRY, CALORIMETRY AND THERMAL ANALYSIS

A tribute to professor Vladimír Šatava, DrSc, a mastermind of theoretical basis of thermal analysis, who celebrates his 90th birthday dedicating also the 55th anniversary since he becomes the Editor of the journal Ceramics-Silikáty

*PAVEL HOLBA, JAROSLAV ŠESTÁK

New Technologies - Research Centre of the Westbohemian region, University of West Bohemia in Pilsen, Universitní 8, 301 14 Plzeň, Czech Republic

*E-mail: holbap@gmail.com

Submitted March 15, 2012; accepted May 16, 2012

Keywords: History, Thermal analysis, Calorimetry, Kinetics, DTA

A short history on the development of thermometric methods are reviewed accentuating the role of Rudolf Bártu in underpinning special thermoanalytical conferences and new journal Silikáty in fifties as well as Vladimir Šatava mentioning his duty in the creation of the Czech school on thermoanalytical kinetics. This review surveys the innovative papers dealing with thermal analysis and the related fields (e.g. calorimetry, kinetics) which have been published by noteworthy postwar Czechoslovak scholars and scientists and by their disciples in 1950-1980. Itemized 227 references with titles show rich scientific productivity revealing that many of them were ahead of time even at international connotation.

Historical roots of thermal sciences
- from thermoscopy to thermal analysis

One of the first modern-times considerations of heat and cold can be found in the treatise published in 1563 by B. Telesio. At the end of the 16th century the first air thermoscope appeared (G. Galileo about 1597) and in 1626 the word „thermometer“ was for the first time used to describe thermoscope equipped with scale with eight degrees (Leurechon in book „La Recreation Mathematique“). Shortly after, the world-known Czech educator J. A. Comenius inserted reflections on the role of heat and cold in nature into his work „Physicae Synopsis“ (1633) and then, in 1659, published another worth noting book „Disquisitiones de Caloris Frigoris et Natura. “The first quantitative thermal law expressing the dependence of temperature of a cooling body (expressed in the scale of 8 degrees) on the time was published by J. Newton in 1701.

Meanwhile, other scientists had invented various types of the dilatation thermometers and had proposed various temperature scales. Romer (1701) had filled glass tube of thermometer with red wine and proposed a 60-degree scale. Fahrenheit (1724) proposed a temperature scale of 100 degrees from 0°F at the temperature of mixture of ammonium chloride, water and ice and 100°F at the human body temperature. Reaumur (1731) introduced the temperature scale with 80 degrees between 0°Re at water melting point and 80°Re at boiling point of water. A year later Delisle introduced an exotic scale with 240 degrees, which was later (1738) modified and adjusted to 150°D corresponding to the melting point of water and to 0°D at boiling point of water (240°D = -60°C), and this scale was being used in Russia for the whole hundred years. Only then Celsius (1742) came with its 100-degree scale (between the melting 100 and boiling 0 points of water, later switched to nowadays 0-100 by Linné).

The crucial experimental studies, thanks to which temperature became a clearly measurable physical quantity, was executed by Regnault in the 1840th, that is long after the Black (1761) distinguished between the specific heat (heat capacity) and the latent heat, Laplace and Lavoisier (1786) performed their first calorimetric measurements. In 1822 Fourier published his laws of heat transfer. Yet after detailed results of Regnault’s dilatometric and heat capacity measurements (1842), together with Carnot’s theorem (1824) and its consequent interpretation by Clapeyron (1834) - the basis was formed for the introducing of absolute temperature scale by W. Thomson (Kelvin 1848) and for the inception of thermodynamics as a new science.
The first noted use of thermometry as a method of thermal analysis took place in Uppsala in 1829 where F. Rudberg (1800-1839) recorded inverse cooling-rate data for various alloys, [1,2]. In 1883, H. L. Le Chatelier (1850-1936) adopted a somehow more fruitful approach plotting the time vs. temperature curves easily convertible to the relation of sample temperature vs. environmental temperature.

