

Theory and Kinetics

THERMAL TREATMENT AND ANALYSIS
The art of adjacent (near-equilibrium) studies*

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Heating and/or cooling of substances is one of the oldest and basic methods for preparing materials with defined properties. This always leaves a definitive fingerprint of the thermal history. Beside knowing the structure we need to specify such materials by their thermodynamic behaviour, i.e., stability/metastability, phase relations and transitions, particularly establishing corresponding characteristic points. All this can be based on ordinary thermodynamics but its validity must be approved for non-equilibrium conditions of temperature changes where equilibrium and kinetic effects overlap. The slower the phase transition proceeds the greater is the deviation of the system state (kinetic curve) from its equilibrium state (equilibrium background). This makes possible to locate the actual phase boundary between two states investigated, resulting in the so-called kinetic phase diagrams. Most of modern technologies are intentionally based on non-equilibrium phenomena in order to create metastable/nonstable phases of specific properties. In this sense thermal analysis is understood as the method for determining the sample state on the basis of the sample interactions with the surroundings whose intensive parameters are controlled. Temperature is here considered as a basic parameter that connects all thermophysical measurements and thermal treatments.

Keywords: history, kinetics, near-equilibrium studies, thermodynamics

Early roots of thermal analysis

I would like to dedicate this award address to the four-hundredth anniversary of the birth of Johannes Amos Comenius (born 28.3.1592 in Nivnice, Moravia; died

* ICTA-TA Award lecture

15.11.1670 in Amsterdam) [1], see Fig. 1. A theology graduate (from the Universities of Herborn and Heidelberg), he served as a teacher (at Prerov) and pastor (at Fulnek) in Moravia after 1619. After the disastrous battle of 'Bila hora' in 1620, life for Czech people become desperate, so he, among many others, was forced to go into hiding in various places before emigrating to Poland, and then moving to England, Sweden and Hungary; he was finally invited to help improve the Dutch school system (1657) using his famous approach called 'teaching by playing'.

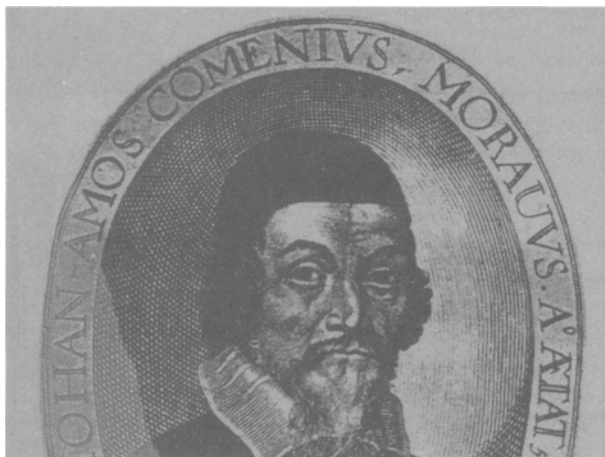


Fig. 1 J. A. Comenius

With respect to our field of thermal analysis (TA), we can recall his work dealing with heat [2] 'Discourses on the Nature of Heat and Cold, a True Knowledge of which is the Key to Many Secrets of Nature' started in the Polish town Leszno but completed in Amsterdam. Although not without faults, its main purpose was to establish that heat and cold are forms of motion. What is worth noting is chapter 3 which somehow gave a prologue to present-day thermal analysis (using Mackenzie's interpretation): 'to observe clearly the effect of heat and cold, let us take a visible subject and let us observe the changes that occur on heating and/or cooling, so that the effects of heat and cold are apparent to our senses' as well as his observation of the adjacent character of heat treatment: 'by a well burning fire we can melt ice to water and heat it quickly to very hot water. But there is no means of converting hot water to ice quickly enough even when exposed to very intense frost'. However, neither Comenius nor Newton nor other scientists prior to Black's 'caloric hypothesis' [1] were able to differentiate clearly the notion of 'heat' from that of 'temperature'.

