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Review

Thermodynamic basis for the theoretical description and correct interpretation of thermoanalytical experiments*

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ABSTRACT

The basic principles of the description and processing of thermal analysis (TA) curves are examined. A rational approach is used to investigate the limits of the validity of phenomenological thermodynamics under non-isothermal conditions. The necessary thermodynamic relations and response functions are derived for thermophysical measurements of thermal and non-thermal (dielectric, magnetic and mechanic) property. Sixteen basic thermal coefficients are listed. Simple phase transformations are analyzed (including generalized Clausius–Clapeyron and Ehrnfest equations for the first- and second-order processes) and their theoretical courses are related to the experimental TA curves. Variant and invariant processes are distinguished with regard to the thermal development of their equilibrium background. Actual conditions of dissociation processes are also discussed.

INTRODUCTION

For the correct interpretation of an arbitrary physical measurement, where a particular physical property of the sample is measured as a function of an externally controlled parameter, it is necessary to consider the conditions under which the experiment is conducted and, consequently, the effect of these conditions upon the resulting data[1]. The term conditions (or experimental conditions) means the way by which the studied material is transferred into the form of a sample and the properties of the environment which surround the sample during the whole course of measurement. From the definition of thermal analysis (usually abbreviated TA) as recently proposed by us elsewhere[2] it follows that dynamic TA covers the group of selected thermophysical measurements where the state of the sample is investigated on the basis of its interaction with the heat of the surroundings if the temperature of the

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* See author's note, p. 226.

surroundings is intentionally programmed, preferably as a linear function of time. The complexity of relations between the assumingly dynamic experimental conditions and the resulting TA record is the major obstacle in utilizing TA methods exactly in physical chemistry, particularly if theoretical thermal analysis is still diverse and yet disproportional[3].

With regard to the dynamic character of TA methods the generalized quantitative description must be looked for through the flux relations, as introduced in our previous works[4-6], i.e. the flux formulation of energy conservation law, principles of heat and mass transfer, chemical kinetics, etc. The application of these laws is not easy and is not unambiguous because many of them were originally derived for the conditions which are not always fulfilled during TA experiments. We face the greatest difficulty, however, when coordinating the ordinary equilibrium thermodynamics with the dynamic character of TA measurements. Hence, the aim of this comprehensive work is the analysis of the validity of some generally used relations in non-isothermal conditions, the systematization of these relations within the logistic of TA and, last but not least, the correlation between thermodynamic processes and the types of resulting curves.

Chapter 1

ANALYSIS OF THERMOPHYSICAL MEASUREMENTS

The unifying element of all thermophysical measurements to be looked after is the investigated sample itself and the way in which the sample is thermally treated. The detected physical property of the material is understood to represent the instantaneous state of the sample and it is up to the investigator to which temperature it is ascribed and in what manner it is analyzed. Qualitative applications, as common in DTA, are a frequent subject of most TA books[7]. Quantitative measurements at an equilibrated (constant) temperature (static methods) are the most general methods of extracting thermodynamic information in solid state chemistry and physics. From the moment when temperature becomes time-dependent (dynamic methods) we face all possible problems connected with temperature gradients, hysteresis, supercooling and/or superheating, etc. Utility of dynamic measurements is thus not general and strongly depends upon the sort of material investigated and its capability to equilibrate fast enough to follow changing temperature; it must, of course, be tested for each experimental case. The comparison of mutual advantages of the equilibrium but time-consuming static methods with the comparatively fast but non-equilibrium dynamic methods provides the basis for the appropriate set up of our experiment. For the study of reversible processes the dynamic methods were found satisfactory.

Nowadays the TA measurements are often understood in their broad sense and may cover almost all thermophysical measurements if the temperature is continuously varied and if the physical property is also continuously registered. Although this all-covering approach provokes assumingly numerous physicists (because many thermophysical measurements have their origin in experimental physics) we, in fact, have frequent reports on such TA techniques[1] as thermospectrometry, thermoluminiscence, thermorefractometry, thermoacoustimetry, thermomicroscopy or even high-temperature (oscillation) X-ray diffraction and/or spectroscopy. These methods evidently belong among the *measurements of structural properties*. These methods can be contrasted with the more classical methods of TA based on the *measurements of thermodynamic properties* as temperature (Direct TA, DTA), heat content (DSC), volume, density, weight (TG), content of volatile products (EGD), as well as less common magnetization (MTA), polarization (ETA), deformation (TMA) and pressure (DPA). The theoretical description of later methods lies within the proposed scope of our introductory thermodynamics and hence is dealt with in detail later.

Almost all TA measurements yield merely single valued data of a given physical property although its local value within the mass of the sample may vary. Averaging such space inhomogeneities* (as well as most important temperature distribution) is in accordance with the theory of phenomenological thermodynamics where all quantities are assumed and characterized by their mean values. The neglect of gradients, however, is a most serious simplification particularly in determining the true state of solids but, on the other hand, is adequate to the present level of TA instrumentation. The use of gradient theory (particularly assuming most effective temperature gradients) is thus not actual unless a more sophisticated instrumentation is introduced as, for example, space multidetection devices.

The framework of phenomenological thermodynamics[8] seems to be the most useful tool in finding the unifying groundwork of TA. For the sake of simplicity, we start by treating a simple one-component system to illustrate the principles of caloric and volume TA measurements, see Chapter 3 (In Chapter 2 we attempt to investigate the validity of basic thermodynamic relations in a more general sense of non-equilibrium condition of non-isothermal studies.) Consequently, the system is complicated by assuming the externally applied fields necessary for the description of dielectric, magnetic and thermomechanic TA and finally generalized for multicomponent materials to describe TG, EGD, etc., based on the detection of volatile products, see Chapter 6. Although all these TA methods never take place at the same time, even as multisimultaneous techniques, their joint description well demonstrates the principal features of a complex thermodynamic approach. To achieve a uniform link and to ease our understanding we commence each of our system descriptions by listing the so-called *constitutive equations* (material relations), see Chapter 2, e.g., $Y = \hat{Y}(X_1, X_2, ..)$ where the state quantity Y is a function $\hat{Y}$ of variables X_1, X_2, etc.

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* We are not concerned with the magnitude of the system[3, 14] when considering its influence on the extent of, for example, temperature gradients (macro- versus micro-methods of investigation and their accuracy of measurements), neither with the description of the microscopic state of the system[3, 4] as ordering of crystallographic sites, distribution of species (and vacancies) on, for example, cation regular and intersticial sites, nor with their thermodynamic potentials which were dealt with in detail elsewhere[4].

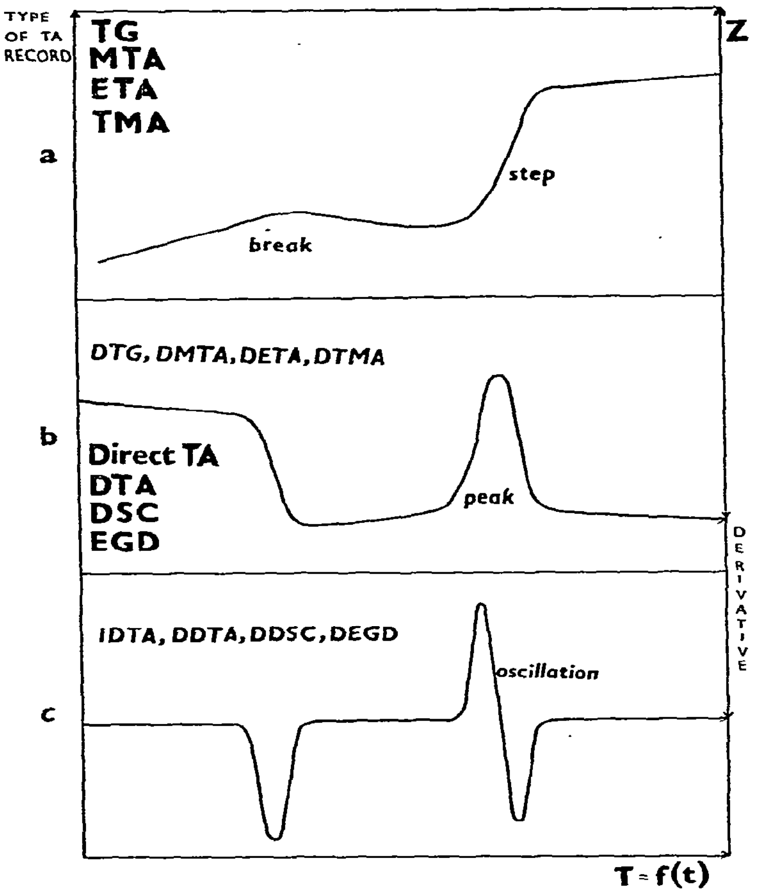

Fig. 1. Graph of typical TA curves as recorded for the individual TA techniques, where a corresponding physical property Z of the sample is plotted versus temperature T.

It should be noted that we intentionally delete from this approach the description of electric conductivity (amperometric TA) because this method is directed to investigate the flux property of materials, i.e. the detection of electric current passing through the sample layer which is evidently a case similar to the purely kinetic studies of mass diffusion and/or heat conductivity bearing their own values of the energy of activation. Neither have we dealt with the description of the energetics of surfaces and interfaces which is discussed in the forthcoming text at a minimum level just to give the basis of heterogeneous new phase formation.

Let us now turn our attention to the possible kinds of TA records[9] as shown schematically for the above selected methods of TA in Fig. 1. Every record can be divided into smooth lines called *base lines* and their sudden changes called *effects*. The upper part of Fig. 1 exhibits two sorts of effects: the change of the base line slope called *break* and the stepwise displacement of base lines called *step* (wave). This is typical for thermogravimetry, thermodilatometry, thermomechanical and electromagnetic measurements. Another effect called *peak* arises from a sudden increase and decay of the measured property Z and occurs at direct TA (heating and cooling curves), DTA, DSC and methods associated with evolved gas detection, see middle part of Fig. 1(b). A similar effect, however, can be obtained through an electronic derivation of upper curve (a) sometimes presented as an independent measuring technique as DTG, similarly DDTA, DDSC, IDTA and DEGD shown in the lower part of Fig. 1. Here also an additional effect called *oscillation* appears. It follows that each TA technique provides only that kind of record appropriate for further analyzing. Additional electronic, analogic as well as numerical treatment merely provides a derived record which can serve as complementary information only[10] or for an advanced characterization when using computers.

To extract the desired data, we must identify mathematically individual base lines and effects and then relate them to a given thermodynamic and/or kinetic description. Base line can be analytically expressed in the form of a series, most conveniently as $Z = a_{i=1} + a_2T + a_3T^2 - a_4T^3$, where T is the temperature and a_i are constants. In most cases, a linear approximation (first two terms of the series) is satisfactory (linear materials). The thermodynamic meaning of thermal coefficients for individual TA methods in question is thus analyzed in Chapter 3 where a simple development of the thermal state of the sample is described. Chemical reactions and structural transformations are indicated by a base line discontinuity and the resulting effects should be analyzed with regard to their *position* (characteristic temperatures), *size* (integral change of the measured property), see Chapter 4, and *shape* (time-development of the measured property), see Chapter 5. The last two phenomena, however, may exhibit a mutual interference of reaction kinetics and thermal development of equilibrium (thermodynamics), compare Chapter 5. The mathematical description of individual effects falls into two categories: determination of *characteristic points*[11], e.g. the beginning and end of the break, extrapolated point of base lines intersection; beginning and end of the step inflection point, step width and height[12]; beginning and end of the peak, extrapolated onset and offset, front and rear inflection point, peak width and height, extrapolated peak width, actual and linearly interpolated peak background, etc., and determination of *instantaneous values* (compare Chapter 5) which may be eased by fitting the curve with a suitable function[13], e.g. higher-order polynomials $Z = p_1(T)/p_2(T)$, exponentials $Z = 1/[1 + a_1 \exp(a_2T)]$, logarithm $Z = a_0 + [a_1/\ln(a_2T)]a_3$ and hyperbolic tangent $Z = \tanh(T^a)$. To establish the total change of the measured property, Z, the step is the most appropriate curve because the peak must be gradually integrated as well as the break derived. Evidently a satisfactorily readable record is the essential requirement for a successful interpretation of TA data[*].