Several years later Le Chatelier (1887) had used Pt/PtRh thermocouple and the new era of thermometry as well as of calorimetry has arrived. In 1891, W. C. Roberts-Austen (1843-1902) [3] became known to construct a device to give a continuous record of the output from thermocouple and he termed it as "thermoelectric pyrometer". Later with his assistant A. Stanfield published in 1899 heating curves for gold, which almost stumbled upon the idea of DTA ("Differential Thermal Analysis"). They improved the sensitivity by maintaining the thermocouple 'cold' junction at a constant temperature and by measuring the differences between two high temperatures [4]. Among other well-known inventors was Russian N. S. Kurnakov (1860-1941) improving registration of his pyrometer by the photographic continuously recording drum [5]. The term “thermal analysis” was coined by G. H. J. Tammann (1861-1938) [6] around the year 1904 demonstrating the significance of cooling curves in phase-equilibrium studies of binary systems.

The first Czech university textbook on the physics of heat was “Thermika” by Č. Strouhal (1850-1922) published in 1908 [7] maintaining its informative value until today’s. The historical development and practical use of DTA in the territory of former Czechoslovakia [1, 2, 8] was linked with the names J. Burian (1873-1942), O. Kallauner (1886-1972) and J. Matějka (1892-1960) who introduced thermal analysis as the novel technique during the period of the so called “rational analysis” of ceramic raw materials [9] in order to investigate behavior of kaolinite [10, 11] at heating.

Worth a special attention is an original development of weight measurements that is connected with the name Š. Škramovský (1901-1983), who, at the Charles University, investigated thermal decomposition of complex oxalates which led him in 1932 to his own construction of an apparatus named “stathomograph” (from Greek “stathmos” = mass, weight) [12] that made it possible to measure mass changes. Independently (twenty years later), C. Duval used for his way of weight measurements the Latin-based term “thermogravimetry” that later became generally accepted in thermal analysis [13]. As the principle scheme of the stathomograph instrument is not generally known, it is perhaps worth mentioning to describe this early arrangement. Škramovský placed a weighted sample into the drying oven on a dish suspended on a long filament passing through a hole in its upper wall (forming the balance case) and hooked to an arm of an analytical balance. A mirror attached to the beam was reflecting the image of alight slit into a slowly rotating drum lined with photosensitive paper. The unwanted vibration was reduced by an attached glass rod immersed into paraffin oil and temperature was registered automatically by means of a mercury thermometer provided by platinum contacts distributed along the whole length of capillary.

In the first years after World War II the other monographs appeared in the world literature (besides that by Duval [13]), which were devoted to microcalorimetry [14] and thermal analysis [15, 16] and an initial paper dealing with theory of DTA [17] was also published. At the end of 1950th a commercial device combining DTA and TG appeared under the name “Derivatograph” [18] for long providing a useful service to the Eastern scientists.

Much credit for the further development of modern thermal analysis was attributed with Rudolf Bárta (1897-1985) who stimulated thermal analysis activity at his fellow workers (V. Šatava, S. Procházka, J. Vášiček, M. Čáp or I. Proks) at the Institute of Chemical Technology Prague (abbreviated as VŠChT) [19, 20, 21, 22]. Bárta organized premature thermoanalytical meetings, the earliest was “the 1st Conference on DTA” (Prague 1956), the 2nd (Prague 1958) and the 3rd Conference on Thermography (Prague 1961) followed by the 4th Conference on DTA (Bratislava 1966). His friend R. C. Mackenzie (1920-2000) [23, 24] from Scotland was an invited guest at the 1961 meeting who was also one of the pioneers of applied DTA [23, 24]. Upon the previous communication with Russian L.G. Berg, Americans P. D. Garn and C. B. Murphy as well as Hungarian L. Erdey an idea for the creation an international society ICTA was cultivated and realized during the first international thermoanalytical conference in London 1965 [24] (where one of the authors also participated as invited speaker). It aimed to enabling easier contacts between national sciences, particularly across the separating “iron curtain”, which in that intricate time politically divided the East and West Europe.