Czech contribution to the development of thermal analysis

Three hundred years of subsequent chaos during the so-called 'darkness' period in Czech history ended with the establishment of modern Czechoslovakia aided by Thomas Garique Masaryk in 1918. This darkness was accompanied by a deep depression of Czech culture which fortunately survived chiefly in the spoken Czech language of the countryside, giving thus bases for the creation of a respectable democratic state in the very historic territories of Bohemia and Moravia with its roots reaching back to the first millenium. Nevertheless the art of science was kept alive as well since methods of studying changes of material properties on heating and/or cooling their part of the tradition during the period of flourishing alchemy, so much supported in Prague by the Emperor Rudolph the 2nd in the turn of the 16th century. The purpose of science, however, lay in chemical analysis and latterly in the determination of the course of reactions.



Fig. 2 Committee of the Czech Group for Thermal Analysis photographed fifteen years ago (those having a moustache or beard took an active part in the amusements)

Following Tammann's introduction of the term 'thermal analysis' at the beginning of this century [3, 4], it was restricted to the determination of composition of crystal types without mechanical separation based on cooling curves. Czech development of classical thermal analysis [5] is linked with the names of the Czech professors Otakar Kallauner, Josef Matejka and Stanislav Škramovský, and development of modern theory with Vladimír Šatava and Ivo Proks; the latter cannot be separated from the development of classical thermodynamics because the history of thermodynamics is closely related to that of measurements of heat effects and the gradual understanding of the nature of heat [6, 7]. The Czech ther-

modynamics school has its recognized place; I mention particularly those (Hala, Reichert, Regner etc.) who assisted with the newly-formed Technical University of Chemical Technology in Prague (1950) where I studied and graduated in 1962. This was already during another period of political depression under the communistic autocracy which we scientists fought by our own sort of resistance. A serious working group on thermal analysis was founded (Fig. 2), but we also used to amuse ourselves by creating a fictitious person whom we made responsible for the introduction of thermal analysis by frost experiments. This was the source of many funny stories which we enjoyed writing and playing as a cabaret at our TA meetings, and we were later interrogated by Czech secret police about their underlying meaning.

Perspectives of eastern thermoanalysts

Another darkness in Czech history (1948–1989) touched our lives completely, and during it we prayed for liberty. The long-wished for transformation of the past communist (eastern-block) countries (where Czechoslovakia was trapped) to the desired state of a democratic society created, however, a not too favourable situation for science and particularly for scientists themselves. The hated 'iron curtain' politically separating nations and forcing many people to immigration was dismantled, but, unfortunately, it was immediately replaced by a new restrictive division caused by the unbalanced economies. The feed-back of the past communist adventure resulted in the fact that the eastern-block scientists now must face an equally strict and thus cruel 'economic curtain' when travelling to the countries of the west. Such a monetary boundary is particularly painful for scientists as they form an essential part of the cultured people who deserve the greatest credit for the gradual disintegration of communism and the final disappearance of the anti-human 'iron curtain' effectively surrounding the former eastern-block countries.

It is no secret that we researchers engaged in all the arts of science including our beloved field of thermal analysis are a special class of people who often put enthusiastically their wealth on the altar of science, serving patiently in an imaginary common wealth. We often sublimated our business and/or political careers in favour of scientific knowledge, thus sacrificing better financial security for our families and being thus considered by our neighbours as harmless and confused individuals. However, without such foolish missionaries of all kinds, the world would never benefit from all the tiny as well as essential achievements inevitable for the steady development of societies and for the everyday luxuries used by wealthy business and political men. Such simpleton missionaries, however, can be of two kinds, rich and poor, dividing themselves into those who carry out their scientific profession more as a hobby, being assured of a certain living standard, and those who make their scientific craft their entire mission, having more or less empty pockets.