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[*] The discussion of partial or whole curve fitting and smoothing with regard to further computer treatment which is usually accomplished by applying more complex, e.g. orthogonal functions possibly under curvature tension (i.e. spline-functions to avoid the creation of inevitable inflections), is not the aim of this review. Neither do we assume the backwards consequence of certain mathematical operations such as derivation or integration which result in changing the scatter and/or smoothness of the originally recorded trace. A detailed mathematical approach will be dealt with elsewhere[14].

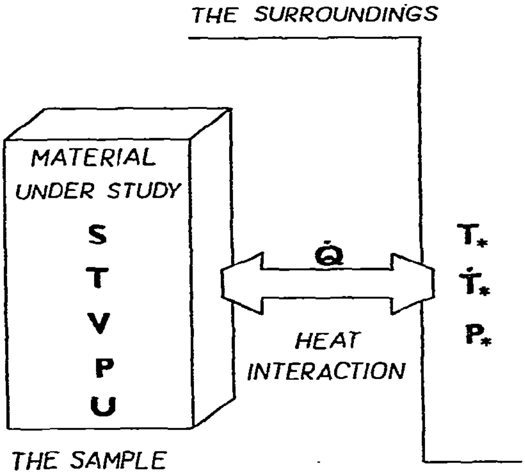

Fig. 2. Simple closed thermodynamic system, where the state of the system under TA study is represented by the entropy S, temperature T, volume V, pressure P and internal energy U. Externally controlled parameters of the surroundings are the temperature T_*, pressure P_* and the time progress of temperature $\dot{T}_*$.

Chapter 2

RATIONAL DESCRIPTION OF A THERMODYNAMIC SYSTEM WHILE EXTERNALLY HEATED

The basic need of a rational approach is to choose the minimum number of variables necessary to describe a system satisfactorily. For the sake of simplicity, we assume a simple (homogeneous) system with constant (one component) composition where no chemical reactions occur. In order to give a mathematical description of such a system, we must define it as a physical object in which we can specify certain *basic quantities*. They may be temperature, T, volume, V, pressure, P, entropy, S, internal energy, U, and heat exchange, $\dot{Q}$ ($= \mathrm{d}Q/\mathrm{d}t$), between the sample and its surroundings (*). Such a system is shown schematically in Fig. 2 and exhibits all the basic features of a simple thermoanalytical arrangement.

The temperature, T, pressure, P, and the rate of heating, $\dot{T}$ ($= \mathrm{d}T/\mathrm{d}t$), can be externally controlled and are thus independent while the remaining quantities behave as the dependent variables. It is assumed that the system is not in its equilibrium state and the possibility of obtaining its description by means of ordinary thermodynamics must be first analyzed.

The main idea of how to make a more flexible framework for the thermodynamic description of the system can be obtained on the basis of *rational thermodynamics*[15-17] as recently summarized by Kratochvíl[18]. To this effect, let us define our thermodynamic process in question as continuous sequences of the state of the system. Simply, the process is fully described when the basic quantities are given as functions (superscript $\wedge$) of time, t, or

$$\left.\begin{aligned} T &= \hat{T}(t) \\ V &= \hat{V}(t) \\ P &= \hat{P}(t) \\ S &= \hat{S}(t) \\ U &= \hat{U}(t) \\ \dot{Q} &= \hat{Q}(t) \end{aligned}\right\} \text{process} \tag{1}$$

The term $\dot{Q}$ is the typical phenomenon accompanying any thermoanalytical experiment and can always be obtained from the energy conservation law

$$\dot{U} = \dot{Q} - P\dot{V} \tag{2}$$

where superposed dotts mean the time derivative.

Specific properties of the sample can be characterized by three material relations, G, V and S, expressed as functions of the state of the sample. The state is now identified with the instantaneous values given for the three externally varied parameters, say pressure, P, temperature, T, and its time change, $\dot{T}$, namely

$$\begin{aligned} G &= \hat{G}(P, T, \dot{T}) \\ V &= \hat{V}(P, T, \dot{T}) \\ S &= \hat{S}(P, T, \dot{T}) \end{aligned} \tag{3}$$

The entropy principle requires that for all processes of this system the rate of heat exchange, $\dot{Q}$, be limited by the maximum value of entropy change, $\dot{S}$, or

$$\dot{S} \geq \dot{Q}/T \tag{4}$$

Employing this requirement, we can draw important conclusions. Introducing a state function in the form

$$G = U - TS + PV \tag{5}$$

which is conveniently called the Gibbs free energy, we have from eqns. (2) and (4)

$$0 \geq \dot{G} + S\dot{T} - V\dot{P} \tag{6}$$

Using eqn. (3) we proceed by introducing the partial derivatives into the inequality (6) to obtain

$$0 \geq \left[\left|\frac{\partial G_{(P,T,\dot{T})}}{\partial T}\right|_{P,\dot{T}} + S(P, T, \dot{T})\right] \dot{T} + \left[\left|\frac{\partial G_{(P,T,\dot{T})}}{\partial P}\right|_{T,\dot{T}} - V(P, T, \dot{T})\right] \dot{P} +$$

$$+ \left[\left|\frac{\partial G_{(P,T,\dot{T})}}{\partial \dot{T}}\right|_{P,T}\right] \ddot{T} \tag{7}$$

Equation (7) must be fulfilled for any process so that the values of T, P and their time derivatives $\dot{T}$, $\dot{P}$ can be chosen independently and arbitrarily. Hence for $\dot{T} = 0$ and $\dot{P} = 0$, eqn. (7) is reduced to $(\partial G/\partial \dot{T})\ddot{T} \leqslant 0$, which can be identified for all possible values of $\ddot{T}$ only if the term in the parentheses is equal to zero. From this it follows that the function G cannot be dependent on $\dot{T}$; thus G in eqns. (3) is only $G = \hat{G}(P, T)$, i.e. Gibbs free energy obtains the form known from ordinary thermodynamics.

Similarly, if we choose $\dot{T}$, we have eqn. (7) in the form $[\partial G/\partial P + V]\dot{P} \leqslant 0$ being already aware that $\partial G/\partial \dot{T} = 0$. Because the term in square brackets is independent of $\dot{P}$, and $\dot{P}$ can be chosen arbitrarily, we obtain

$$\left|\frac{\partial G_{(P,T)}}{\partial P}\right|_{T,T} = V(P, T) \tag{8}$$

The analysis of the last term of eqn. (7) is more complicated. Let us divide the entropy, S, into its equilibrium part, $S_{\mathrm{eq}} = \hat{S}_{\mathrm{eq}}(P, T) \equiv \hat{S}(P, T, \dot{T} = 0)$, and the complementary part $[S - S_{\mathrm{eq}}]$. What remains from the inequality (7) can now be rewritten as

$$0 \geq \left[\left|\frac{\partial G_{(P,T)}}{\partial T}\right|_{P,\dot{T}} + S_{\mathrm{eq}}(P, T)\right] \dot{T} + [S(P, T, \dot{T}) - S_{\mathrm{eq}}(P, T)]\, \dot{T} \tag{9}$$

For fixed P and T, this inequality expresses the variable $\dot{T}$ in the analytical form of $0 \geq a\dot{T} + b(\dot{T})\dot{T}$, where $b(\dot{T})$ approaches zero if $\dot{T} \to 0$. Such inequality can be satisfied for arbitrary $\dot{T}$ only if $a = 0$ and $[b(\dot{T})\dot{T}] \leqslant 0$, or

$$\left|\frac{\partial G_{(P,T)}}{\partial T}\right|_{P,\dot{T}} = - S_{\mathrm{eq}}(P, T) \tag{10}$$

$$[S(P, T, \dot{T}) - S_{\mathrm{eq}}(P, T)]\, \dot{T} \leq 0 \tag{11}$$

Equation (11) represents here the so-called *dissipation inequality*, i.e. the non-ideality of our material under study. If the term $b(\dot{T})$ is negligible or small enough, we come to the so-called *quasistatic processes*, where an ordinary description by means of classical thermodynamic relations [see eqns. (8) and (10)] is satisfactory.

The application of our approach now depends on the kind of material investigated and on the rate of temperature change. It is evident that, for example, a perfect gas will always behave ideally regardless of the conditions externally applied. However, in thermal analysis we often encounter rather non-ideal materials such as solids and, hence, the heating rate becomes decisive. Nevertheless, for ordinary TA runs ($\dot{T} > 0$, $\ddot{T} = 0$), where the heating rates are of the order of magnitude of 10^{-1} K sec^{-1}, the state functions of G, V and S depend predominantly on P and T and the effect of $\dot{T}$ is negligible. This, in fact, is in accordance with the well-known result following from thermodynamics of irreversible processes which says that for the systems which are not too far from their equilibrium state and where the processes proceed fast enough, the ordinary thermodynamics can be utilized[19–21].

It is evident that this "classical" thermodynamics or "*thermostatics*" forms a limiting case of a general rational approach and thus its applicability must be carefully investigated for each experimental case. For example, if we start to deal with greater and non-uniform heating rates ($\dot{T} \gg 0$, acceleration $\ddot{T} \neq 0$), the system of eqns. (3) may not be adequate because it does not include the systems possible dependence upon the second (or even higher) derivatives in T, e.g. $G = \hat{G}(P, T, \dot{T}, \ddot{T})$. This holds true for some extreme conditions when, for example, some explosive reactions are studied and/or for such a non-ideal material which can remember its thermal history. The ordinary Gibbs free energy then alters by an additional term[18], $\partial G/\partial \dot{T} \neq 0$ expressing higher dissipation. The discussion of such a system, however, is beyond the scope of this review and also beyond an ordinary thermoanalytical experiment.

Chapter 3

BASIC THERMODYNAMIC RELATIONS AND MEASURABLE QUANTITIES

When investigating quasistatical transformations of the energy [see eqn. (2)] of our studied macro-system into its particular forms, the so-called *phenomenological thermodynamics*[3, 8] is of great help to a better understanding of the general principles of a TA experiment. It aids our interpretation of how to construct mutual interconnections between the thermal and non-thermal properties of the system. The most ready-to-use result of such a description is the set of relations, conveniently called *response functions*, correlating thermodynamic quantities with those which can be detected by means of a direct thermophysical measurement. For the simplest case of a closed system discussed above we readily transform[3] internal energy $U = \hat{U}(S, V)$ and $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$ into the form of Gibbs free energy $G = \hat{G}(T, P)$ and $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$ by replacing the extensive parameters S and V by the intensive ones, T and P, which do not depend upon the quantity of the system and which can be more easily externally controlled. On the other hand, we should bear in mind that the experimentally measurable state of the system is best reflected by the instantaneous values of the *extensive parameters* V and S as functions of the *intensive parameters* P and T [see eqns. (3)] with regard to the size of the system*.

