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## Thermal analysis of Micro, Nano- and Non-Crystalline Materials

Transformation, Crystallization, Kinetics and Thermodynamics

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*Thermal Analysis of Micro-, Nano- and Non-Crystalline Materials: Transformation, Crystallization, Kinetics and Thermodynamics* complements and adds to volume 8 Glassy, Amorphous and Nano-Crystalline Materials by providing a coherent and authoritative overview of cutting-edge themes in the field of crystalline materials. In particular, the book focuses on reaction thermodynamics and kinetics applied to solid-state chemistry and thermal physics of various states of materials. In this volume the fundamental and historical aspects of phenomenological kinetics and the equilibrium background of processes are detailed. Crystal defects, non-stoichiometry and nano-crystallinity, reduced glass-transition temperatures and glass-forming coefficients are covered. The determination of the glass transition by DSC, the role of heat transfer and phase transition in DTA experiments, and the explanation of DTA/DSC methods used for the estimation of crystal nucleation are reviewed. Structural relaxation and viscosity behaviour in glass and associated relaxation kinetics are also examined, together with the influence of preliminary nucleation and coupled phenomenological kinetics nucleation on both the strongly curved surfaces and nano-particles. The book investigates crystallization of glassy and amorphous materials including oxides, chalcogenides and metals, non-parametric and fractal description of kinetics, disorder and dimensionality in nano-crystalline diamond. Moreover, it analyzes thermal analysis of waste glass batches, amorphous inorganic polysialates and bioactivity of hydroxyl groups as well as reaction kinetics and unconventional glass formability of oxide superconductors. Written by an international array of distinguished academics, *Thermal Analysis of Micro-, Nano- and Non-Crystalline Materials: Transformation, Crystallization, Kinetics and Thermodynamics* is a valuable resource to advanced undergraduates, postgraduates, and researches working in the fields of applied material thermodynamics, thermal analysis, thermophysical measurements and calorimetry.

- Presents different aspects of thermal properties of glassy and amorphous structures in a comprehensive, yet accessible way
- Complements and adds to the previous HTTC volume Glassy, amorphous and disordered materials: thermal analysis, structure and properties
- Written by an international array of distinguished researchers in the field of Thermal Analysis

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and Thermodynamics

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## Preface

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### Nucleation, Glass Crystallization, and Nonisothermal Kinetics

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There are thousands of researchers, scientists, and engineers worth mentioning who have contributed to a better understanding of glass science. However, in this book we can present only some of them. Already in 1830 M. Faraday noted that “*glass is a solution of different substances one in another rather than a strong chemical compound.*” S. Arrhenius (1889) and then H. Eyring (1935) gave the requisite meaning to the reaction rate constant.

Some of the most significant scientific achievements worth mentioning are Griffith's theory of the strength of brittle materials (1921) and X-ray diffraction analysis, which paved the way for W.H. Zachariesen's principles (1932) on how the nearest-neighbor coordination was maintained without imposing an exact long-range order so far common for crystalline materials. Equally important are the studies pertaining to vitrification and crystallization that can be found in the early works of both G. Tammann and G.O. Jones: *States of Aggregation* (1925) and *Glass* (1956), respectively. We also must mention various fundamental research work by such as D.H. Vogel, S. Fulcher, W. Kauzman, A.Q. Tool, E.A. DiMarzio, D. Turnbull, W.E.S. Turner, J. Frenkel, R.O. Davis, H.A. Davies, J.H. Gibbs, M. Cohen, R.W. Douglas, M. Cable, P.F. McMillan, C.A. Angel, J.C. Fisher, J. Tauc, B.T. Kolomiets, N.F. Mott, A. Hruby, L.L. Hench, N.J. Kreidl, H. Schaeffer, G. Frischat, J.C. Maxwell, H. Rawson, R.S. Elliot, R. Roy, P.K. Gupta, J.E. Shelby, O.V. Mazurin, E.A. Porai-Koshitz, S.V. Nemilov, G.P. Johari, W. Götz, C.T. Moynihan, E. Donth, A.R. Cooper, G.N. Greaves, A.L. Greer, K.F. Kelton, A. Feltz, D.R. Uhlmann, J.D. Mackenzie, R.E. Moore, R.K. Brow, P.C. Schultz, E.N. Boulou, C.R. Kurkjian, J.P. Davis, S. Procházka, M.B. Volf, J. Voldán, V. Bouška, I. Fanderlík, J. Hlaváč, M. Frumar, A. Duran, B.G. Potter, X. Zhang, P. Balta, K. Moorjani, Z. Strnad, M. Liška, P. Hrna, L. Němec, L. Koudelka, L. Tichý, Z. Košíšek, L. Stoch, G. Beall, L. Leuzzi, T. M. Nieuwenhuizen, M. Choudhary, F. Nicoletti, A.A. Cabral, R.A. Weeks, J.M. Parker, H. Kawazoe, N. Soga,