The financial strength of the better-organized western society killed the ill-minded communism of the east which economically could not compete with the west. However, nobody could have imagined that the destruction would bring so many disastrous and unexpected side-effects; from national wars to cultural misery. It is now up to the west to make up its mind and decide where to start to help repairing the destructed east. Evidently, a first move is the incorporation of the mental strength of eastern scientific manpower into existing projects of the west. Scientific knowledge is as rare as raw materials and should be explored similarly to the cheap resources in the past in underdeveloped countries. One has to promote joint scientific ventures, possible 'renting' eastern scientist at substantially lower, but still quite acceptable, salaries to carry out the research tasks in well-equipped western laboratories or providing outdated equipments for the possible creation of new eastern centres ready to provide services for the west. What we can do is to start a qualitatively new period of cooperation in agreement with the newly developed state of the politically undivided world. Let us start to seek financial resources for making our thermal analysis activity recognized. Let us present the work of our ICTA committees as joint international scientific projects to be funded either from Brussels, Washington or Tokyo. Let us make the effort to keep our ICTA alive and effective within the structure required to obtain money for carrying on the scientific work at any well-established institutions. We should not hide ourselves any more behind the convenient statement that our International Society is and always should be a strictly non-political body and for these reasons we can support administration but we cannot do anything in favour of scientists. Economy and science have become political issues and such hiding is just turning a blind eye to the situation which does need a solution.

Thermodynamic basis of thermal analysis

The term 'thermodynamics' [7] is quite appropriate as a description of thermal analysis (TA) [8] in comparison with 'thermostatics' known as textbook thermodynamics. This is evident because TA studies are carried out under truly thermally dynamic (and thus non-equilibrium) conditions, as being dependent on the heating/cooling rate applied. Therefore the validity of so far known classical thermodynamic treaties must be approved for such equilibrium adjacent conditions which is the most important issue of the theoretical basis of TA [9].

For easy understanding we should classify all the variables into two sorts: those which characterize the sample (extensive quantities, X) and those defining the experimental setup of measuring conditions (intensive quantities, I). The sample is characterized by its weight, volume, composition and thermophysical properties (specific heats, enthalpy, etc.) which have fixed starting values corresponding to the material investigated. Experimental conditions are given by the controlled (and often even uncontrolled) action of external field forces intentionally (or incidentally) applied from the surroundings during TA measurements. Not accounting for pressure, the most important parameter is temperature (T accom-

panied by the extensive heat/enthalpy, H) which is always associated with all kinds of investigations. For a general description, a thermodynamic potential (Φ) is conventionally employed as a function (\wedge) of all intensive parameters which are effective to control the sample surroundings during the entire course of measurement. The changes can be infinitesimally small for equilibrium (thermostatic, dI) and definite for near-equilibrium (thermodynamic, ΔI) studies. Introducing the heating rate $dT/dt = \dot{T}$ as the essential condition of TA experiments we can distinguish:

Equilibrium:		Near-equilibrium
$I_i(dI) - X_i$	—————→	$I_i(\Delta I_i) - X_i$
$T(dT) - H$	(introducing \dot{T})	$T, \dot{T}(\Delta T) - H$
$\Phi = \hat{\Phi}(T, I_i)$	—————→	$\Phi_T = \hat{\Phi}_T(T, \dot{T}, I_i)$

However, it is fortunate that the mathematical analysis [9] yields, for the most frequent cases (i.e., $\dot{T} < 0$ and $\dot{T} = 0$), a negligible effect of the questioned variable \dot{T} which results in the identity $\Phi_T = \Phi$ making it possible to use the standard form of mathematics known from classical equilibrium thermodynamics.

This certainly is a textbook example showing mainly the importance of externally applied (experimental) conditions where the temperature plays a crucial role, but which can be equally true for pressure, electromagnetic fields, gravity etc. For the description of real cases of material behaviour we have to make our simplified example more complex to include, e.g., a second-phase formation. If such a new phase is to occur, another pair of variables becomes inevitable for an adequate description, namely introducing the intensive surface energy and the extensive surface area (being proportional to the squared radius r of created nuclei). Furthermore a chemical reaction should be accounted for by considering the intensive chemical affinity and the extensive fraction reacted (a). As the best example a diffusion process (mass transport across a flat phase boundary between two phases 1 and 2 where $r \rightarrow 00$) can serve to describe a transformation using the intensive chemical potential (μ) and the extensive concentration (C) which is convenient for further analysis. The complex thermodynamic potential then reads:

$$\Phi = \hat{\Phi}(T, \mu_1, \mu_2) \quad (1)$$

Phase transformation dynamics between the phases 1 and 2 is a common aim of TA studies which, however, cannot be accomplished solely on the mere basis of Eq. (1) because the inherent intensive parameters do not reflect the entire state of the sample investigated and thus Eq. (1) must be completed by the extensive parameters which are state-dependent. Therefore we have to transform Eq. (1) by exchanging μ for C to obtain $\Phi' = \hat{\Phi}'(T, C_1, C_2)$ neglecting further I 's is again. Because we can assume that $(d\Phi'/dC_1 - d\Phi'/dC_2 = a\Delta\Phi')$ we can write the resultant equations in the form:

$$\begin{aligned}\dot{a} &= \hat{a}(T, a) \\ T &= \hat{T}(T, a)\end{aligned}\quad (2)$$

which is known as the basic (constitutive) equations of reaction kinetics, showing the interdependence of reaction rate \dot{a} ($= da/dt$) and temperature changes (T) produced during the course of a phase transformation (certainly if the other I 's are kept strictly constant). In practice, however, we merely control the temperature of the sample surroundings (isothermally $\dot{T} = 0$ or non-isothermally $\dot{T} = \beta$) and we seldom measure the entire temperature of the sample (except that for DTA). The use of the externally controlled values of temperature instead of the true ones of the sample is thus the essential oversimplification of all kinetic evaluations.

Such simple mathematical manipulations were illustrate an important philosophy of TA description as the adjacent field of known thermodynamics often hidden in too complicated [8] or controversially oversimplified treatments. Moreover it presents an idea how to bridge two normally separate categories of textbook 'thermostatistics' and reaction kinetics.

Thermal analysis as applied science

Thermal analysis is the domain or field of interdisciplinary cooperation of various specialists and is often referred to as integrated thermophysical research [8]. A common drawback to its development is the insufficient transfer of skills from branches that are not closely related, although they might serve as an inspiration. Specialists who often lack time to study information from overlapping branches find invaluable assistance in interdisciplinary publications. The often neglected field of thermal analysis kinetics [8, 11] demonstrates a typical situation: prior to the 2nd World War, the centre of attention was the evaluation of geometrical models for solid-state reactions under strictly isothermal conditions. Principles of non-isothermal kinetics were introduced in the period 1950–1970, chiefly directed to the phenomenology of evaluation methods treated by analogy with homogeneous-like kinetics. After the establishment of the validity of formal kinetic procedures, it was found important to match truly non-isothermal conditions creating, however, the side effects of uncertainty of rate constant, the problem of apparent activation energy, kinetic compensation effect, etc. It may well be exemplified in the practical setup of thermal analysis methods, the type of heating and constitutive equations employed, (Figs 3 and 4). There remains a certain analogy with a very important field of basic and applied material science of the seventies and eighties, as witness the program of formulating the principal objectives and targets projects in the selection, study and preparation of important materials with the aim of improving the properties of existing materials, finding new functional materials with more advantageous properties, and trying to lower their production costs. Progress essentially involved the integrated thermophysical study of phenomena influencing the properties from slowly-grown single

crystals to rapidly solidified multi-component crystalline and non-crystalline substances including both the experimental and theoretical research focused mainly on the description of the behaviour of solid/liquid phase interfaces subjected to the action of external force fields beside the essential temperature. Thermal analysis served as a four-fold source of information regarding material fingerprinting, characteristic temperatures, quantity and the course of reaction (i.e. amount of heat and its rate of generation or lost), the latter factor being most important in preparing advanced materials in metastable and/or unstable states by controlled formation kinetics. At random, I can mention some principal branches