By the use of thermoanalytical convention the state of this system can be investigated in two different ways: by volume measurements $V = \hat{V}(P, T)$ and/or

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* The greater the magnitude of the system investigated, the better the sensibility and resolution achieved for the detection of an extensive parameter. On the other hand, the accuracy of determination of an intensive parameter improves for smaller systems (mainly due to decreasing gradients). There, however, arises the controversy of how to measure experimentally intensive parameters through which the representative extensive quantity is estimated. The typical case is that of temperature[10] (thermometric measurements as DTA, spontaneous heat flux measurements as DCC) or pressure (non-isobaric measurements, isochoric measurements as DPA), etc.

enthalpy measurements $H = \hat{H}(P, S) = \hat{H}[P, \hat{S}(P, T)]$. As both functions are the state functions, we can express their total differential as

$$\mathrm{d}V = \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T \tag{12}$$

and

$$\mathrm{d}H = \left(\frac{\partial H}{\partial P}\right)_S \mathrm{d}P + \left(\frac{\partial H}{\partial S}\right)_P \left[\left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial S}{\partial T}\right)_P \mathrm{d}T\right]$$

$$= V\mathrm{d}P + T\left[-\left(\frac{\partial V}{\partial T}\right) \mathrm{d}P + \left(\frac{\partial S}{\partial T}\right) \mathrm{d}T\right] \tag{13}$$

where the partial derivatives can be identified with the following experimentally attainable coefficients

$$\text{thermal compressibility} - \beta = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial^2 G}{\partial P^2}\right)_T \frac{1}{V}$$

$$\text{thermal expansion } \alpha_v = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_{T_1 P} \frac{1}{V}$$

and

$$\text{heat capacity } c_P = \left(\frac{\partial H}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Finally, it yields

$$\mathrm{d}V = \alpha_V V \mathrm{d}T - \beta V \mathrm{d}P \tag{14}$$

$$\mathrm{d}H = V(1 - \alpha_V T)\mathrm{d}P + c_P \mathrm{d}T \tag{15}$$

It can be seen that the change of the thermal state of our macro-system is accompanied by the changes of all the macroscopic properties in question and, conversely, the change of any macroscopic property results in changing the thermal property. This fact documents the major importance of thermodynamics in describing a TA experiment in its broad sense of a general thermophysical measurement. In addition, the change of temperature will not only affect the above-listed thermal properties but will also change mechanical, electromagnetic[22–25] and optical properties, and will affect the rate of chemical reactions[3], heat and mass transfer, etc.

Consequently, let us consider a more complex system assuming the exchange of a volatile component between the sample and its surroundings (a partly open system) as well as new externally applied fields: electromagnetic and mechanical, as schematically shown in Fig. 3. New intensive parameters which are to be externally

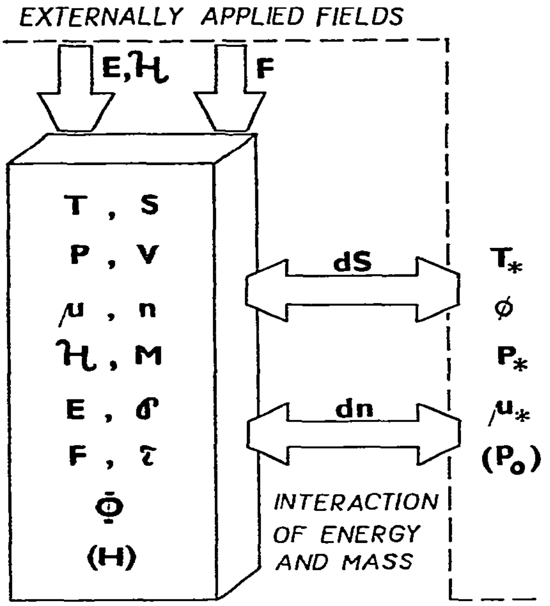

Fig. 3. Partly open, quasistationar thermodynamic system suitable for the portrayal of TA methods as calloric, thermodilatometric, weight, evolved gas, magnetic, dielectric and thermomechanical measurements (symbols see text).

controlled are μ, $\mathscr{H}$, E and F called the chemical potential, magnetic and electric fields and mechanical tension, respectively. Corresponding extensive parameters representing the state of the sample are n, M, $\mathscr{P}$ and τ, known as the mole number, magnetization, polarization and deformation. We certainly cannot control directly the chemical potential of the surroundings but we choose the partial pressure p_0 (assuming the validity $\mu_* = \mu_0 + RT \ln p_0$). It should also be noted that the previously used term VdP retains its real meaning only if the material investigated does not become anisotropic under the action of the external fields (i.e. homogeneity condition)*. The chemical potential term $nd\mu$ is expressed in the form of a summation according to the number of phases in the system.

Let us imagine a generalized state function Φ depending exclusively on the intensive parameters as independent parameters of our TA experiment

$$\Phi = \Phi(T, P, \mu, \mathscr{H}, E, F) \tag{16}$$

The differential form of this thermodynamic potential is analogical to Gibbs free energy G but more comprehensive

$$\mathrm{d}\Phi = -S\mathrm{d}T + V\mathrm{d}P - n\mathrm{d}\mu - M\mathrm{d}\mathscr{H} - \mathscr{P}\mathrm{d}E - \tau\mathrm{d}F \tag{17}$$

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* For a more rigorous analysis of electromagnetic and mechanic measurements it is more convenient to replace the term $P\mathrm{d}V$ by the term $\rho\mathrm{d}\varphi$ which indicates the energy change in a unit volume of the sample as a result of a mass change for given $E, \mathscr{H}$ and F. The symbol ρ is density and φ means here a chemical potential of a unit amount of the mass of the sample.

TABLE 1

THERMAL COEFFICIENTS DERIVED ON BASIS OF A GENERAL THERMODYNAMIC POTENTIAL $\Phi = \Sigma\, Y\, \mathrm{d}X$

Experimentally controlled intensive parameter X	*Corresponding extensive parameter to be detected* $Y(=\partial\Phi/\partial X)$	$\dfrac{\partial^2\Phi}{\partial X^2} = \dfrac{\partial Y}{\partial X}$	$\dfrac{\partial^2\Phi}{\partial X \partial T} = \dfrac{\partial Y}{\partial T} = \dfrac{\partial S}{\partial X}$	$\dfrac{\partial^2\Phi}{\partial T \partial Y} = \dfrac{\partial S}{\partial Y} = \dfrac{\partial X}{\partial T}$
Pressure P	Volume V	$-\dfrac{1}{V}\dfrac{\partial V}{\partial P} = \beta$ thermal compressibility	$\dfrac{1}{V}\dfrac{\partial V}{\partial T} = \alpha_V$ thermal expansion	$\dfrac{\partial P}{\partial T} = \dfrac{\alpha_V}{\beta}$ thermal expansivity
Chemical potential μ	Mole number n	$\dfrac{\partial n}{\partial \mu} \approx$ (logarithm of activity)	$\dfrac{\partial n}{\partial T} = K_{nT}$ thermal solubility	$\dfrac{\partial \mu}{\partial T} = \bar{S}$ partial molar entropy
Magnetic field $\mathscr{H}$	Magnetization M	$\dfrac{\partial M}{\partial \mathscr{H}} = \chi$ magnetic susceptibility	$\dfrac{\partial M}{\partial T} = \alpha_M$ magnetocaloric effect	$\left.\begin{array}{l}\dfrac{\partial \mathscr{H}}{\partial T} = \dfrac{\alpha_M}{\chi} \\ \dfrac{\partial E}{\partial T} = \dfrac{p_P}{\chi_P}\end{array}\right\}$ thermal susceptibilities
Electric field E	Polarization $\mathscr{P}$	$\dfrac{\partial \mathscr{P}}{\partial E} = \chi_P$ diel. susceptibility	$\dfrac{\partial \mathscr{P}}{\partial T} = p_P$ pyroelectric effect	
Mechanic tension F	Deformation τ	$\dfrac{\partial \tau}{\partial F} = C_\tau$ elastic stiffness coef.	$\dfrac{\partial \tau}{\partial T} = \alpha_\tau$ thermal strains coefficient	$\dfrac{\partial F}{\partial T} = K_{FT}$ thermal stress coefficient
Temperature T	Entropy (enthalpy) $S\,(H)$	$T\dfrac{\partial S}{\partial T} = \left\{\dfrac{\partial H}{\partial T}\right\} = c_X$ thermal capacity, essential term in TA		

By making partial derivatives we obtain an extended number of thermal coefficients as listed in Table 1. Here we are merely concerned with the derivatives between the intensive (X) and the corresponding extensive (Y) parameters and the mixed derivatives with temperature as the essential coefficients for theoretical thermal analysis. The parameters which are kept constant during the derivation and which are usually marked as the subscripts of individual partial derivatives are, for the sake of simplicity, omitted. Some coefficients are evidently simplified when we assume real materials. The electromagnetic field and particularly the mechanical tension must be understood as tensors which may yield for an anisotropic material as many as six coefficients for each c_τ, α_τ and K_{FT}. Some interesting coefficients can also be obtained on the basis of interactions between non-thermal properties only, as e.g. electromagnetic field with mechanical tension (piezoelectric coefficient $\mathrm{d}\tau = \partial \mathscr{P}/\partial F$ or $= \partial\tau/\partial E^{22}$, magnetoelastic coefficient $C_M = \partial M/\partial F = \partial\tau/\partial\mathscr{H}$) and/or pressure with mole number (molar volume $\bar{V} = \partial\mu/\partial P$ or $= \partial V/\partial n$, change of concentration with pressure $V\, K_{nP} \cong \partial n/\partial P$ or $= \partial V/\partial\mu$), etc.

Following Table 1 we can derive a set of equations in analogy with the procedure given for volume by eqns. (12) and (14) suitable to describe thermodilatometry or differential pressure analysis and/or experiments carried out in sealed ampoules ($\mathrm{d}V = 0$). These relations describing the change of the selected extensive property Y as a function of the corresponding intensive parameter X and the temperature T then hold the form

$$n = \hat{n}(\mu, T) \qquad \mathrm{d}n = (\partial n/\partial\mu)_T\, \mathrm{d}\mu + K_{nT}\, \mathrm{d}T \tag{18}$$

$$M = \hat{M}(\mathscr{H}, T) \qquad \mathrm{d}M = \chi \mathrm{d}\mathscr{H} + \alpha_M\, \mathrm{d}T \tag{19}$$

$$\mathscr{P} = \hat{\mathscr{P}}(E, T) \qquad \mathrm{d}\mathscr{P} = \chi_P \mathrm{d}E + p_P\, \mathrm{d}T \tag{20}$$

$$\tau = \hat{\tau}(F, T) \qquad \mathrm{d}\tau = C_\tau\, \mathrm{d}F + \alpha_\tau\, \mathrm{d}T \tag{21}$$

These equations become essential for the respective thermogravimetric, thermomagnetic, thermodielectric and thermomechanical measurements under given experimental conditions.