M. Tomozawa, J. Lucas, S. Kaschiev, C. Rüssel, R.H. Doremus, F.I. Gutzow, 30  
I. Avramov, W. Vogel, J.C. Philips, C.G. Pantano, C.A. Wright, M. Tatsumisago, 31  
F. Speapan, R. Conrat, A. Inoue, P.K. Gupta, K. Hirao, D.E. Day, W. Höland, 32  
M. Poulain, P.F. James, W.P.J. Schmelzer, B.P. Macedo, M.C. Weinberg, H. Suga, 33  
S.L. Simon, B. Wunderlich, L.D. Pye, M.D. Ingraham, A.V. Tobolsky, K.J. Rao, 34  
M.H. Fernandes, A.K. Varshneya, K.A. Jackson, W.A. Philips, M.E. Glicksman, 35  
F.E. Luborski, J.H. Simmons, and many others. 36

As a result of the enhanced understanding of (often controlled) melt-enhanced 37  
cooling and consequent recrystallization of glasses, the data on glass formation 38  
have rapidly expanded and required systematic classification, leading to the early 39  
foundation of specific journals and symposia. Associated theoretical studies on 40  
nucleation, crystallization, and crystal growth have also escalated, evaluating both 41  
limiting sides: on the one hand it was the solidification upon a slow (self-cooling) of 42  
melts and on the other hand the purposefully suppressed crystallization of quenched 43  
(freeze-in) melts. 44

Thermal analysis, and differential thermal analysis (DTA) in particular, became 45  
effectively involved from the very beginning of thermometry, simply discriminating, 46  
for instance, bulk and surface nucleation by simple DTA comparing the thermal 47  
behavior of the as-cast (sample) and subsequently powdered (reference) tasters 48  
(R.L. Thakur in the 1960s). 49

Some other fundamental and complementary methods of thermal physics arrived 50  
at sophisticated levels of research, as presented in the previous volume entitled 51  
*Glassy, Amorphous and Nano-Crystalline Materials: Thermal Physics, Analysis,* 52  
*Structure and Properties* published by Springer in 2011 (ISBN 978-90-481-2881-5; 53  
DOI [10.1007/978-90-481-2882-2](https://doi.org/10.1007/978-90-481-2882-2)). 54