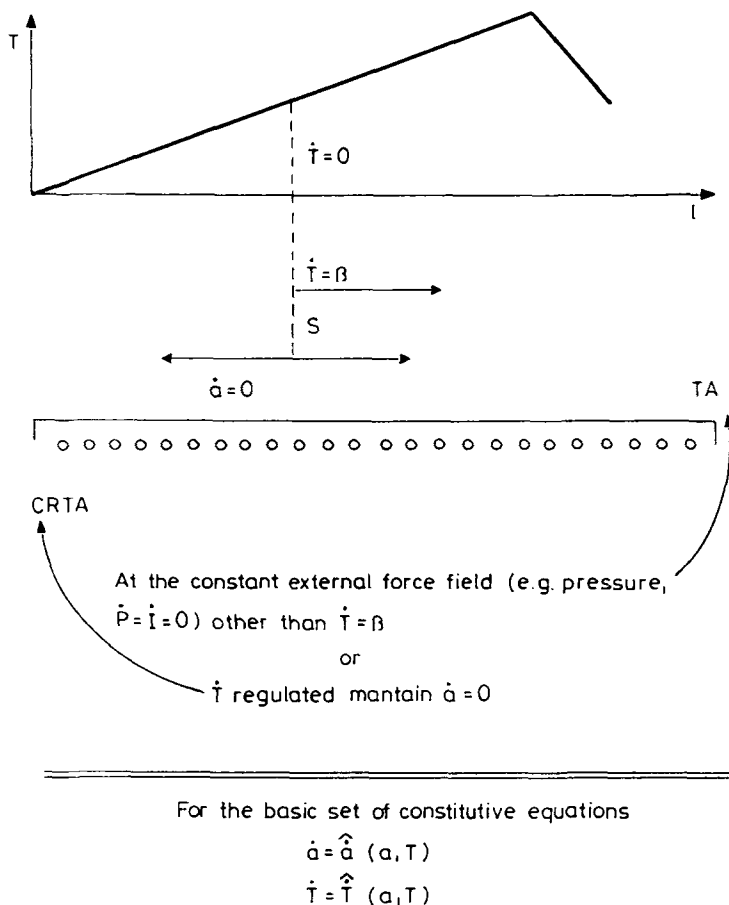


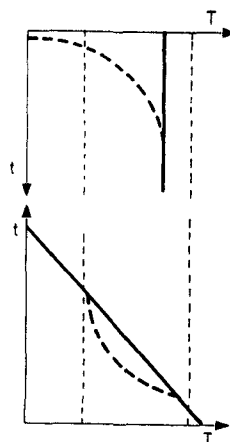
Fig. 3 Temperature control and two basic types of TA measurements: classical TA (controlling \dot{T} by a controlled movement of the sample s along the constant temperature T gradient in furnace l and measuring \dot{a}) and constant rate TA (controlling and measuring \dot{T} in order to keep \dot{a} constant)

- Neglecting $T = \hat{T}(a, T)$
- 1) Isothermal kinetics -- $\dot{T} = 0$

$$\dot{a} = \hat{a} \quad (\{T = \text{const}\}, a)$$
 - 2) Linear non-isothermal kinetics -- $\dot{T} = \beta$

$$\dot{a} = \hat{a}(T, \beta, a)$$
 - 3) Truly non-isothermal kinetics -- $\dot{T} = \beta + \hat{a}^* \{\Delta H\}$
 (including the effect of self-heating and self-cooling due to the enthalpy change ΔH)

$$\dot{a} = \hat{a}(T, \hat{a}^* \{\Delta H\}, a)$$



Considering $T = \hat{T}(T, a)$

- 4) General non-isothermal kinetics
 (like drop-in calorimetry where the sample heats up to the working temperature of thermostat according to an exponential $T \sim \Delta T \exp(t / \tau)$) or computer simulated DTA where the sample is inserted into pre-heated furnace and its exponential heating curve is computer-evaluated and compared with the heating curve of inert sample standard)
- 5) Constant rate thermal analysis (where the reaction is controlled that its rate \dot{a} is constant)

\dot{T} under the regulation

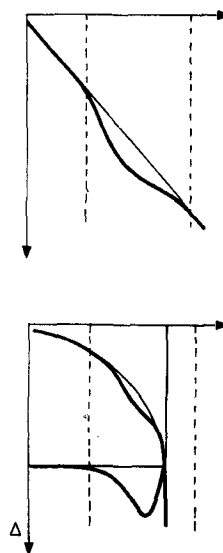


Fig. 4 Possibilities of controlling temperature during various types of kinetic studies; plots of temperature (vertical) vs. time (horizontal axis) show considered (bold full), actual (dashed) and furnace (thin full line) temperatures; dotted lines bounding the reaction interval