In analogy with the well known form of entropy equation suitable to describe caloric measurements

$$\mathrm{d}S = \alpha_V V\, \mathrm{d}P - c_p/T\, \mathrm{d}T \tag{22}$$

we can distinguish four particular forms of investigations common in physical chemistry and physics

$\mathrm{d}Y = 0$	isolated (thermally closed) system	(e.g. $\mathrm{d}S = 0$ adiabatic or for eqn. (14) $\mathrm{d}V = 0$ isochoric)
$\mathrm{d}X = 0$	system under constant external field	(e.g. $\mathrm{d}P = 0$ isobaric)
$\mathrm{d}T = 0$	system at constant temperature	(e.g. $\mathrm{d}T = 0$ isothermal)
$\mathrm{d}T =$ const.	system under constant heating (TA)	(e.g. $\mathrm{d}T = \phi$ non-isothermal)

$$\left\{ \mathrm{d}Y,\ \mathrm{d}X,\ \mathrm{d}T \neq 0 \ \text{system out of control} \qquad \text{(e.g. undefined experimental condition)} \right\}$$

Equations (14) and (18)–(21) express the thermal development of *non-thermal (non-caloric) property* of the sample. In basic TA methods, however, we are usually concerned with the thermal development of *thermal (caloric) property* of the system which is essential to any calorimetric work. Thus we can derive the relations of the enthalpy-like term H upon a given intensive parameter X [compare eqns. (18)–(21)] and the temperature T in analogy with eqns. (13) and (15).

$$H = \hat{H}(\mu, \hat{S}(\mu, T)) \qquad \mathrm{d}H = (n - T K_{nT})\mathrm{d}\mu + c_\mu \, \mathrm{d}T \tag{23}$$

$$H = \hat{H}(\mathscr{H}, \hat{S}(\mathscr{H}, T)) \qquad \mathrm{d}H = (M - T\alpha_M)\mathrm{d}\mathscr{H} + c_\varkappa \, \mathrm{d}T \tag{24}$$

$$H = \hat{H}(E, \hat{S}(E, T)) \qquad \mathrm{d}H = (\mathscr{P} - T p_P)\mathrm{d}E + c_E \, \mathrm{d}T \tag{25}$$

$$H = \hat{H}(F, \hat{S}(F, T)) \qquad \mathrm{d}H = (\tau - T\alpha_\tau)\mathrm{d}F + c_F \, \mathrm{d}T \tag{26}$$

Chapter 4

THERMODYNAMICS OF SIMPLE PHASE TRANSFORMATIONS

In the preceding part we shown the thermodynamic picture of a heated system where no chemical reactions and structural transformations occur which, in fact, corresponds to the base line of respective TA records. Moreover, it demonstrates well the necessity of a proper definition of the set of intensive parameters to be chosen in accordance with the externally applied, so-called experimental conditions to achieve a successful description and classification of individual TA methods[1, 6, 12]. In our experiments with rising temperature, however, we are more concerned with the characterization of thermal effects which change the smooth course of the base line of a TA record. Such turns are usually caused by the process of phase transformation[26, 27], where a stable (or metastable) phase A is transformed into the other, thermally more stable phase B; or A with $\Phi(T_A, P_A, \mu_A, \mathscr{H}_A, E_A, F_A) \rightarrow$ B with $\Phi(T_B, P_B, \mu_B, \mathscr{H}_B, E_B, F_B)$. There arise two basic problems: (1) how to find the conditions of the two equilibrium phases and, (2) where and how one phase transforms into the other.

The principal condition of equilibrium is given by the minimum of the potential Φ ($\mathrm{d}\Phi = 0$) associated with the secondary conditions valid for all the extensive parameters, $\mathrm{d}Y_A + \mathrm{d}Y_B = 0$. It follows that such a system must be in thermal as well as mechanic and electromagnetic equilibrium, where $X_A = X_B = X_{eq}$. In other words, with a continuous change of temperature, the other intensive parameters must also change continuously [which is particularly important for the chemical potential μ as classically assumed for multicomponent systems]. With regard to the given couples of intensive variables T and X chosen in eqns. (18)–(22), we obtain for a single component system the equality

$$\Phi(X_A, T_A) = \Phi(X_B, T_B) \tag{28}$$

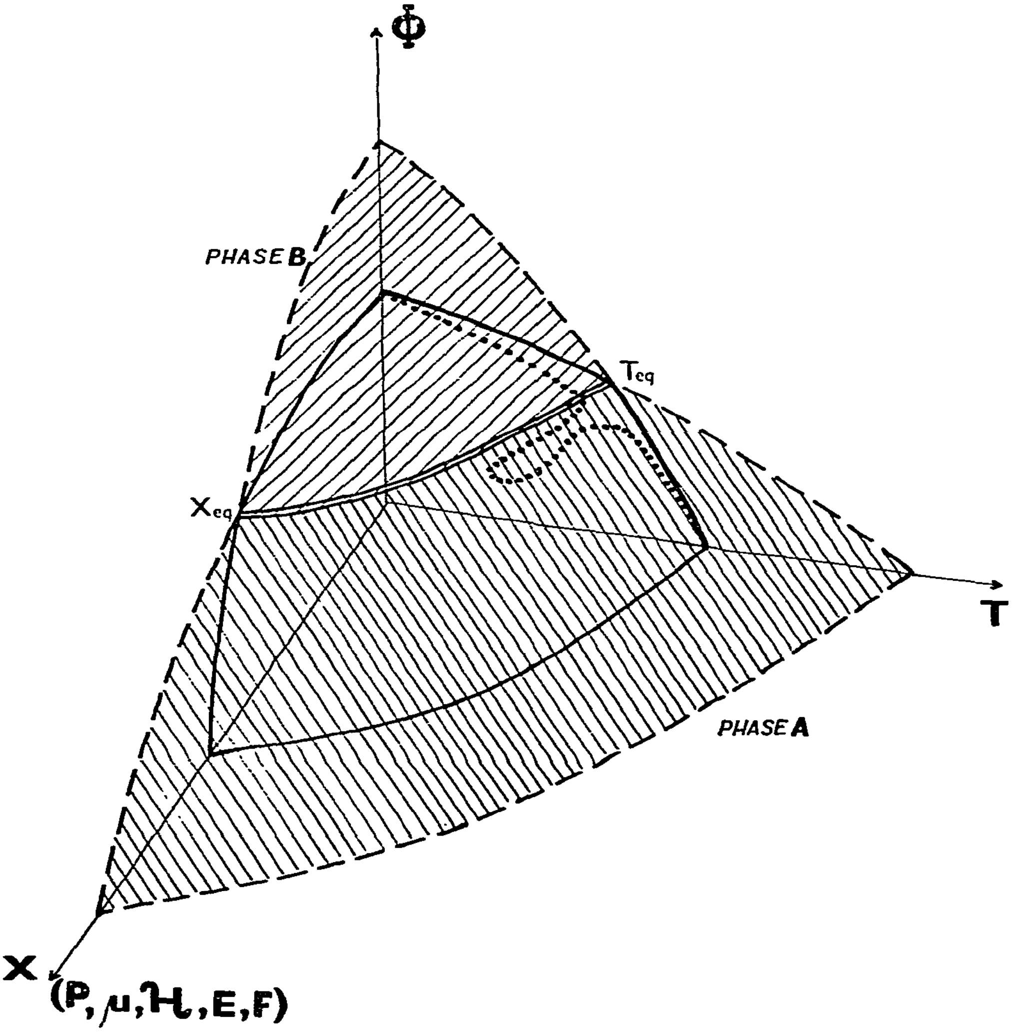

Fig. 4. Three-dimensional representation of the state of two phases (A and B) mutual relation. The equilibrium (eq) is described by the double solid line, which holds for the general thermodynamic potential $\Phi_A(T_A, X_A) = \Phi_B(T_B, X_B)$, see text.

(see Fig. 4) the solution of which are the curves $X = X(T)$ usually represented in the form of diagrams, P–T for liquids, μ–T for solid solutions, $\mathscr{H}$–T for ferromagnetics, E–T for dielectrics and F–T for mechanically stressed systems[25].

The conditions of a thermodynamic equilibrium do not put any limitation on the change of the derivative of the general potential with an intensive variable, $\partial\Phi/\partial X$, which may have in the different phases different values. As each phase represents here a homogeneous system and the coexistence of two phases, A and B, becomes discontinuous (i.e. a heterogeneous system defined as the sum $Y = \Sigma_i\ Y_i$), the two phases must differ by the value of at least one property, as, for instance, the density, specific heat, magnetization, etc. The discontinuity in $\partial\Phi/\partial X$ is thus most suitable for the classification of phase transformations and the characteristic value of X, at which the transformation occurs, is the equilibrium value of the given intensive

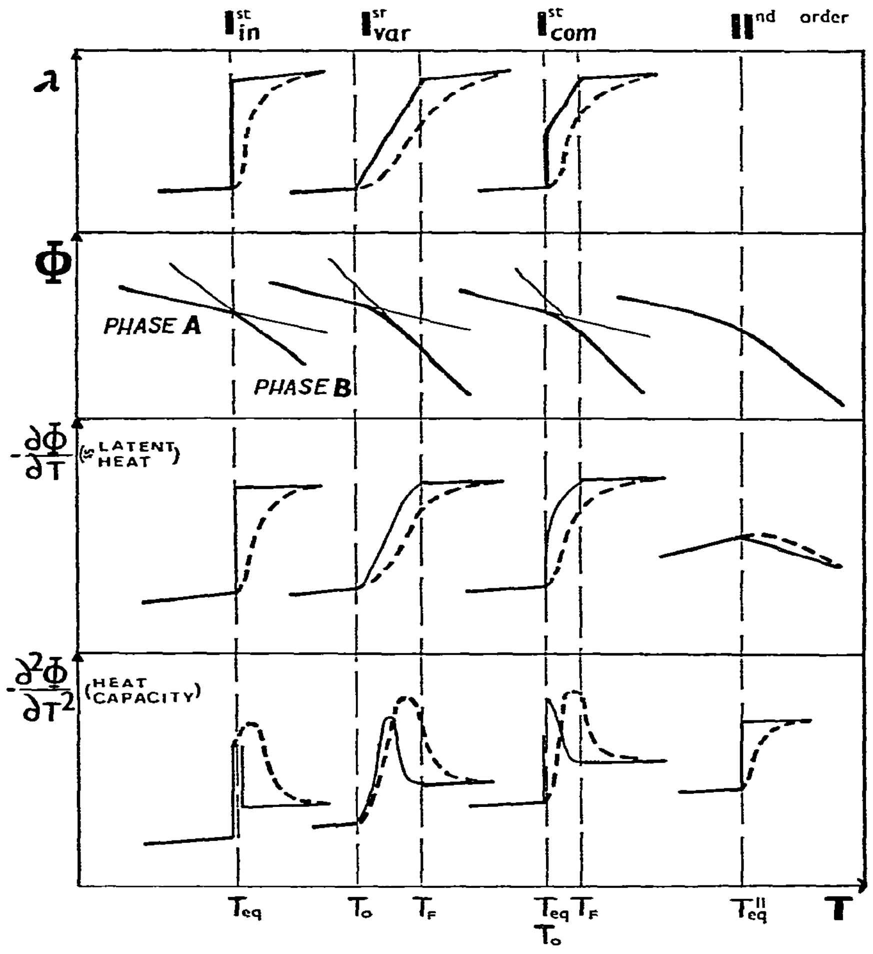

Fig. 5. Graphical illustration of possible types of phase transformation for the non-isothermal degree of transformation, λ, and the general thermodynamic potential, Φ, as a function of temperature. The underscripts in, var, com, eq, o and F mean invariant, variant, composed, equilibrium, initial and final, respectively and dashed line indicates actual "response" curves.