The best theoretical endeavor, however, was made in the field of oxide glasses 55  
where the traditional symposia on advances in nucleation and crystal growth, 56  
originally held every 10 years, have resulted in valuable proceedings. Starting from 57  
the early 1970s, we list *Advances in Nucleation and Crystallization of Glasses*, 58  
edited by L.L. Hench and S.W. Freiman and published by the American Ceramic 59  
Society (Columbus, Ohio, 1972); *Nucleation and Crystallization of Glasses*, edited 60  
by J.H. Simmons, D.R. Uhlmann, and G.H. Beall and published in *Advances of* 61  
*Ceramics* (American Ceramic Society, Columbus, Ohio, 1982); *Nucleation and* 62  
*Crystallization in Liquids and Glasses*, edited by M.C. Weinberg and published in 63  
*Ceramic Transactions* (American Ceramic Society, Westerville, Ohio, 1993); and 64  
finally *Crystallization in Glasses and Liquids* (the symposium in Vaduz, Liechten- 65  
stein, 2000), edited by W. Höland, M. Schweiger, and V. Rheinberger and published 66  
in *Glass Science and Technology – Glastechnische Berichte (Glastech. Ber. Glass.* 67  
*Sci. Technol.)* 73C, 2000 (425 pp). We earnestly hope that the present book will 68  
credit the above listed prestigious publications receiving as many positive responses 69  
as our previous title “*Glassy, Amorphous and Nano-Crystalline Materials*” (already 70  
~ 2500 e-book downloads entries). This 350 page thematically preceding Volume 8 71  
(containing 21 chapters under the editorial of J. Šesták, J.J. Mareš and P. Hubík) was 72  
coauthored by H. Suga, A.C. Angell, B. Wunderlich, C.A. Queiroz, B. Hlaváček, 73

I. Krakovský, Y. Ikeda, B. Kratochvíl, Z. Černošek, I. Holubová, J. Shánělová, 74  
J. Málek, M. Liška, P. Šittner, R. Delville, B. Malard, V. Balek, I. Beckman, 75  
J.-P.E. Grolier, P. Thomas, K. Heide, E. Füglein and/or P. Šimon. 76

This project originated from a special issue of the journal *Thermochimica Acta* 77  
(Vol. 280/281) in 1996 entitled *Vitrification, Transformation and Crystallization* 78  
*of Glasses* (Elsevier, Amsterdam), edited by J. Šesták (and dedicated to the 79  
life anniversaries of H. Suga, V. Šatava, and D.R. Uhlmann). In 1993, when 80  
Šesták was visiting professor at the University of Arizona in Tucson (see the 81  
photograph at the end of the Preface), he started a cooperation with N.J. Kreidl, 82  
D.R. Uhlmann, and M.C. Weinberg that extended to many renowned glass 83  
scientists in the United States, such as C.A. Angel, D.E. Day, L.L. Hench, 84  
P.M. Mehl, C.T. Moynihan, C.S. Ray, J.H. Flynn, and S.H. Risbud. The book 85  
resulted in a collection of 40 chapters coauthored by several other famous 86  
scientists, such as C.J.R. Gonzales-Oliver, O.F. Martinez, Argentina; E.D. Zanotto, 87  
Brazil; Z. Kožíšek, Z. Chvoj, B. Hlaváček, J. Málek, P. Demo, Czechoslovakia; 88  
P.F. James, M.J. Richardson, United Kingdom; I. Avramov, A. Dobrev, 89  
I.B. Gugov, I. Gutzov, Bulgaria; H.D. Gollf, Canada; M. Poulain, France; K. Heide, 90  
R. Müller, Germany; L. Granasy, Hungary; K.S. Dubey, P. Ramachandrarao, India; 91  
A. Buri, F. Branda, Italy; W. Höland, V. Rheinberger, Liechtenstein; T. Kokubo, 92  
T. Komatsu, M. Matusita, M. Tatsumisago, M. Koide, Y. Masaki, Japan; W. Hölland, 93  
Liechtenstein; V. Filipovich, V. Fokin, G. Moiseev, A. Kalinina, I. Tomilin, Russia; 94  
and J.M. Barandiarán, I. Tellería, Spain. Recently, this tradition has been followed 95  
by a similarly anticipated compendium entitled *Interplay between Nucleation,* 96  
*Crystallization and the Glass Transition* with almost 30 contributed papers 97  
published as a special issue of *Thermochimica Acta* (Vol. 503, 2011) under the 98  
editorial care of C. Schick and C.W. Höhne. 99