Besides significance of the early Czech-written books on thermal science [7, 26], which appeared before and/or simultaneously with the credited international literature [8, 22] the indispensable figure in the Czechoslovak development of thermal analysis was undoubtedly Vladimir Šatava (*1922) [27-31]. He brought to the Czech scientific circles necessary theoretical basis on solid-state chemistry and physics [29, 30], pioneered methods of thermal analysis [18, 19, 27, 26], educating his students who thus followed his professional guidance and published esteemed books [27-33] completing thus the rich spectrum of Czech thermoanalytical literature [31-38], cf. Fig. 1. The individual contributions and innovative approaches have been affluent and focal which is worth of a more detailed portrayal, as exposed in the next paragraph, especially accentuating Czechoslovak source journals. Unfortunately, most of these rather cru-
cial papers disappeared in the shadows of time due to the Czech written texts. Only consequently a supply role started playing the novel thermoanalytical journals, Thermochimica Acta, which was cofounded by one of the authors back in the year 1970 as well as Journal of Thermal Analysis instigated by R. Bártá in 1969.

Less known book by J. A. Komenský “Investigation of the nature of heat and cold.” (Amsterodam 1659) in which the predicament of heat and cold is well discussed; “Thermics” by Č. Strouhal (1908) was an unique book describing the early but elementary treaties on heat, the almost unknown book on DTA (1957) was published ahead of time, basic book of solid-state chemistry and material thermal behavior was also published (1965) beforehand of international literature (unfortunately never translated). Far right is the Russian translation of Czech original book on theoretical basis of thermal analysis (1988), which became curiously a scientific bestseller as whole 2000 issues were sold in the former USSR within one week.

Methodical footpath identifiable on the territory of former Czechoslovakia

The greatest promotion of thermoanalytical methods came after fifties when the methodical bases were formed [39] and new techniques specified. In this period various Czechoslovak scientists played an important role as it is documented in the achievement book [40] and citation records [41]. Below listed papers relating the field of TA promoted in the former Czechoslovakia are assorted into several (but not very strict) categories. The referenced papers are supplied by original titles (given in English) and they are chronologically ordered within individual categories. All references were checked and corrected according to database WoS (Web of Science).

The first category „TA generally” consists of articles [42-57] deals mostly with thermal analysis in a general way including papers published mainly in Czech journals Silikáty and Chemické listy, and in Slovak journal Chemické Zvesti.

The second category “Special methods of TA” is devoted to original principles and unique techniques developed and put into operation by Czechoslovak scientists. The articles described e.g. dielectric TA [58], thermogravimetry [59, 60, 63], accelerated TA [62], permeability TA [65], photometric TA [66], periodic TA [68] (becoming a forerunner of today’s temperature modulated methods of TA), differential hydrothermal analysis [70] and [71, 74], quick TA [78], thermoelectrometry [79, 80], decrepitating TA [82] and thermomagnetometry [83]. A distinctive consideration should be allocated to the characterization of radioactive measurement called emanation thermal analysis (ETA) which is connected mainly with authors V. Jesenák [64], V. Bálek [67, 75, 76] and J. Tölgyessy [81].

An explicit part of the papers was devoted to the description of own constructions of apparatuses for TA measurement as a consequence of at that time existing inaccessibility of commercial TA instruments. This type of articles is included into category Apparatuses of TA [84-101]. Early instruments as were opportunely produced by laboratory groundwork, such as DTA belong into this category. The production way of latterly produced TG apparatuses was paved by the development of a Czech thermogravimetric instrument named “TEGRA” and constructed by A. Blažek [37, 87]. Early instruments were opportunely produced by laboratory groundwork, such as DTA [84, 86, 91, 97].

A rich sphere of Czechoslovak research was also formed by calorimetric contributions [103-127] registered in category Calorimetry. Worth accentuating is an initial classification of calorimeters according to the temperature difference between the sample-block $T_S$ and surrounding jacket $T_J$, as early suggested by J. Velíšek [117].