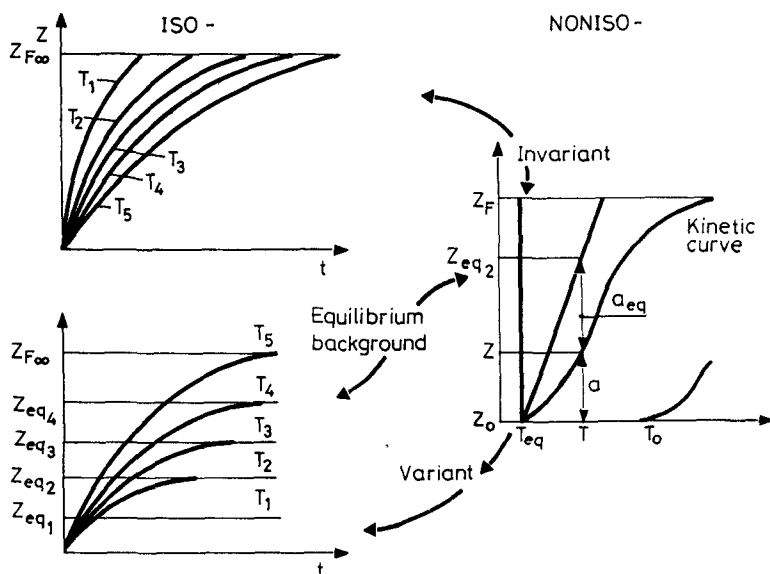
of science involved in the theory of solids, such as physics and chemistry of semiconductors, dielectrics, metals, magnetics, and superconductors. An important aspect of further progress is an attempt to solve universal problems that have to be tackled in the coming decades involving also problems of applied thermal analysis in searching for the production of new materials in the solution of the energy crisis, processing of information, searching and renewal of raw materials, recycling wastes, and generally preserving environment qualities, and, last but not least, attaining a certain equilibrium between the relatively overdeveloped natural science and the under-developed sphere of social science and particularly human relations.

Thermal analysis and material engineering

The available technologies show considerable variability. As a rule, one particular technology can be used to prepare a whole range of materials and, vice versa, each material can be fabricated usually prepared by a number of different techniques, which is true even considering those for thermal treatment. One of the objectives of applied thermal treatment and analysis is to find the criteria permitting the selection of the right method for treating and/or studying the given material. This implies not only finding new technologies but also improving the existing ones with the aim of making better use of the raw materials, saving energy, reducing production costs, etc. In many respects there are diminishing differences between the laboratory technologies and those used for small-scale production. In this respect thermal analysis procedures may enable us to be discriminating in studying integrated data of changes of heat as well as weight, etc. On preferably larger samples or in fine measurements of characteristic points (temperatures) on very small samples with negligible gradients but possibly an unfavourable proportion between the effects of volume and surface. Kinetics of technological important processes would require a technology-like setup of a thermal analysis experiment. The problem of adequate measurements of averaged samples may become crucial for the experimental setup necessary for investigation of large samples, possibly reaching over a kilogram in weight.

Out of a large body of necessary information that contributes to finding techniques best suited for the production of a partial new material, the most essential is the information contained in the phase diagrams of the system in question. By the term 'phase diagram' of a chemical system we understand the whole complex of knowledge that makes it possible to co-ordinate the partial properties of the individual phases co-existing in so-called equilibrium (i.e. data on balance phase conditions) for a given overall chemical composition. However, the entire production relies increasingly on the processes that occur under conditions far removed from equilibrium. Examples of such processes are rapid cooling of melts, laser processing of solid surfaces, cvd techniques, and glass-formation in general. These extreme conditions may lead to new structures and compositions of solids that cannot be described within the standard framework of the equi-

librium phase diagrams [6]. Therefore the notion of metastable and kinetic phase diagrams emerged depending on the kinetic factors of the system normally not included or intentionally neglected in traditional 'thermostatics' [8]. It is best exemplified on the basis of the so-called 'equilibrium background' [12] of a



Thermodynamic data

characteristic T

(T_{eq}, T_o)

total change off Z

$$\Delta Z_{\infty} = Z_{F\infty} - Z_o$$

partial change of Z

$$\Delta Z_i = Z_{eq(i)} - Z_o$$

equilibrium background

$$a_{eq} = (Z_{eq(i)} - Z_o) / (Z_{F\infty} - Z_o)$$

Kinetic data

degree of conversion

$$a = (Z - Z_o) / (Z_{F\infty} - Z_o)$$

reaction rate

$$\dot{a} = da/dt$$

hysteresis

$$T = T_o - T_{eq}$$

(induct. period)

Multidisciplinary field

Kinetic phase diagrams

(extrapolated phase bound.)