The idea of collecting broader points of view on the formation and devitrification 100  
of glasses, particularly aimed at confronting various aspects of descriptive theories, 101  
evaluative treatments, and applied technologies, represented the main purpose 102  
of the renowned Kreidl's memorial conferences. Worth mentioning are the last 103  
two: *Advances of Glasses*, held in Liechtenstein in 1994 (proceedings edited by 104  
D.R. Uhlmann and W. Hölland), and *Building the Bridges between Glass Science* 105  
*and Glass Technology*, held in Slovak Trenčín in 2004 (proceedings published in 106  
*Glass. Ber. Glass. Sci. Technol. 77C*, 2004, and edited by J. Šesták and M. Liška). 107

Some of the following compendiums are also particularly relevant: *Reaction* 108  
*Kinetics by Thermal Analysis*, published as a special issue of *Thermochimica Acta* 109  
(Vol. 203, 1992, edited by J. Šesták and dedicated to the former chairman of Kinetic 110  
Committee of ICTAC, the late J.H. Flynn, on the occasion of his seventies); *Thermal* 111  
*Studies beyond 2000*, published as a special issue of the *Journal of Thermal Analysis* 112  
*and Calorimetry* (Vol. 60, 2000, by Kiado, Budapest and Kluwer, Dordrecht), edited 113  
by M.E. Brown, J. Málek, N. Koga, and J. Mimkes (and dedicated to J. Šesták's 114  
sixties). Furthermore, we would like to draw the reader's attention to two recent 115  
monographs: *Glass: the Challenge for the 21st Century* (published by Trans Tech 116

Publications, Switzerland 2008, 692 pp, edited by M. Liška, D. Galusek, and R. Kandlement as the Proceedings of the International IX ESG/ICG conference held in Trenčín, Slovakia 2008) and *Some Thermodynamic, Structural and Behavioral Aspects of Materials Accentuating Non-Crystalline States* (published as a university internal booklet by the Public Weal Society, OPS, at the West Bohemian University – ZČU Pilsen 2009 and 2011, 620 pp, edited by J. Šesták, J. Málek, and M. Holeček).

Quite a few books have been published recently on the topic of nucleation, such as those by S. Kaschiev, *Nucleation: Basic Theory with Application* (Butterworth 2000); D. Jürn and J.W.P. Schmelzer, *Nucleation: Theory and Application* (Wiley 2005); H. Vehkamäki, *Classical Nucleation Theory in Multicomponent Systems* (Springer 2006); K.F. Kelton and A.L. Greer, *Nucleation in Condensed Matter: Applications in Materials and Biology* (Elsevier 2010); and V.I. Kalikhmanov, *Nucleation Theory* (Springer 2011). Other influential books on glass formation stand: E.J. Donth, *Glass Transition, Relaxation Dynamics and Disordered States* (Springer, Berlin 2001); T. Egami, A.L. Greer, A. Inoue, and S. Ranganathan (eds.), *Supercooled Liquids, Glass Transition and Bulk Metallic Glasses* (Cambridge 2003); K.A. Jackson: *Kinetic processes. Crystal Growth, Diffusion, and Phase Transitions in Materials*. Wiley, Weinheim (2004); J. Šesták: *Science of Heat and Thermophysical Studies: a generalized approach to thermal analysis kinetics*. Elsevier, Amsterdam (2005); B. Wunderlich, *Thermal Analysis of Polymeric Materials* (Springer, Berlin 2005); M. Henkel, M. Pleimling, and R. Sanctuary (eds.), *Ageing and the Glass Transition* (Springer, Berlin 2007); and J.W.P. Schmelzer, I.S. Gutzow, O.V. Mazurin, A.I. Priven, S.V. Todorova, and B.P. Petroff (eds.), *Glasses and the Glass Transition* (Wiley, New York 2011).

Concerning the field of continuous upgrading, particular attention should be paid to the *Committee on Glass Nucleation and Crystallization* (abbreviated as ‘CT 7’) as a part of the ICG (*International Commission on Glass*) (see Fig. 1).