Consequent category Theory of DTA/DCS is associated with a gradual development of theoretical basis of thermal measurements mostly focused on the DTA [128-140] curiously noting early the associated effect of gradients [129, 130]. It involved problems of...
calibration and standardization of temperature and heat measurements by employing solid solution [135, 140], application of heat pulses [134], conductivity issues [138] as well as a detailed analysis of the complex composition of a DTA peak including the effect of heat inertia [135, 137]. One of the frequently cited and widely applied treaties was the Hrubý glassforming coefficient [133] based on the DTA determination of characteristic temperatures during glass crystallization (inquisitively becoming the best cited paper in the history of Journal Czechoslovak Physicists with 372 citations). Such achievements were only possible by the impact of prosperous Czechoslovak school on thermodynamics [27-34]. The other corresponding papers [141-162] are included into category Thermodynamics and phase equilibria.

Another special attention is paid to the studies on reaction dynamics which topic is included into the category Kinetics [163-199]. Early kinetic studies were explicitly offered by studies of V. Šatava whose kinetic evaluation method [175] have been broadly exploited and quoted by international resources (several hundreds of citations) and frequently named as the “Šatava kinetic method” [31, 34, 35, 174, 183]. Such a popularity of theoretical works aimed to elucidate predicaments of reaction kinetics [34, 35, 183] became the heart of the so-called Czech school of nonisothermal kinetics recently continued both in Czech [195-198] and Slovak republic [190, 191, 199]. Worth noting is the first ever published algorithm for the computer calculation of kinetic data [171] and the review paper [170] which despite the Czech language became the best cited article in the journal history. In feedback stance the papers [177, 179] undertook abundant citation responses becoming thus the best cited papers in relevant journals (562 and 132 respectively) and bringing into literature the notations named in the international literature after the authors (i.e., the Šesták-Berggren [178] as well as the Holba-Šesták [180] kinetic equations). Not less important have been the contributions by recently deceased Ivo Proks (1926-2011), who factually paved the way to the development of methods using the modulated temperature modes [68], early accounting on temperature gradients and measurement accuracy [129, 132], improved solution calorimetry [104, 113, 118] thus significantly contributing the elementary attributes of thermochemistry and thermodynamics. Worth mentioning are also his imperative studies on historical root of thermodynamics [8, 220, 222, 224, 225] as well as the work by J. Brandštetr [93, 100, 108, 115, 120, 125] in the field of titrimetry.

Not less important were also the related articles about mechanic properties (which was one of favored of the Šatava’s research topics [208, 217]), diffusion studies [203-212] and early measurements of electrical and heat conductivity [202, 214-217] inserted into category Mechanical and transport properties [200-216]. The last category of Czechoslovak papers dealing with TA is labeled as History and nomenclature. It contains reviews of historical aspects of thermometry and thermodynamics [221-227] and associated nomenclature issues [219, 220].

CONCLUSIONS

The Czech researches have richly contributed to thermal science and it would be a misfortune to allow their input to slip into oblivion. Clearly, one of the most important moments in the development of modern thermal analysis was the establishment of the journal Ceramics-Silikáty, launching 1956 by Rudolf Bára. Vladimír Šatava was its chief editor within the years 1957-1967. This period was also credited with creating the foundations of thermal analysis and physical chemistry in general [29-31]. Šatava inspired his students and coworkers, cf. photo, by continuously broaden his own scientific interest in elucidating solid-state reactions which subsequently flourished into publication of various thermoanalytical books [34-39]. Equally important was the introduction of various novel thermoanalytical methods [58-83] which preceded the international know how, e.g. the emanation thermal analysis [50, 64, 67, 75, 76, 99] that has become the source of a commercially produced instrument. Specially the Czech contribution to the DTA technique [62, 71, 84-86, 91, 96, 97, 128, 131, 133, 136, 137] deserves a distinctive attention, the Czech written book published in 1957 [26] preceded international publications and was later followed by well cited Czechoslovak books [31-38]. Solid grounds of DTA were accomplished in 1976 by the consistent theory made up by Holba and Šesták and published in Ceramics-Silikáty [135, 136]. Fundamental contributions already appeared in the first issues of the journal Silikáty. Unfortunately, they did not get into a wider attention of international public due to the Czech language,. Nevertheless the Czech journal
Czechoslovak footprints in the development of methods of thermometry, calorimetry and thermal analysis

Ceramics – Silikáty 56 (2) 159-167 (2012)