property, X_{eq}. From the viewpoint of TA the most interesting are the derivatives with temperature, see Fig. 5, as the caloric term $-SdT$ always takes part in any of the so far used forms of our potential Φ. This yields the discontinuity in entropy ΔS, which means that during this so called *first-order transformation* a certain amount of latent heat ($T\Delta S = \Delta H$) is always absorbed or generated. If the first derivative in Φ is continuous, at least the second derivative is stepwise showing the so-called *second-order transformations* (as also illustrated in Fig. 5) which are always accompanied by the change in the value of thermal capacity Δc_X. It follows that the thermophysical measurement of the enthalpy content is the principal and most general method of thermal analysis because it can detect any physico-chemical process. The most important result may be found in generalized Clausius–Clapeyron and Ehrnfest relations which are listed in Table 2[21, 25, 27]. The set of these relations is experimentally very useful as they reflect the alternation of externally applied parameters

TABLE 2

GENERALIZED CLAUSIUS–CLAPEYRON AND EHRNFEST RELATIONS

Balance condition	*First-order transformation*	*Second-order transformation*			
	$\left(\frac{\partial\Phi}{\partial X}A\right) - \left(\frac{\partial\Phi}{\partial X}B\right) \neq 0$	$= 0;\ \left(\frac{\partial^2\Phi A}{\partial X^2}\right) - \left(\frac{\partial^2\Phi B}{\partial X^2}\right) \neq 0$			
Term $(Y_B - Y_A)\,\mathrm{d}X$	for $(S_B - S_A)\,\mathrm{d}T$	$\lim\limits_{T \to T_{eq}} \left(\frac{\Delta Y}{\Delta H}\right) \to 0 \equiv >$	$\frac{(\partial\Delta Y/\partial T)_X}{(\partial\Delta H/\partial T)_X} \equiv >$	$-\frac{(\partial\Delta Y/\partial X)_T}{(\partial\Delta Y/\partial T)_X} \equiv >$	change of thermal capacity, ΔC_X
$(V_B - V_A)\,\mathrm{d}P$	$\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{\Delta V}{\Delta H}T_{eq}$	$\frac{\mathrm{d}T}{\mathrm{d}P} = V\frac{\Delta\alpha_V}{\Delta C_p}T_{eq}$		$= \frac{\Delta\beta}{\Delta\alpha_V}$	$\Delta C_p = TV\frac{(\Delta\alpha_V)^2}{\Delta\beta}$
$(n_B - n_A)\,\mathrm{d}\mu$	$\frac{\mathrm{d}T}{\mathrm{d}\mu} = \frac{\Delta n}{\Delta H}T_{eq}$	$\frac{\mathrm{d}T}{\mathrm{d}\mu} = \frac{\Delta K_{nT}}{\Delta C_\mu}T_{eq}$		$= -\frac{\Delta(\partial n/\partial\mu)}{\Delta K_{nT}}$	$\Delta C_\mu = -T\frac{(\Delta K_{nT})^2}{\Delta(\partial n/\partial\mu)}$
$(M_B - M_A)\,\mathrm{d}\mathscr{H}$	$\frac{\mathrm{d}T}{\mathrm{d}\mathscr{H}} = \frac{\Delta M}{\Delta H}T_{eq}$	$\frac{\mathrm{d}T}{\mathrm{d}\mathscr{H}} = \frac{\Delta\alpha_M}{\Delta C_\chi}T_{eq}$		$= -\frac{\Delta\chi}{\Delta\alpha_M}$	$\Delta C_\chi = -T\frac{(\Delta\alpha_M)^2}{\Delta\chi}$
$(\mathscr{P}_B - \mathscr{P}_A)\,\mathrm{d}E$	$\frac{\mathrm{d}T}{\mathrm{d}E} = \frac{\Delta\mathscr{P}}{\Delta H}T_{eq}$	$\frac{\mathrm{d}T}{\mathrm{d}E} = \frac{\Delta p_P}{\Delta C_E}T_{eq}$		$= -\frac{\Delta\chi_P}{\Delta p_P}$	$\Delta C_E = -T\frac{(\Delta p_P)^2}{\Delta\chi_P}$
$(\tau_B - \tau_A)\,\mathrm{d}F$	$\frac{\mathrm{d}T}{\mathrm{d}F} = \frac{\Delta\tau}{\Delta H}T_{eq}$	$\frac{\mathrm{d}T}{\mathrm{d}F} = \frac{\Delta\alpha_\tau}{\Delta C_F}T_{eq}$		$= -\frac{\Delta C_\tau}{\Delta\alpha_\tau}$	$\Delta C_F = -T\frac{(\Delta\alpha_\tau)^2}{\Delta C_\tau}$

in terms of the stepwise changes of experimentally measurable extensive quantities.

During a TA experiment, the temperature is gradually raised so that the whole transformation does not have time to proceed instantly at a single temperature, T_{eq}. Thus, it is of great importance to determine the temperature dependence of ΔH including the simultaneous effect of the second intensive parameter X, i.e. $\Delta H = \widehat{\Delta H}(X, \widehat{\Delta S}(X, T))$. Making partial derivatives we can proceed according to eqn. (13) to obtain

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}T} = \left(\Delta Y - T\frac{\partial \Delta Y}{\partial T}\right)\frac{\partial X}{\partial T} + \Delta c_X \tag{29}$$

By the substitution for $\partial T/\partial X$ from Table 2 we have

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}T} = \Delta c_X + \frac{\Delta H}{T} - \frac{\partial \ln \Delta Y}{\partial T}\Delta H \tag{30}$$

where ΔY equals respective ΔV, Δn, ΔM, $\Delta \mathcal{P}$ and $\Delta \tau$, according to the type of transformation listed in Table 2. In the sense of Fig. 4, eqn. (24) expresses the shift of ΔH along the transformation boundary shown as the double-solid line. This equation is most often used for the simplified description of sublimation and/or melting $(X = P, \Delta Y = \Delta V \gg)$, where the second and the last term of the right-hand side of eqn. (30) cancel each other yielding $\mathrm{d}\Delta H/\mathrm{d}T \cong \Delta c_P$. If multiple effects of $\partial X_1/\partial T$, $\partial X_2/\partial T \cdots$ are assumed, the last two terms in eqn. (24) reappear for each new ΔY.

According to the preceding scheme, we can derive the required increase of any non-thermal property $\mathrm{d}X_1$ to balance the equilibrium of transformation if the other non-thermal property is changed by $\mathrm{d}X_2$, i.e. $\mathrm{d}X_1/\mathrm{d}X_2 = X_{eq}\Delta Y_2/\Delta Y_1$ (compare Table 2), as well as to find out the non-thermal dependence of any ΔY in analogy with eqns. (29) and (30) $[\Delta F = \widehat{\Delta F}(X_1, \widehat{\Delta Y}(X_1, X_2))]$ which, of course, falls beyond the normal TA practice.

It should be emphasized that all preceding equations are correct only if the experimental conditions are well defined and restricted to given values. If one of the externally applied parameters is out of control, the process of transformation becomes undetermined within our measures which can be graphically illustrated by the dotted line in Fig. 4. This is particularly important for the so-called *self-generating conditions* which are often applied in terms of non-constant pressure P and/or partial pressure p_0 $(\cong \mu)$ usually found when the dissociating sample is placed in a partly sealed crucible or when applying undefined vacuum. Similar effects may result from a free motion of the sample, which is suspended in a non-homogeneous electromagnetic field.

Chapter 5

DESCRIPTION OF THEORETICAL AND EXPERIMENTAL CURVES

The object of the majority of TA measurements is to find out and to describe the effects which occur during the heating of the material under investigation. The analyses of TA data are thus directed to establishing the relation between the experimentally obtained curves and the actual course of our thermodynamic process, compare eqns. (1). Let us focus our attention to the simple one-component transformation, see eqn. (28), $n_A \rightarrow n_B$. For the sake of simplicity the set of eqns. (1) may be reduced to

$$n_A = n_A(t) \qquad (\text{or } -n_B = n_B(t))$$
$$T = \hat{T}(t)$$

where, however, we intentionally neglect the energetics of A–B interface formation. As the transformation cannot take place at temperature T_{eq} infinitesimally fast, it is necessary to define the progress of transformation by a dimensionless parameter ξ, called the *true degree of transformation*[28] (or generally conversion)

$$\xi = n_A/(n_A + n_B) \quad \text{or} \quad (1 - \xi) = n_B/(n_B + n_A) \tag{31}$$

where n_A and n_B are the instantaneous mole numbers of the respective phases. The choice of non-dimensional parameters normalized within the interval (0,1) is in accordance with ordinary kinetic convenience.

The practice of TA measurements is to collect all information on the instantaneous state of the sample and on the time progress of the change of its state on the basis of a certain physical property of the sample, which is experimentally measured and chosen to represent the state of the sample. This property must be evidently dependent on the quantity of the sample, i.e. it must be an extensive parameter characterizing the material investigated such as enthalpy content, density, weight, length, volume, magnetization, polarization, mechanic deformation, possibly weight loss and/or amount of volatilized component, as will also be shown later on. The experimentally detected course of the process is thus best described by the *effective degree of transformation*, λ, defined on the basis of an experimentally measured property Z by the equation[28, 29]

$$\lambda = \frac{Z - Z_0}{Z_F - Z_0} \tag{32}$$

where Z_0 is the initial and Z_F is the final (ultimate) value of Z. One of the principal premises of TA is the identity between ξ and λ which is usually accepted without proofs as proportionality

$$\xi = K_\lambda \lambda \tag{33}$$

Hence it is interesting to compare the thermal development of both these degrees. We can assume that the measured property is proportional to an extensive parameter of the system, $Z = K_Y Y$. For the constant mole number of the system $(n_A + n_B) =$ const. we have by eqns. (31)–(33)

$$\frac{d\xi}{dT} = \frac{dn_A}{dT}\left(\frac{1}{n_A + n_B}\right) = K_\lambda \frac{d\lambda}{dT} = K_\lambda \frac{dY}{dT}\left(\frac{1}{Y_F - Y_0}\right) \tag{34}$$

For the total change ($\Delta Y = Y_F - Y_0$) the proportionality coefficient K_λ keeps a certain value in accordance with the corresponding thermal coefficients in Table 1, e.g.

$$K_\lambda = \frac{K_{nAT}}{(\partial Y/\partial T)} \frac{\Delta Y}{(n_A + n_B)} \tag{35}$$

which is approximately constant for a narrow temperature interval of the process duration.

The experimental task of TA measurements is the transformation of experimentally recorded signal $Z_{\text{meas.}}$ to the true value of measured physical property Z. For most TA apparatus there exists a direct or almost direct proportionality in the form

$$Z = Z_{\text{meas.}} K_{\text{app.}} \tag{36}$$

where $K_{\text{app.}}$ is known as *apparatus constant* to be established by calibration. This is adequate, for example, for weight measurement of magnetization, compensation heat flux measurements in DSC or length measurements in thermodilatometry. For some special instrumentation, however, the proportionality (36) reaches the form of a more complicated function as[30-32]

$$Z = \hat{Z}(Z_{\text{meas.}}, \dot{Z}_{\text{meas.}}, T, \dot{T}, P, \dot{P}, K_{\text{app.}}, \cdots) \tag{37}$$

the typical example of which is the case of DTA[13], DCC or DPA.