The notable element of randomness is the variation of bond angles is sometimes assumed to be crucial in auxiliary distinguishing of constrained states of glassy and amorphous materials. The flexibility of the covalent bond is larger for the twofold coordination groups of VI elements and is lower for the tetrahedrally coordinated groups of IV elements. For instance, in the SiO<sub>2</sub> glasses the oxygen atoms are bridging the Si-tetrahedral, providing the essential flexibility, which is considered necessary to form a random covalent network (without exhibiting excess of strain). However, if such a covalent random network is formed without the flexing bridges of the group VI elements, the structure becomes amorphous (as the deposited strain-confined films of, e.g., As<sub>2</sub>S<sub>3</sub>), which can exist in several forms of non-crystalline configurations (often experimentally irreproducible). The glass-forming tendency occurs greatest when the short-range order imposed by bond stretching and bending forces is just sufficient to exhaust the local degrees of freedom. The internal strain increases with the average coordination number, *m*, whereas entropy follows the opposite trend because the non-crystalline state





**Fig. 1** Group photograph of the members of the 2001 TC7 committee (of ICG) working in the historical configuration. From the *right*: G. Völksch (Germany), V.M. Fokin (Russia), M. Davis (USA), R. Müller (Germany), late P. James (UK), E. Zanotto (kneeling; present chairman, Brazil), late M.C. Weinberg (USA), W. Hölland (past chairman, Liechtenstein), T. Kokubo (Japan), late I. Szabo (Hungary), I. Donald (UK), L. Pinckney (USA), W. Panhorst (former chairman, Germany), and J. Šesták (Czech Republic)

becomes insufficiently interconnected (i.e., ‘cross-linked’). Therefore, the con- 160  
 conventionally “stable” state of chalcogenide glasses is typically restricted to lie in 161  
 the region  $3.3 > m > 2$ ; with  $m > 3.3$ , glass becomes overconstrained amorphous 162  
 (shown by J.C. Phillips in the 1970s); when yet higher, with  $m > 4.3$ , it associates 163  
 with the unusual state of non-crystalline metals obtained by ultrafast quenching. 164  
 On the other hand, those having the lowest connectivity ( $m < 2$ ) are assumed to be 165  
 under-cross-linked amorphous materials, such as typically thin films. The highly 166  
 constrained nature of variously obtained amorphous films suggests that defects 167  
 might not be randomly distributed but could be predominantly located as internal 168  
 blocks, voids, and strain-relief interfaces between low-strain regions. In contrast to 169  
 glasses, the amorphous films can thus exist in many non-crystalline configurational 170  
 states, the thermal annealing of which can lower their tense energy. However, it 171  
 cannot transform the overconstrained amorphous configuration from one ranking to 172  
 another. A drastic atomic rearrangement would be enforced as to accomplish such 173  
 an ‘unstructured’ reconstruction, which would, instead, commence overlapping by 174  
 unprompted crystallization. 175

However, a possible interference of the so-called medium-range order (or ‘mod- 176  
 ulated structures’) becomes common when determining various non-crystalline 177  
 materials, typically pertinent semiconductors. The concept of a homogeneously ran- 178  
 dom network and its heterogeneity has been extensively studied in this area, which is 179

closely connected with the fashionable use of the adjective 'nano' (nanotechnology or nanomaterials) and touches the limits where the ordered and disordered states transpire, and became known as a guarantee threshold ('delimitability'). The standard observations, based on measuring crystallographic characteristics and the amount of crystalline phases (such as typical XRD) are capable to detect the crystalline phase down to about 2% within the glassy matrix and definitely under certain crystal-size discrimination ('detectability').