(shifted phase boundary)

(T - T - T and H - T diagrams)

Fig. 5 Possible types of isothermal curves obtained for invariant and variant processes and resulting equilibrium background ($\beta \rightarrow 0$) and kinetic curve (TA trace for $\beta > 0$) with associated types of thermodynamic and kinetic data

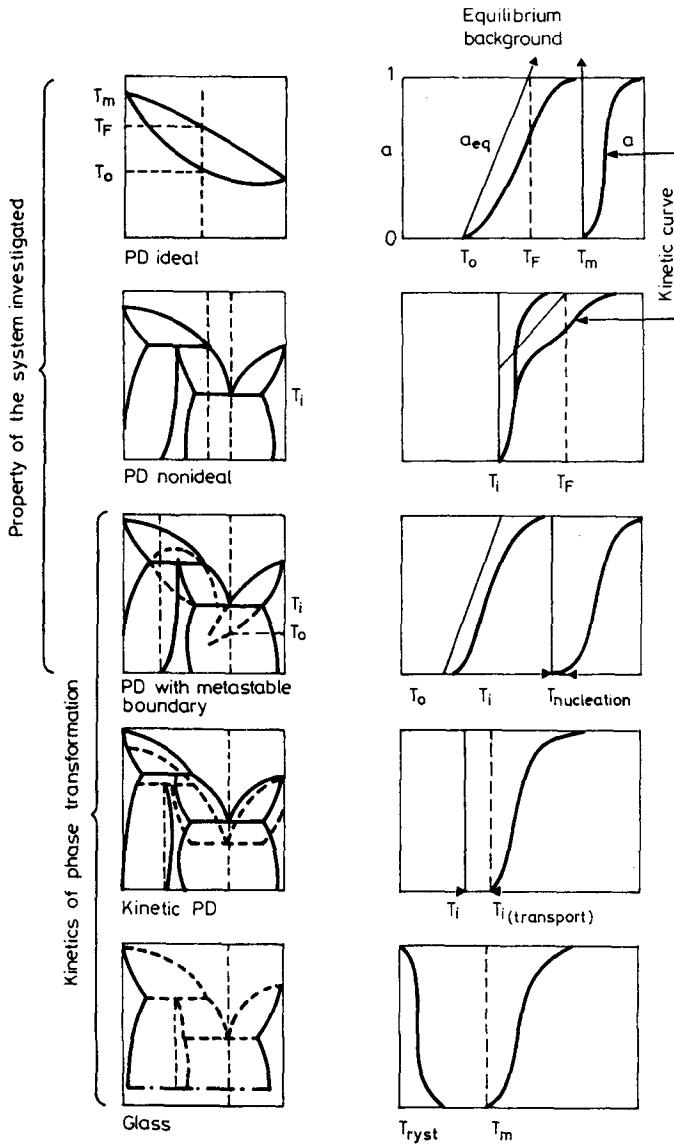


Fig. 6 Hypothetical picture to illustrate overlapping effect of material thermochemical properties (from ideal to non-ideal solution creating tectic points at phase diagrams) with transformation kinetics (nucleation and mass transport) and externally applied conditions of experimental setup (changes of temperature) as exhibited on a binary phase diagram (PD) showing possible extrapolation and/or shift of boundary lines (left column) and the position of equilibrium background and associated kinetic curve (right column) for given isoconcentration cuts (dotted verticals, left column)

