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RATIONAL APPROACH TO THERMODYNAMIC PROCESSES AND CONSTITUTIVE EQUATIONS IN ISOTHERMAL AND NON-ISOTHERMAL KINETICS

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Isothermal and non-isothermal kinetics are classified according to the viewpoint of rational approach. The appropriate selection of basic quantities and constitutive equations is stressed. The extensive discussion recently focused to the meaning of the partial derivatives is reinvestigated and clarified considering the origin of following equation

\[ \alpha = f(T, t) \]

where \( \alpha \) is the extent of reaction, \( T \) and \( t \) are the temperature and time respectively, and \( f \) represents a function. The meaning of partial derivatives is demonstrated in details. The disagreement sometimes claimed between the data evaluated by means of isothermal and non-isothermal kinetics is also reviewed, but no fundamental differences are established.

A recent article by MacCallum and Tanne~ [1] on a non-isothermal rate equation has created an extensive discussion as to the applicability of the isothermal mathematical treatment to non-isothermal conditions for which it is assumed that the concentration, \( C \), under non-isothermal conditions in a homogeneous system is a function of both the temperature, \( T \), and the time, \( t \). This assumption leads to the following equation, based upon a normal mathematical procedure for partial differentiation

\[ \frac{dC}{dt} = \left( \frac{\partial C}{\partial t} \right)_T + \left( \frac{\partial C}{\partial T} \right)_t \frac{dT}{dt}. \] (1)

Some authors [1, 2] have claimed that the term \( (\partial C/\partial t)_T \) is appropriate to describe the isothermal rate of a process only. Hill [3] first argued that the term \( (\partial C/\partial T)_t \) is effectively zero, comparing the situation to that of the arrow in flight. Although the arrow is in motion, at any instance it is at rest, similarly to the state of a chemically reacting system defined at any instant of time without reference to change. Felder and Stehel [4] later pointed out that such an instantaneous rate of Eq. (1) would depend not only on the present state of the system (e.g. the frequency of collisions, relative energies and the orientation of the molecules of the system), but also on previous and future states. They emphasized that Eq. (1) is invalid because \( C \) is a path function rather than a state function of the variables \( t \) and \( T \). Holba and Šesták [5] made a mathematical attempt to calculate possible consequences of Eq. (1) upon the analytical form of the non-isothermal rate equa-
dition. By assuming that the degree of reaction, \( \alpha \), is a state function of \( T \) and \( t \), they arrived at a relationship yielding a non-isothermal rate about ten times faster than the isothermal one. Hrma and Šatava [6] discussed the actual meaning of partial derivatives using the established form and significance of the specific rate constant. They concluded that the non-isothermal \( \alpha \) of Eq. (1) would then depend only on the total duration of the process and its final temperature.

In his defence of the validity of Eq. (1), MacCallum [7] assumed that the temperature is only one of the physical parameters which may be varied during a kinetic reaction; the volume of the reactant solution, the pressure of volatile products, etc., could also be changed during an isothermal decomposition, just as in non-isothermal experiments the temperature is linearly raised holding other variables constant. He considered the case of adding an inert diluent at a constant rate during a process, resulting in a mathematical description analogous to Eq. (1), for the volume, \( V \):

\[
\frac{dC}{dt} = \left( \frac{\partial C}{\partial t} \right)_V + \left( \frac{\partial C}{\partial V} \right)_t \frac{dV}{dt} \tag{2}
\]

where the partial terms were further analytically expressed.