In this case, if we do not consider the ability to distinguish 'yet-crystal-magnitude' nor can we account for a specialized diffraction measurement at low diffraction angles (radial distribution function), we can concentrate on the critical amount of crystalline phase in the glassy sample. This issue has not yet been faced with a crucial question: how can we relevantly define the limit of 'true glassiness' from 'nano-crystallinity'? A few proposals have been put forward; however, to date, the generally accepted value is  $10^{-6}$  vol.% (revealed by D.R. Uhlmann in the 1970s) of crystallites to exist within the glass matrix, yet not disturbing its non-crystalline portrayal and the consequent characterization of glassines. Nevertheless, the appropriateness of this value is difficult to ascertain being based on acute convenience and reiteration.

With regard to the process of crystallization, the early theories of solid-state reactions (D.A. Young, K. Haufe, H. Schmelzried, J.P. Tretyakov, C.S. Smith, F.C. Tompkins, R.F. Mehl, V.V. Boldyrev, E.A. Prodan, B.V. L'vov, S.F. Hulbert, A.K. Galwey, D. Dollimore, M.E. Brown) should be mentioned as they prepare the ground for generalized kinetic studies. Such premises were preceded by the diffusion-controlled kinetics (introduced by E. Kirkendall, W. Jander, C. Kroger, V.F. Zhuravlev, A.M. Ginstling, B.I. Brounshtein, R.E. Carter, W. Komatsu, M.E. Fine, and others).

The methods of kinetic evaluation played a specific role in the use of thermal analysis, specifically DTA, which was inaugurated to the study of reaction kinetics by P. Murray and J. White (1949), H.J. Borchard and F. Daniels (1950), D.W. VanKrevelen and F.J. Hutjens (1951), H.E. Kissiner (1957), E.S. Freeman and B. Carroll (1958), H.H. Horowitz and G. Metzger (1963), A.W. Coats and J.P. Redfern (1964), H.L. Friedman (1964), and T. Ozawa (1965), and introduced in the practice of solid-state reactions in the 1960s/1990s (by such workers as L. Reich, J. Norwitz, C.D. Doyle, J.H. Flynn, L.A. Wall, J. Zsako, P.D. Garn, J.R. MacCallum, G.R. Heal, T. Sunose, T. Akahira, E. Koch, J.H. Sharp, K. Heide, V.M. Gorbachev, M.E. Brown, J.M. Criado, F.O. Piloyan, D. Dollimore, M. Balarin, G. Varhegyi, Z. Adonyi, J. Pysiak, J. R. Opfermann, M. Maciejewski, T. Mitsushashi, H. Tanaka, M. Ochiai, K. Matusita, T. Komatsu, M. Tatsumisago, S. Sakka, S. L. Liu, L.C. Chen, Y. Cheng, A. Buri, F. Branda, J.M. Barandiaran, S. Suriñach, M.D. Baró, M.T. Clavaguera-Mora, L.A. Perez-Maqueda, J. Suñol, C. Várheley, C.S. Ray, M.L.F. Nascimento, E. Illekova, P. Šimon, J. Málek, J.A. Augis, M. Harmelin, J.E. Bennet, D.W. Henderson, M.C. Weinberg, N. Doca, C. Popescu, N. Sbirrazzuoli, A. Broido, H. Anderson, D. Fatu, R.N. Rogers, T. Kemény, S. Montserrat, J. Rouquerol, E. Segal, V. Jesenak, V. Šatava, A. Mianowski, and A. Malecki).