reaction which well separate the measured kinetic curve and its limit as the heating rate approaches zero (Fig. 5). Such a 'kinetic' state of phase compatibilities (Fig. 6) makes it possible to describe the dependences of composition and/or structure of the solid phase obtained by 'freezing-in' of the liquid/solid phase on the quenching process or on the effect of external fields (gravity, pressure, electromagnetics). Here also belongs the effort to improve the quality of casting which is required to solve the non-equilibrium ordering process of liquid and consequent crystalline phase with the aim of controlling the microstructure and plasticity, traditionally connected with a kind of kinetic phase diagrams called 'surroundings' [13]. Specifying the requirements also poses the problem of preparation of oriented eutectics of a particular shape for machine parts exposed to extreme loads and/or superconductors with high current density. It requires the study of temperature/concentration dependences of nucleation and growth under various conditions of undercooling and supersaturation and the possibility to measure it by modified methods of thermal analysis in three and even two-dimensional arrangements. No less important is the thermophysical study of hydrodynamic processes in fluid media (solutions, melts, gases from which the phase interface is formed or diminished) particularly for exploring their influence on the surface processes when studying heat and mass transfer under various conditions of material make-up and external control. Although these methods have found broad practical application in a number of technologies, their potential is far from being exhausted. With the required knowledge one can go as far as the preparation of two-dimensional structures which, however, are difficult to study in the conventional 3-D sample setup of existing TA instruments.

Conclusions

The basic task of all TA measurements is to obtain reliable knowledge about the sample temperature which can be detected either directly or indirectly (contactless if the temperature of a reference point is measured and related to the true sample temperature by calibration). Single point measurements of the so-called centred temperature assures the gradient averaging by high enough thermal conductivity of the sample/holder. Multipoint measurements make it possible to scan temperature gradient or to localize the reaction interface or to read a mean surface temperature. In particular, DTA is the only method where the entire course of the true sample temperature is monitored, thus being the centre of an increased interest if analysed with respect to non-equilibrium behaviour. When seeking for a gradientless experimental setup, the sample size or heating rate have to be minimized to possibly reach a limit when a DTA effect is diminished. Miniaturization of the sample weight brings problems associated with a precise determination of starting weight, interaction of surfaces (sample vs. holder particularly during the course of melting) and effect of the powdered sample interfaces itself particularly disturbing the investigation of bulk properties. Thin layer (2D) measurements are unfortunately not convenient yet as they can conflict with common requirements

of the sufficiently sensitive measurements of the sample extensive properties. Thus the further development of TA apparatuses designed to indicate either extensive (e.g. heats) or intensive (e.g. temperatures) properties may not follow the same path [14].

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Zusammenfassung — Das Erhitzen und/oder Abkühlen von Stoffen ist eine der ältesten Methoden zur Herstellung von Substanzen mit ganz bestimmten Eigenschaften. Dies hinterläßt stets einen definitiven Fingerabdruck der thermischen Vorgeschichte. Außer mittels der Struktur solcher Substanzen müssen diese auch durch ihr thermodynamisches Verhalten, z.B. Stabilität/Metastabilität, Phasenbeziehungen und -übergänge angegeben, insbesondere entsprechende charakteristische Punkte spezifiziert werden. All dies kann auf gewöhnlicher Thermodynamik begründet werden, die Gültigkeit muß jedoch für Nicht-Gleichgewichtsbedingungen von Temperaturänderungen erprobt werden, bei denen sich Gleichgewicht und kinetische Effekte überschneiden. Je langsamer die Phasenumwandlung erfolgt, umso größer ist die Abweichung zwischen dem Systemzustand (kinetische Kurve) und dem Gleichgewichtszustand (Gleichgewichts-Background). Dies ermöglicht die Lokalisierung der Phasengrenze zwischen zwei untersuchten Zuständen, wobei man ein sogenanntes kinetisches Phasendiagramm erhält. Die meisten modernen Technologien beruhen absichtlich auf Nicht-Gleichgewichterscheinungen, um metastabile/unstabile Phasen bestimmter Eigenschaften zu schaffen. In diesem Sinne wird Thermoanalyse als eine Methode zur Bestimmung des Probenzustandes auf der Grundlage der Wechselwirkungen zwischen Probe und Umwelt mit kontrollierten intensiven Eigenschaften verstanden. Dabei wird die Temperatur als ein grundlegender Parameter berücksichtigt, der alle thermophysikalischen Messungen und thermischen Behandlungsvorgänge miteinander verbindet.