Another more experimental approach to this discussion was based on a long kinetic practice which has exhibited that the reaction rate, \( \frac{d\alpha}{dt} \), is proportional to the product of two separate functions; the first, \( k(T) \), is temperature-dependent, and the second, \( f(\alpha) \), is related to \( \alpha \) only:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha). \tag{3}
\]

The validity of Eq. (3) has also been confirmed in non-isothermal kinetics, e.g. by Šesták [8], who showed a simple accumulation procedure based on infinitesimal changes in \( \alpha \) scanned along a non-isotherm, and by Simmons and Wendlandt [9], who made a similar stepwise calculation of the instantaneous rate constant under isothermal conditions with linearly or hyperbolically elevated temperature. Gilles and Tompa [10] stressed the fact that the value of \( \alpha \), as the solution of a special form of the differential equation (3), \( \frac{d\alpha}{dt} = k(T)\alpha \), depends at time \( t \) on the functional relationship between \( T \) and \( t \), and in general therefore is not a function of two independent variables \( T \) and \( t \).

Because the situation is still not completely clear, the aim of this article is to review the problem employing a well-defined concept.

* Concentration \( C \), as well as any other physical property which is chosen to represent the system investigated, can be normalised in the form of a so-called fraction conversion \( \alpha \), by the equation

\[
\alpha(t) = \frac{[C(t) - C_0]}{[C_\infty - C_0]}
\]

where subscripts indicate the value of \( C \) at the initial time \( (t = 0) \) and at \( t \to \infty \). The case where \( C_\infty \) is not constant and varies with the temperature [5], is not considered here.
Rational approach to the kinetics

In our opinion the misunderstanding arose from a vague definition of the concepts which appear in the considerations. A convenient framework in which all necessary concepts can be exactly defined is the rational thermodynamics developed by Coleman and Noll [11] (for applications in chemical kinetics see e.g. [12]). This method does not introduce new physical principles but its progressiveness is based on the precise establishment of logical connections between the thermodynamic notions. In contrast to classical thermodynamics which is suitable for the description of a reversible equilibration, rational thermodynamics may also be used for processes distant from equilibrium and hence may cover the field of kinetics as well. Only some general features of the rational thermodynamic approach which are relevant to the present discussion will be utilized here, namely to clear the definition of a thermodynamic process and a constitutive equation and their mutual relations [13].

Any theory which attempts to describe a physical phenomenon requires drastic assumptions as to what is to be included and what can reasonably be neglected. These assumptions are set up in a list of basic quantities which unambiguously describe the given thermodynamic system (e.g. volume $V$, pressure $P$, heat exchange $Q$, temperature $T$, fraction conversion $\alpha$, etc.). We say that the thermodynamic process (i.e. continuous sequences of the states of the system), or just a process, is completely described if the basic quantities are specified as a function of the time*, $t$ [e.g. $V = V(t)$, $P = P(t)$, $Q = Q(t)$, $T = T(t)$, $\alpha = \alpha(t)$ etc.]. We neglect here all quantities except a kinetic variable $\alpha$, and the temperature $T$. Hence a process in our system is represented by the pair of functions $\alpha = \alpha(t)$, and $T = T(t)$, denoted $[\alpha(t), T(t)]$.

A special class of processes in which $T(t) = K = \text{constant}$ is called the class of isothermal processes $[\alpha(t), K]$. Similarly we can have the class of linear processes $[\alpha(t), K't]$ where $T$ is given as a linear function of $t$, and $K'$ is a constant; the class of quadratic processes $[\alpha(t), K''t^2]$, etc.

The basic quantities are not independent. They must satisfy constitutive equations which are characteristic for a given system (in general the basic quantities must satisfy both the constitutive equations and balance laws. The balance laws express properties common to all systems covered by the theory, and the constitutive equations formalised diversities in the system allowed by the balance laws**).

A process which satisfies the constitutive equations is called admissible. From this point of view isothermal kinetics concerns the class of admissible isothermal processes; non-isothermal kinetics concerns the class of admissible linear, quadratic

* The dependence of basic quantities on the position can generally be considered. A process independent of the position is called homogeneous.

** The balance laws, e.g. the conservation of mass and energy, are not considered here as they do not appear in the present discussion.

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or other dynamic processes. According to the class of processes involved, we have linear non-isothermal kinetics, quadratic non-isothermal kinetics, hyperbolic non-isothermal kinetics, etc.