Having determined Z we can evaluate the so-called reaction kinetics from the time-dependence of our process using $\lambda = \hat{\lambda}(t)$ and $T = \hat{T}(t)$. The kinetics of the

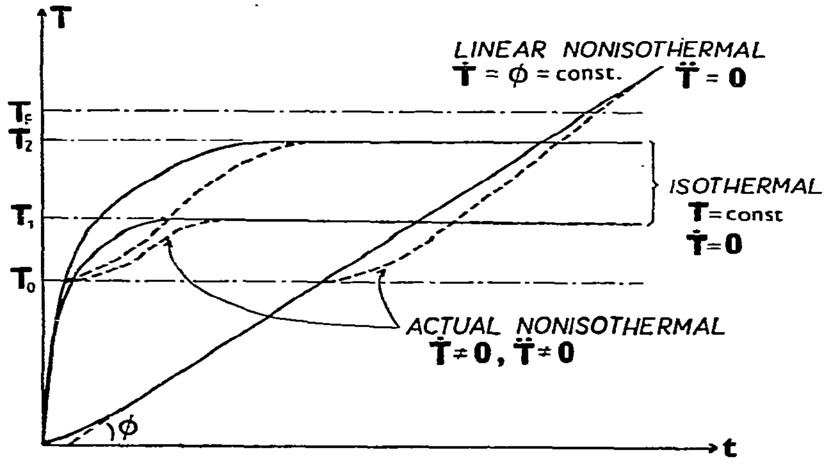

Fig. 6. Exemplification of the most common methods of thermal treatments. Solid lines show the idealized course of temperature while dashed lines express the actual course of temperature due to the heat absorbed (assuming an endothermic process). Dashed-and-dott lines specify the characteristic temperatures, compare Fig. 5.

simple first-order transformation can be expressed by two basic constitutive equations[33, 34]

$$\begin{aligned} \dot{\lambda} &= \hat{\dot{\lambda}}(\lambda, T) \\ \dot{T} &= \hat{\dot{T}}(\lambda, T) \end{aligned} \qquad (38)$$

They are practically evaluated in three different ways, see Fig. 6,

(i) *isothermal kinetics* assuming

$$\begin{aligned} T &= \text{constant (and } \dot{T} = 0) \\ \dot{\lambda} &= \mathrm{f}(\lambda)\,\mathrm{k}(T) \end{aligned} \qquad (39)$$

where $\mathrm{f}(\lambda)$ and $\mathrm{k}(T)$ are functions called the model relation and the rate constant respectively being dependent on the separable variables λ and T only.

(ii) *linear non-isothermal kinetics* assuming[35]

$$\begin{aligned} \dot{T} &= \phi = \text{constant (i.e. } T = T_{t=0} + \phi\, t) \\ \dot{\lambda} &= \mathrm{f}'(\lambda, T)\mathrm{k}'(T, \phi) \cong \mathrm{f}(\lambda)\mathrm{k}(T)\phi \end{aligned} \qquad (40)$$

where ϕ is the constant heating rate.

(iii) *actual* (*nonlinear*) *kinetics*, where eqns. (38) are to be applied without simplifications. Here we are not able to separate individual parameters as in eqns. (39) and (40)[29, 36]. Simple numerical determinations of ordinary kinetic parameters, e.g. activation energy which is popular in isothermal and linear non-isothermal kinetics, are not possible in this complex case (iii).

Let us investigate in greater detail the speciality of a thermoanalytical description of an actual "kinetic" curve, particularly if the process $n_A \rightarrow n_B$ is not thermodynamically to take place at a point temperature T_{eq} but within a certain temperature interval $T_0 - T_F$, where phases A and B can coexist. The terminal state of the system may thus become temperature dependent due to the change of equilibrium with temperature. This effect is important in all non-isothermal studies and ought to be incorporated into the calculation. Considering eqn. (32), where the value Z_F reaches evidently its maximum value, we can imagine that this equation is composed of two parts: kinetics and equilibrium. Accordingly, we may introduce a new term[28] called the *advancement of equilibrium* of the process λ_{eq} defined as

$$\lambda_{eq} = \frac{Z_F - Z_0}{Z_{TF} - Z_0} \qquad (41)$$

where Z_T is the terminal equilibrium value of Z for the given temperature T, compare Fig. 6, while Z_F is its ultimate value reached at the end of whole process evidently independent of temperature. This term, in fact, describes the propagation of equilibrium under the conditions of an infinitesimally slow temperature increase. Combining eqns. (41) and (32), we obtain[28]

$$\lambda = \lambda_{eq} \frac{Z - Z_0}{Z_T - Z_0} = \lambda_{eq}\, \alpha \qquad (42)$$

where α is the *isothermal degree of transformation* defined in accordance with ordinary isothermal studies. It follows that λ can be understood as the *non-isothermal degree of transformation* containing all complex information about the process normally provided by a set of α determined for a series of $T(Z_{TF})$ within the interval $T_0(Z_0)$ to $T_F(Z_F)$ (compare Fig. 6).

From the point of view of the equilibrium background of the process we can classify the first order process into invariant (single temperature T_{eq}), *variant* (temperature interval T_0–T_F) and *combined* (where the process proceeds partly as invariant and partly as variant), as it is graphically demonstrated in Fig. 5, where dashed lines show the actual course of the process owing to kinetic retardation.

For TA practice there follow important considerations^{29}.

(i) For invariant processes, where $\lambda = \alpha$, it is not necessary to take any precaution for the curves interpretation.

(ii) For variant and combined processes we should either use the truly non-isothermal degree of transformation, which is not common as yet, or to employ enough high heating rates which enable us to evaluate the major part of TA curve above T_F, i.e. above two-phase region where again $\lambda = \alpha$.

(iii) For the description of the second-order processes it is only convenient to use the derivative of the experimentally obtained curve which can then be treated in the same way as first-order processes (compare Fig. 5) last column, i.e. the transformation of the break with no inflections to the step with one inflection point.

Let us concentrate our attention on Fig. 5, which is instructive enough to find analogy between the graphical demonstration of increasing derivatives in Φ with the kind of experimental curves and their derivatives (compare Fig. 1). With the gradual transition from lower to higher derivatives, the curve changes its character; it be-

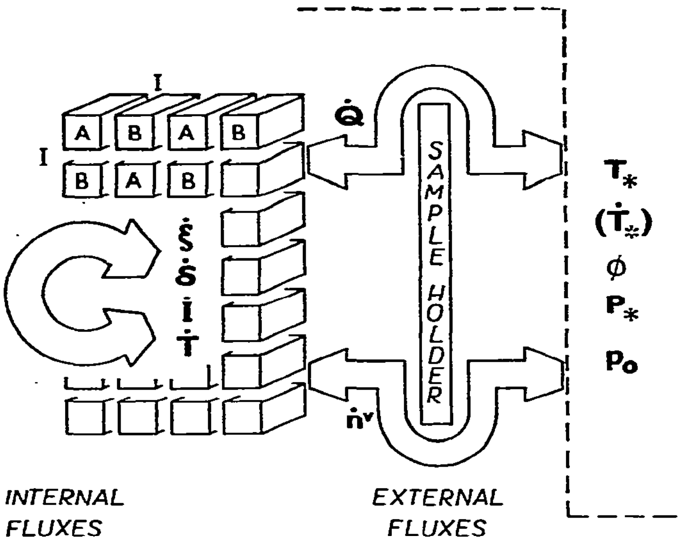

Fig. 7. Actual conditions of a heterogeneous system during a TA experiment, where externally applied fields (compare Fig. 3) are absent but where we consider internal fluxes across the phase A and B interface I.

comes mathematically more distinguishable as the number of inflection points and extremes increase[9, 12, 37]. From a certain stage, however, the effect cannot be quantitatively evaluated as, for example, oscillation (see Fig. 1), defined by three inflection points. Therefore, it is important to know the proper form of any experimental curve for a given TA instrumentation and to distinguish its electronically derived analogue to make possible a correct determination of a *true ("kinetic") curve.*

Chapter 6

ACTUAL CONDITIONS OF DISSOCIATION PROCESSES

So far we have not considered the content of a volatile component (v) in our sample, i.e. the transformation well known as dissociation process and often encountered in TA practice. Let us imagine our system in the form illustrated in Fig. 7. Two basic external fluxes take place between the sample and the surroundings: $\dot{Q}$ (heat flux) and $\dot{n}^{\mathrm{v}}$ (mass flux). The overall behaviour of the system can be expressed on the basis of the energy and mass conservation law, compare eqn. (2), as already shown in our previous works[4-6]

$$\dot{U} = \dot{Q} - P\dot{V} + \mu_{*}\dot{n}^{\mathrm{v}} \tag{43}$$

which, in fact, is the flux formulation of the first law of thermodynamics. As the enthalpy is a more convenient parameter in TA measurements, then

$$\dot{H} = \dot{Q} + V\dot{P} + \mu_{*}\dot{n}^{\mathrm{v}} \tag{44}$$

where H is the system enthalpy which for our heterogeneous system composed of phases A and B holds as the sum of H_{A} and H_{B}. In accordance with eqn. (13), we have to assume H as the state function of S, P and n, i.e. $H = \hat{H}(P, n, \hat{S}(P, n, T))$, so that

$$\dot{H}_{\mathrm{A}} = V_{\mathrm{A}}\dot{P} + \bar{H}_{\mathrm{A}}\dot{n}_{\mathrm{A}} + T\left[-\frac{\partial V_{\mathrm{A}}}{\partial T}\dot{P} - \frac{\partial \mu_{\mathrm{A}}}{\partial T}\dot{n}_{\mathrm{A}} + \frac{\partial S}{\partial T}\dot{T}\right] \tag{45}$$

where the superposed strip describes molar values for the given extensive property $(\bar{Y})$. By combining with $\dot{H}_{\mathrm{B}}$ we get

$$\begin{aligned}\dot{H} = (V_{\mathrm{A}} + V_{\mathrm{B}})\dot{P} + (\bar{H}_{\mathrm{A}} - T\bar{S}_{\mathrm{A}})\dot{n} + (\bar{H}_{\mathrm{B}} - T\bar{S}_{\mathrm{B}})\dot{n} - T(\alpha_{V\mathrm{A}} + \alpha_{V\mathrm{B}})\dot{P} +& \\ + (c_{p\mathrm{A}} + c_{p\mathrm{B}})\dot{T}&\end{aligned} \tag{46}$$

if $(V_{\mathrm{A}} + V_{\mathrm{B}}) = V$, $\bar{H}_{\mathrm{A}} - T\bar{S}_{\mathrm{A}} = \bar{G}_{\mathrm{A}} = \mu_{\mathrm{A}}$ and $P_{*} = P = \text{const.}$, i.e. $\dot{P} = 0$, we have by eqn. (44)

$$\dot{Q} = (c_{p\mathrm{A}} + c_{p\mathrm{B}})\dot{T} + \mu_{\mathrm{A}}\dot{n}_{\mathrm{A}} + \mu_{\mathrm{B}}\dot{n}_{\mathrm{B}} - \mu_{*}\dot{n}^{\mathrm{v}} \tag{47}$$