References

4. Stanfield A.: On some improvements in the Roberts-Austen recording pyrometer, with notes on thermo-electric pyrometry; Phil. Mag. 46, 59 (1898).
10. Matějka J.: Chemical changes of kaolinite on firing; Chemické listy 13, 164 (1919); and 182 (1919).
12. Škvramovský S.: Apparatus for automatic registration of dehydration at rising temperature; Chemické listy 26, 521 (1932).
20. Šatava V.: Significance of DTA in the industry of cements; Stavivo 31, 15 (1953).
27. Šatava V.: Documentation on thermal analysis; Silikáty 1, 240 (1957).
29. Šatava V.: Úvod do fyzikální chemie silikátů; (Introduction to Physical Chemistry of Silicates), SNTL, Praha 1965.
41. Šesták J.: Citation records and some forgotten anniversaries in thermal analysis; J. Thermal Anal. Calor. in print 2012 (DOI:10.1007/s10973-011-1625-3).

TA generally

42. Šatava V.: Temperature regulators for thermography; Silikáty 7, 204 (1957).


Special methods of TA


59. Šatava V.: Simple registration thermobalans; Silikáty 1, 188 (1957).


61. Šatava V., Stránský K.: Gradient furnace with defined atmospheres; Silikáty 3, 343 (1959).


70. Vepřek O., Rykl D., Šatava V.: The study of hydrothermal processes by the DTA method; Thermochim Acta 12, 7 (1974).


72. Šatava V., Vepřek O.: Effect of the sample thermal conductivity on the calibration constant in DTA; Thermochim Acta 17, 252 (1976).


77. Hrabě Z., Svetík S.: The application of heat flow sensor to study the hydration of inorganic binders; Thermochim Acta 93, 299 (1985).


Apparatuses of TA

84. Sokol L.: Automatic apparatus for DTA; Silikáty 1, 177 (1957).

85. Šatava V., Trouslí Z.: Simple construction of apparatuses for automatic DTA; Silikáty 4, 272 (1960).


90. Malingre M., Brandstetter J.: Use of Czechoslovak ther-

Calorimetry

111. Pekárek V.: Possibilities and present state of calorimetric experiments; Chem. Listy 69, 785 (1975).

Theory of DTA/DCS

128. Šťava V.: Differential thermal analysis; Silikáty 1, 207 (1957).
129. Proks I.: Influence of rate of temperature increase on the quantities important for the evaluation of DTA curves; Silikáty 5, 114 (1961).
130. Šetlík J.: Temperature effects influencing kinetic data accuracy obtained by thermographic measurements under constant heating; Silikáty 7, 125 (1963).
Thermodynamics and phase equilibria

141. Šatava V.: Contemporary foresight on the structure of glasses; Skláň a keramik 13, 6 (1956).


143. Holb P.: On calculations of activities of chemical individuals from disorder models; Thermochim Acta 3, 475 (1972).


151. Holb P.: Thermodynamic aspects of thermal analysis; Silikáty 20, 45 (1976).


164. Šatava V.: Reactions of solids; Silikáty 4, 67 (1960).

165. Šatava V.: Reaction of solids with liquids; Silikáty 5, 171 (1961).


169. Hulinsky V., Šatava V.: Gypsum solubility within temperatures 100-140 °C; Silikáty 11, 47 (1967).


171. Šesták J., Šatava V., Rihák V.: Algorithm for kinetic data computation from thermogravimetric data obtained at increasing temperature; Silikáty 11, 153 (1967).


186. Matoušová M., Nývt J.: Theory of crystallization rate; Ceramics – Silikáty 56 (2) 159-167 (2012)
Czechoslovak footprints in the development of methods of thermometry, calorimetry and thermal analysis


Mechanical and transport properties

218. Šatava V.: Strength and microstructure of cast gypsum; Ceramics-Silikáty 40, 72 (1996).

History and nomenclature

221. Hlaváč J.: The present state and perspective view of the material research; Silikáty 29, 169 (1985).
227. Proks I.: Celok je jednoduchší ako jeho časti; (Whole is simpler than its parts), Publ. House of Slovak Academy of Sciences, Bratislava 2012.