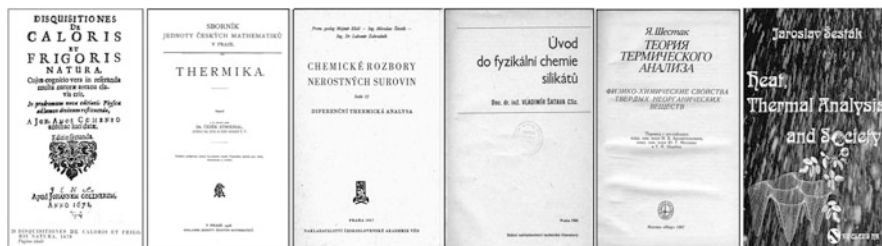
Kinetic theory was preceded by the traditionally calculated mode of the so-called isothermal crystallization mechanism using a comprehensive form of the Johnson–Mehl–Avrami–Yerofeeyev–Kolmogorov equation (abbreviated as JMAYK and pioneered around the 1940s) as well as by detailed analysis of nucleation (by D.R. Uhlmann 1967 and 1972). Its validity was based on its derivation mode under more general (“nonisothermal”) conditions, therefore respecting the standardized thermal regime of the temperature linear increase (common, e.g., during DTA measurements). It was necessary to introduce the temperature-dependent integration (D.W. Henderson, T.J.W. DeBroijjn, W.A. DeJong, T. Kemény, J. Šesták) yielding the concealed but anticipated fact that that the nonisothermal equivalent of the isothermally derived JMAYK relationship is almost indistinguishable. It enabled one to simplify the kinetic rate equation to all types of interface-controlled and/or diffusion-controlled crystallization in a comprehensive form of  $\ln(1-\alpha) = -k_T t^r$  where the general exponent,  $r$ , can be seen as a multipart number of a robust analysis of the basic JMAYK equation effortlessly analyzable in terms of DTA measurements. It reveals that the apparent (overall) values of activation energies,  $E_{app}$ , is frequently correlated to the partial activation energies of nucleation,  $E_N$ , growth,  $E_G$ , and/or diffusion,  $E_D$  (J. Šesták, M.C. Weinberg, C.T. Moynihan, J.W. Christian).

To sum it up, it should be pointed out that numerous variously adapted methods of kinetic analysis and evaluation cannot be easily covered in a single communication. These manners have been treated repeatedly, generating many publications, which were dealt with by a range of well-known kineticists (see Fig. 2).

The editors and authors are positive that this compendium of distinctive contributions will improve the readers in kinetics and will become a valuable resource to the scientific community. Let us point out that the topic of nucleation-crystallization kinetics has been extensively quoted in the literature. For example, according to WOS database 2011, Avrami’s fundamental paper on general kinetics of phase changes (1939) received 5,368 citations, Kissinger’s reaction kinetics by DTA (1957), 4,461, and Ozawa’s kinetic method of analyzing thermogravimetry data (1965), 2,096 respective citations. Similarly, the renowned kinetic equations by Jander (1927) on diffusion received 551, Šesták-Berggrenn (1971) on fractal (autocatalytic) kinetics received 566 responses, and Uhlmann’s kinetic treatment (1972) 473 responses. These figures are comparable with 1,913 and 1,396 citations for the basic papers on glass behavior by Fulcher (viscosity, 1925) and Mott (conduction, 1968), respectively. The citation data illustrate that the theme of reaction kinetics is one of the most popular within the literature on solid-state reactions and does therefore play an important role in this book. Moreover, the pioneering stimulus of the Czechoslovak thermoanalysts toward the early promotion of thermoanalytical kinetics (see Fig. 3; and: *Czechoslovak footprints in the development of methods of thermometry, calorimetry and thermal analysis*. *Ceramics-Silikáty* 56(2012)159) is worth noting, which consequences were also reflected in the selection of the contents of this book. Historical thermal analysis and its development on an international scale were already described by all the details in the Chapter 21 of our preceding Volume 8.