which can be considered as the basic relation of our system. However, there arises the problem of how to treat the terms $\mu\dot{n}$ in an understandable enough way. Therefore, let us use the molar values[4] but related to the sum of conservative components (superscript c) as introduced by Holba as a convenient mean for the description of non-stoichiometry[38]. Hence assuming the transformation of the type

$$\mathrm{ijv(A)} \rightarrow \mathrm{ij(B)} + \mathrm{v}\uparrow\ (*) \qquad (48)$$

where i and j are two conservative components of phases A and B and v is the volatile component (superscript v). For $n^{\mathrm{c}} = \Sigma_{\mathrm{i} \neq \mathrm{c}}\, n^{\mathrm{i}} = n^{\mathrm{i}} + n^{\mathrm{j}}$ we have for example $c^{\mathrm{m}}_{p\mathrm{A}} = c_{p\mathrm{A}}/n^{\mathrm{c}}_{\mathrm{A}}$, $N^{\mathrm{i}}_{\mathrm{A}} = n^{\mathrm{i}}_{\mathrm{A}}/n^{\mathrm{c}}_{\mathrm{A}}$, $N^{\mathrm{i}} = n^{\mathrm{i}}/n^{\mathrm{c}}$, etc. These parameters are stable regardless of the mass lost during dissociation except for the volatile part. Introducing the degree of transformation ξ which expresses the portion of phase A converted to phase B related again to the sum of conservative components for any extensive parameter, we have[4, 6]

$$Y^{\mathrm{m}} = Y^{\mathrm{m}}_{\mathrm{A}}(1 - \xi) + Y^{\mathrm{m}}_{\mathrm{B}}\, \xi \qquad (49)$$

where

$$\xi = n^{\mathrm{c}}_{\mathrm{B}}/n^{\mathrm{c}} = 1 - n^{\mathrm{c}}_{\mathrm{A}}/n^{\mathrm{c}} \qquad (50)$$

Assuming, for example, the fluxes in the form of $\dot{n}^{\mathrm{i}} = \Sigma \dot{N}^{\mathrm{i}}_{\mathrm{A}} n^{\mathrm{c}}_{\mathrm{A}} + \Sigma N^{\mathrm{i}}_{\mathrm{A}} \dot{n}^{\mathrm{c}}_{\mathrm{A}}$ (e.g. $\dot{n}^{\mathrm{v}}_{\mathrm{A}} = \dot{N}^{\mathrm{v}}_{\mathrm{A}} n^{\mathrm{c}}_{\mathrm{A}} + N^{\mathrm{v}}_{\mathrm{A}} \dot{n}^{\mathrm{c}}_{\mathrm{A}}$) together with eqns. (49) and (50), we obtain after some algebraic manipulation[4]

$$\begin{aligned} \dot{Q}/n^{\mathrm{c}} &= c^{\mathrm{m}}_{p\mathrm{A}}(1 - \xi)\dot{T} + c^{\mathrm{m}}_{p\mathrm{B}}\, \xi \dot{T} + (1 - \xi) \sum \mu^{\mathrm{i}}_{\mathrm{A}} \dot{N}^{\mathrm{i}}_{\mathrm{A}} + \xi \sum \mu^{\mathrm{i}}_{\mathrm{B}} \dot{N}^{\mathrm{i}}_{\mathrm{B}} + \\ &+ (1 - \xi)\, \mu_* \dot{N}^{\mathrm{v}}_{\mathrm{A}} + \xi\, \mu_* \dot{N}^{\mathrm{v}}_{\mathrm{B}} + [\sum \mu^{\mathrm{i}}_{\mathrm{B}} N^{\mathrm{i}}_{\mathrm{B}} - \sum \mu^{\mathrm{i}}_{\mathrm{A}} N^{\mathrm{i}}_{\mathrm{A}} + \mu_*(N^{\mathrm{v}}_{\mathrm{B}} - N^{\mathrm{v}}_{\mathrm{A}})]\, \dot{\xi} \qquad (51) \end{aligned}$$

The first three lines of this equation describe the thermal development of the states of the individual phases A and B and (*) while the last line expresses the entire change occurring due to the transformation of A into B. For a better explanation of its physical meaning, let us rewrite eqn. (51) in the following form[4].

$$\begin{aligned} &[K^{\mathrm{cn}}_{\mathrm{s}}(T_* - T) + K^{\mathrm{rd}}_{\mathrm{s}}(T^4_* - T^4)]/n^{\mathrm{c}} = && \text{(a)} \\ &= (c^{\mathrm{m}}_{p\mathrm{A}} + \Delta c^{\mathrm{m}}_{p}\, \xi)\dot{T} + && \text{(b)} \\ &+ (1 - \xi)(\mu^{\mathrm{v}}_{\mathrm{A}} - \mu^{\mathrm{v}}_*)\dot{N}^{\mathrm{v}}_{\mathrm{A}} + \xi(\mu^{\mathrm{v}}_{\mathrm{B}} - \mu^{\mathrm{v}}_{\mathrm{A}})\dot{N}^{\mathrm{v}}_{\mathrm{B}} + && \text{(c)} \qquad (52) \\ &+ (\Delta H_{\mathrm{ef}} + \Delta N^{\mathrm{v}} \mu_*)\dot{\xi} + && \text{(d)} \\ &+ (\Delta \mu^{\mathrm{i}} - \Delta \mu^{\mathrm{j}})\dot{\delta} && \text{(e)} \end{aligned}$$

where the individual lines describe the heat consumption due to:

(a) specific heat flux between the surroundings and the sample, where $K^{\mathrm{cn}}_{\mathrm{s}}$ and $K^{\mathrm{rd}}_{\mathrm{s}}$ are the sample heat transfer coefficients for conduction and radiation;

(b) the change of the system temperature, where Δc_p is the difference between the specific heats of the initial phase A and product phase B;

(c) the change of the content of the volatile component in respective phases (called *stoichiometry*);

(d) the formation of product phase B (where $\Delta H_{\mathrm{eff.}}$ is the effective enthalpy change) including the specific loss of the volatile component (ΔN^{v}) by dissociation taking place during A → B transformation;

(e) the redistribution of conservative components between the phases often called phase separation, where $\Delta\mu^{\mathrm{i}} = \mu^{\mathrm{i}}_{\mathrm{B}} - \mu^{\mathrm{i}}_{\mathrm{A}}$ and δ is a new parameter called *extent of phase separation* (normalized 0-δ-0) by equation $\xi(N^{\mathrm{i}} - N^{\mathrm{i}}_{\mathrm{B}}) = (1 - \xi)(N^{\mathrm{i}}_{\mathrm{A}} - N^{\mathrm{i}}) = \delta$.

This analysis shows that this system must also be described by help of δ besides the previously introduced ξ. Furthermore, it is worth noting that each mass flux is diffusion controlled[39], i.e. is carried out across the interface (I) the area of which must also be introduced to our consideration as a necessary parameter describing, in fact, the energetics of phase A and B discontinuity. From this viewpoint, the set of constitutive equations (38) for this heterogeneous system takes up the form[39, 40]

$$\begin{aligned}
\dot{\xi} &= \hat{\dot{\xi}}(\xi, \delta, I, T)\\
\dot{\delta} &= \hat{\dot{\delta}}(\xi, \delta, I, T)\\
\dot{I} &= \hat{\dot{I}}(\xi, \delta, I, T)\\
\dot{T} &= \hat{\dot{T}}(\xi, \delta, I, T),
\end{aligned} \tag{53}$$

where $\dot{I}$ is bounded with ξ, δ and T by nucleation-growth equation which is usually indicated in the form[29, 36, 39]

$$\dot{I} = \hat{F}_{\mathrm{nucl.}}(\xi, \delta, T)\,\hat{F}_{\mathrm{grow}}(\xi, \delta, T) \tag{54}$$

Equation (54) is well known in the simplified shape of Kolgomorov–Johnson–Mehl–Avrami–Yerofeev equation[3, 36], where the parameter δ is not considered and the course of T is idealized ($\dot{T} = 0$ or $\dot{T} = \phi$).

Equation (52), although having a rather small practical applicability, well demonstrates the complex behaviour of a heterogeneous system and possible interconnections between the individual parameters. It can be seen that the specific properties of such a system can be investigated by, for example, weight loss (TG) and/or evolved gas (EGD) measurements (ΔN^{v}); compensation calorimetry (DSC) and enthalpiometry ($\Delta H_{\mathrm{eff.}}$, $\dot{T} = \phi = \mathrm{const.}$), Calvet microcalorimetry (DCC) and other spontaneous heat flux measurements ($\dot{Q}$, $\dot{T} \neq \mathrm{const.}$)[32, 37], direct TA ($T$) and its derived techniques[32, 37] as DTA measuring the temperature difference $\Delta T = (T - T_{\mathrm{reference}})$ or even possibly high-temperature X-ray diffraction (δ). This approach also yields the virtually new parameter δ as an entire property of a multicomponent heterogeneous system[39, 40] which, for advanced kinetic studies, ought to be incorporated into the calculation. Consequently, for variant processes proceeding in two-phase region the values of ξ and δ again contain the equilibrium parts[40], ξ_{eq} and δ_{eq}, compare eqn. (41).

For the actual interpretation of TA curves, Holba[6] thoroughly analyzed the relations between the change of a measured extensive property Z and the state of the sample. For the transformation of the type eqn. (48) he assumes the state of the sample to be dependent upon the degree of conversion ξ [eqn. (50)], temperature T, pressure P, partial pressure of volatile components p_o^v, total chemical composition $N^i = n^i/n^c$ and composition of product condensed phase B, N_B^i, i.e. $Z = \hat{Z}(T, P, p_o^v, N^i, N_B^i)$. Using eqn. (49) for N^i and the derived derivative for $\dot{N}_B^i$ we can write for the rate of the change of a measured extensive property $\dot{Z}$[6]

$$\dot{Z} = n^c \left\{ \left[\Delta Z^c + \sum \frac{\partial Z_A^i}{\partial N_A^i} \frac{N^i - N_B^i}{1 - \xi} \right] \dot{\xi} + \xi \sum \left(\frac{\partial Z_B^c}{\partial N_B^i} - \frac{\partial Z_A^c}{\partial N_A^i} \right) \dot{N}_B^i + \right.$$

$$\left. + \frac{\partial Z^c}{\partial T} \dot{T} + \frac{\partial Z^c}{\partial P} \dot{P} + \frac{\partial Z^c}{\partial p_o^v} \dot{p}_o^v + \cdots + \frac{\partial Z^c}{\partial X} \dot{X} \right\} n^c \qquad (55)$$

where $Z^c = Z/n^c$ and X mean, in accordance with the above symbolic, any additional intensive parameter varied from the surroundings. The term $\Delta Z^c = Z_A^c - Z_B^c$ is the integral change of Z^c due to the transformation. The following term which is also multiplied by $\dot{\xi}$ is of similar meaning as the extent of phase separation in eqn. (52e). The primitive proportionality $\dot{N}^v = n^c \Delta n^{vc} \dot{\xi}$, often used in TG, holds, however, in the case of daltonides only, i.e. the constant stoichiometry of phase A and B. For a practical use of eqn. (55) it is necessary to assume that the values ΔZ^c and $\partial Z/\partial X$ are not constant but dependent upon the state of the sample. To express their instantaneous values, it is possible to employ Taylor's expansion in the vicinity of equilibrium points of the transformation[6], e.g. $T = T_* + \Delta T$, $p_o^v = p_* + \Delta p^v$, etc., where ΔT and Δp^v have the meaning of the deviation of the sample temperature or partial pressure from those in the surroundings (*).