**Fig. 2** Numerous researchers have been involved in the study of reaction kinetics and particularly in the development of a nucleation theory and associated nonisothermal evaluations. Some of them are listed below, according to the availability of individual portraits. *First row:* Svante A. Arrhenius, Henry Eyring, Andrey N. Kolmogorov, Robert F. Mehl, Raoul Kopelman, Andrew K. Galwey, Paul D. Garn; *next row,* Erwad M.D. Karhanavala, Joseph H. Flynn, David Dollimore, Vladimir V. Boldyrev, Janus Zsako, Boris L. L'vov, Vladimír Šatava; *next row,* Eugene Segal, Ari Varschavski, Viktor Jesenák, Delbert D. Day, Cornelius T. Moynihan, Takeo Ozawa, Donald R. Uhlmann; *next row,* Julia Sempere, Rosa Nomen, Judith Simon, Barbara Malecka, Andrzej L. Malecki, Alan K. Burnham, Michael E. Brown; *next row,* Marek Maciejewski, Zdeněk Kožíšek, Jerzy Czarniecki, Nobuyoshi Koga, Petru Budrugaec, Nae-Lih Wu, Emília Illeková; *next row,* Peter Šimon, Jaroslav Šesták, Jiří Málek, Vladimir M. Fokin, José M. Criado, Sergey Vyazovkin, Bertrand Roduit; *next row,* John M. Hutchinson, Klaus Heide, Isaac Avramov, Lindsay A. Greer, Kenneth F. Kelton, Edgar D. Zanotto, Takayuki Komatsu; *bottom row,* Živan Živkovič, Jurn W.P. Schmelzer, Pavel Hrma, Pavel Holba, Paul S. Thomas, Pavel Demo, Vladimir A. Logvinenko



**Fig. 3** Some authoritative Czech books related to the topic of thermal analysis. *From left:* Less-known book by Czech thinker and Bohemian educator J.A. Comenius (Komenský), *Investigation of the Nature of Heat and Cold* (Amsterdam 1659), in which the predicament of heat and cold was well discussed. Next, *Thermics*, written by Č. Strouhal (1908), was a unique book describing the early but elementary treatise on heat. The almost unknown book on DTA (1957), which was published ahead of time and next, is a basic book on *Solid-State Chemistry and Thermal Behavior of Silicates*, by V. Šatava (1965), again available beforehand of comparable international literature (unfortunately never translated). *Next to right* is the Russian translation of Czech (1982) and English (1984) original book *Thermophysical Properties of Solids and Theoretical Basis of Thermal Analysis*, by J. Šesták, which in 1988 became intriguingly a scientific bestseller in the former USSR as the entire 2,000 issues were sold within 1 week. On the *far right* is the treatise covering a unique scientific, philosophical, and societal approach toward the interdisciplinary science of heat including author's illustration by frontispiece art photos on each chapter

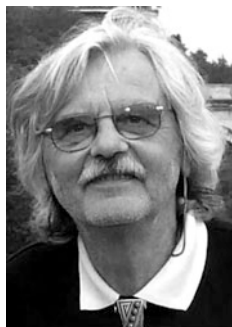
Prague, June 2012



Jaroslav Šesták 269  
 Emeritus scientist of the Academy of Science of the Czech Republic, Program auspice of the West Bohemian University in Pilsen, 'Doctor Honoris Causa' of Pardubice University; Founding professor of both the School of Energy Science of the Kyoto University in Japan, the Faculty of Humanities of the Charles University in Prague, and the New York University, international branch in Prague. He also authored numerous books (the most cited *Thermophysical Properties of Solids*); shown with the distinguished professor of the University of Arizona in Tucson (USA), a truth-seeker of glass crystallization portrayal, Michael. C. Weinberg (+2003, photo upper right). 270  
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Donald R. Uhlmann 282  
 Emeritus professor of the University of Arizona in Tucson (USA) and the former director of the Arizona Research Laboratory; Fellow and Awarder of the American Ceramic Society, the author of both the recognized nucleation-growth theory and the renowned Kingery's fundamental book *Introduction to Ceramics* as well as the book series on glass science co-edited together with the legendary Norbert J. Kreidl (+1994, photo lower left). Recently he is the president of the Donald Uhlmann Incorporation in Tucson. 283  
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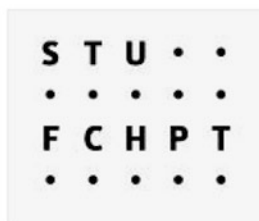
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 complementing thus a coherent and authoritative overview of cutting-edge themes 13  
 of material science focused on solid-state chemistry and thermal physics and 14  
 analysis of various states of matter. 15



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