Chapter 7

DISCUSSION

The importance of thermodynamic relations as elementary rules to be applied in theoretical TA has already been stressed in an earlier review[3]. The present extension with the heating rate as an independent parameter and, particularly, the inclusion of electromagnetic and mechanoelastic measurements comes within the theoretical scope of TA description and is also required with respect to the individual methods classification although, for illustrative purposes, it is still idealized.

It is the matter of mathematical manipulation to extend the above two-parameter description, see Chapter 4, by additional parameters, which is most often P alike always accounted T. For instance, by a mere combination of individual terms in eqns. (23)–(26), we can achieve a generalized relation for H in the form of $H = \hat{H}(P, X, \hat{S}(T, P, X))$.

$$dH = V(1 - T\alpha_v)dP + (Y - T\alpha_x)dX + C_p dT \qquad (56)$$

This equation clearly illustrates the possible interdependence of externally controlled parameters. It can be seen that the originally used symbols of heat capacities, as exhibited by eqns. (23)–(26) and Table 2, and unusually defined under either constant μ, $\mathscr{H}$, E or F, may now be identified with the classical C_p, compare eqn. (13). An analogous result can be reached for the generalized Clausius–Clapeyron equation (Table 2) using the plausible extension to three- or multi-variable relations.

Attention should now be paid to the possibility of practical utilization of the previously listed equations. Above all, it may be the direct numerical extraction or tabulation of the standard enthalpy and/or free energy changes. By approximating the material coefficients in eqn. (56) as, for example, $\alpha_x = a_x + b_x T$ and the heat capacity as $Cp = a_c + b_c T + c_c/T^2$, and after substitution and integration we obtain

$$\Delta H = \Delta H_0 + \Delta V(1 - \Delta a_v T^2/2 - \Delta b_v T^3/3)(P - P_0) +$$

$$+ (\Delta Y - \Delta a_x T^2/2 - \Delta b_x T^3/3)(X - X_0) +$$

$$+ [\Delta a_c T - \Delta b_c T^2/2 - \Delta c_c/T]_{T_0}^{T} \qquad (57)$$

or, for $\Delta\Phi = \Delta H - T\Delta S$, the last term of the right-hand side of eqn. (57) being altered to

$$[\Delta a_c T(1 - \ln T) + \Delta b_c T - \Delta c_c/2T^2]_{T_0}^{T}.$$

These functions are not in a sufficiently convenient form for standardization[*] nor does the second term on the right-hand side of eqn. (57) have any applicability except in the special determination of boundary curves in electromagnetic or mechano-elastic system, cf. eqn. (28). Moreover, the partial derivative of Φ with respect to n does not provide the convenient parameter μ, so useful in the standard description of equilibria[**]. Hence, let us restrict our attention to the ordinary ΔH and ΔG functions and their most frequent use when constructing phase diagrams by the direct determination of either characteristic temperatures or the heats of fusion for a given composition x. For instance, modifying the Clausius–Clapeyron equation into the form of the Le Chatelier–Schrederer equation

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[*] The choice of standard state is solely a matter of convenience for ease of calculation and should not affect the result[41, 42]. So it may be $T_0 = 298$ K, $P_0 = 1$, $X_0 = 0$, etc. The proper selection of the consistent units should be noted, e.g. ΔH (cal mole^{-1}), ΔC_p (cal K^{-1} mole^{-1}), ΔS (e.u.), ΔV (cal bar^{-1} = cm^3/41,84), etc.

[**] This, of course, can be helped by introducing an additional parameter n into eqn. (16) thus yielding the desired term $\mu \mathrm{d}n$ (and $\partial\Phi/\partial n = \mu$), as the additional term of eqn. (17). Presumably this would be more convenient in everyday thermodynamic practice[25] but it is not consistent with our simplified approach to use exclusively the intensive parameters as variables in Φ.

$$R \ln x_A = -\Delta H_A \left(\frac{1}{T} - \frac{1}{T_A}\right) - \Delta a_c \left(\frac{T_A}{T} + \ln \frac{T}{T_A} - 1\right) +$$

$$\Delta b_c \left[T - T_A - T_A^2 \left(\frac{1}{T} - \frac{1}{T_A}\right)\right] + \tag{58}$$

$$\Delta c_c \left[2\left(\frac{1}{T^2} - \frac{1}{T_A^2}\right) - \left(\frac{1}{T_A T} - \frac{1}{T_A^2}\right)\right]$$

where T_A and T are the temperature of fusion and of the system, respectively, and ΔH_A is the change of standard enthalpy at T_A. Practical applicability and common simplifications were surveyed by, for example, Adams and Cohen[43]. Assuming ideal behaviour, the most popular simplification employs only the first term of eqn. (58), plotting $\ln x_A$ versus $1/T$ to obtain a straight line the slope of which yields the enthalpy of fusion ΔH_A. On the other hand, if ΔH_A is known, this equation may be used to give the ratio of the activities instead of x_A. We also should not forget the possibility of using the Hess and Kirchhof additive laws as convenient means in all cases where experimental difficulties in the direct determination of the state functions occur.

Let us now consider a typical TA recording in Fig. 8 to demonstrate the type of information that can be extracted. First of all, we may look for thermodynamic quantities. From the base line we can read the thermal development of the measured property Z as well as non-thermal progress if an additional external parameter is also

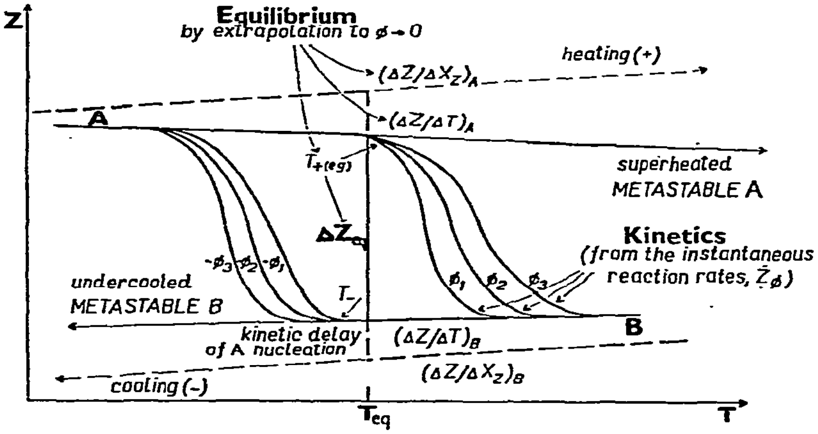

Fig. 8. Graphical illustration of a TA record with regard to possible ways of data selection. The rectangular solid line reflects the development of equilibrium (background) of the phase transformation (A→B) of invariant type assuming an infinitesimal temperature change (Cf. Fig. 5, I_{in}). The possible distortion of its rectangularity (λ-shaped and/or diffuse-like phase transformations[26, 27]) due to fluctuations of concentration, magnetic moments or temperature etc. is not accounted for here (see ref. 14). The horizontal liner-like parts correspond to the base lines representing the change of system state if no reaction occurs. The actual (S-shaped) course of the TA curves for different heating rates ϕ_1, ϕ_2, ϕ_3, is caused by the time relaxation process necessary to reach equilibrium, called kinetics.

time–temperature dependent. The displacement of base lines gives the integral change of the measured property but its equilibrium value can only be achieved by extrapolation to zero heating rate or by recalculation using eqns. (29) and (30) when dealing with the enthalpy change, or by using analogous forms for any non-thermal property. However, one should be careful over the correct interpretation of DTA measurements[30, 31] [cf. eqn. (37)] in ordinary dynamic calorimetry[32, 37]. Equilibrium temperatures can also be obtained by extrapolation to zero heating rate. In determining its equilibrium values, there always remains a certain error proportional to the temperature gradient[44–46]. This was quantitatively estimated by Proks[45] and reduced in practice by, for example, using thin layers of investigated materials spread over the large surface of a well conducting sample holder shaped, for example, in the form of multiplate crucible[46], already convenient for TG measurements. Beside this error due to quasi-stationary gradients, there can arise an additional (kinetic) delay caused by the impingement of interface energetics of new phase formation which is commonly associated with the effect of superheating and/or, most probably, supercooling. This is already connected with the second type of data to be evaluated from TA records: kinetics and mechanism of the process. The logistics of this procedure were briefly touched on in eqns. (38)–(40) and its entire mathematics have been presented with full details elsewhere[3]. Some notoriously discussed and yet unclear points of view, however, are discussed in the form of questions and answers in a subsequent critical review[47].

In conclusion, it should be noted that truly equilibrium thermodynamics cannot be completely sufficient to describe correctly the real dynamic features of TA experiments because even steady temperature increments may give rise to non-equilibrium states, cf. Fig. 6. In other words, the state functions, similar to those used above, must be considered as functions of the space coordinates and time. Kluge[48] has produced a nice approach for generally solving and interpreting the basic differential equations for the independent state fields (e.g., temperature, density, concentration, etc.). This has already received attention in kinetics in the determination of the decisive dimensionless parameters such as diffusion coefficient, rate constant, activation energy, etc.[49]. Such new, actually non-isothermal approaches to non-isothermal kinetics[39, 49, 50] are a good guarantee of a promising theoretical future. It can be anticipated that the development in theoretical TA will also be affected by flux methods as pioneered by Šesták et al.[4, 5] and matured in stating the fundamental equation of TA in the form (cf. Chapter 7)[1, 6].

$$\begin{array}{lcl} \dot{Q} & = & \dot{U} + P\dot{V} - \mu\dot{n} - \mathscr{H}\dot{M} - E\dot{\mathscr{P}} - F\dot{\tau} + \gamma\dot{A} + \varphi\dot{C} \qquad (59) \\ \text{heat interaction with} & = & \text{response change of the state of TA system} \\ \text{the surroundings} & & \text{(according to type of TA method)} \end{array}$$

The additional work terms, such as $\gamma\dot{A}$ and $\varphi\dot{C}$, can be chosen according to the type of TA in question, e.g. emanation TA, where A, γ, C and φ are the surface area, interfacial tension, surface curvature and curvature coefficient, respectively (which would bring desired attention to the surface chemistry, in this article intentionally underestimated). A definite but not yet easy aid for the near future can be sought in a more concise framework of rational thermodynamics$^{15-17}$.

AUTHOR'S NOTE

In some aspects, the nomenclature employed throughout this article slightly but intentionally deviates from the nomenclature recommended by ICTA (see four reports of ICTA nomenclature committee published, for example, in the Proceedings of ICTA Conferences). It was found necessary from the point of view of theoretical TA but it should be stressed that, so far, it is restricted to this article, having no general validity. The notation of the most important, and thus recommendable, basic terms are denoted in the text by the *italic* lettering. In our attempt to present a concise list of symbols suitable in theoretical TA, some replacement of individual symbols may also be found more convenient as, for example, heating rate a or β, compressibility $\mathscr{H}$, deformation ε, stress σ or τ, force F, etc.

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