**Constitutive equations in chemical kinetics**

The entire form of constitutive equations for a given system can be deduced from suitably designed experiments or derived from a microscopic theory. In our case the choice of the constitutive equation should be found through the available kinetic relations justified by both experimental practice and the statistical approach based on the microscopic theory, as for example the Arrhenius rate equation, the collision theory, the activated complex theory, etc. [14].

For the system characterised by the basic quantities \( \alpha(t) \) and \( T(t) \) it seems to be fairly well established that Eq. (3) holds as the constitutive equation; this will be used in the following discussion in a slightly generalised form, i.e.

\[
\frac{d\alpha}{dt} = F(\alpha, T)
\]  

(4)

where \( F \) denotes a function (as well as \( G \) later).

a) In isothermal kinetics we have from Eq. (4)

\[
\frac{d\alpha}{dt} = F(\alpha, K).
\]  

(5)

We denote the solution of Eq. (5), assuming the admissible isothermal process, characterised by \( K \) as

\[
\alpha(t) = \hat{\alpha}(t, K)^*.
\]  

(6)

We may write formally

\[
\frac{d\alpha}{dt} = \left( \frac{\partial \hat{\alpha}}{\partial t} \right)_K + \left( \frac{\partial \hat{\alpha}}{\partial K} \right)_t \frac{dK}{dt} = \left( \frac{\partial \alpha}{\partial t} \right)_K.
\]  

(7)

Eq. (7) follows from \( dK/dt = 0 \) as \( K \) is a constant in an isothermal process. The derivative \( \left( \partial \hat{\alpha}/\partial K \right)_t \) may in general be non-zero. Physically this derivative measures the change of \( \alpha \) at \( t \), if we consider instead of the process with \( T = K \) the process with \( T = K + dK \) (see also Fig. 1 but replace \( K' \) with \( K \)).

b) In linear non-isothermal kinetics we have from Eq. (4)

\[
\frac{d\alpha}{dt} = F(t, K'),
\]  

(8)

We denote the solution of Eq. (8) in the admissible linear process characterised by \( K' \) as

\[
\alpha(t) = \tilde{\alpha}(t, K').
\]  

(9)

and we may proceed

\[
\frac{d\alpha}{dt} = \left( \frac{\partial \tilde{\alpha}}{\partial t} \right)_{K'} + \left( \frac{\partial \tilde{\alpha}}{\partial K'} \right)_t \frac{dK'}{dt} = \left( \frac{\partial \alpha}{\partial t} \right)_{K'}.
\]  

(10)

* Note that the superposed caret in \( \alpha \) serves to distinguish this function from its value.

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(the illustration of which is given in Fig. 1). Similarly to Eq. (7) \( \frac{dK'}{dt} = 0 \) according to the assumption that \( K' \) is a constant for a linear process and \( \left( \frac{\partial \tilde{a}}{\partial K'} \right)_t \) indicates the change in \( \alpha \) in two infinitesimally close processes differing by \( dK' \) (see Fig. 1).

Fig. 1. Diagrammatic representation of the system \( \alpha = \tilde{a}(t, K') \)

Fig. 2. Diagrammatic representation of the system \( \alpha = \bar{a}(t, T) \)

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However, the solution of Eq. (8) may also be obtained in the form
\[ \alpha(t) = \bar{\alpha}(t, T/t) \text{ def.} = \bar{\alpha}(t, T) \] (11)
using \( K' = T/t \). The function \( \bar{\alpha} \) for given values of \( t \) and \( T \) yields the value of \( \alpha \) at \( t \) in the linear process characterised by \( K' = T/t \). In terms of \( \bar{\alpha} \) we obtain
\[ \frac{d \bar{\alpha}}{dt} = \left( \frac{\partial \bar{\alpha}}{\partial t} \right)_T + \left( \frac{\partial \bar{\alpha}}{\partial T} \right)_t \frac{dT}{dt} = \left( \frac{\partial \bar{\alpha}}{\partial t} \right)_T + \left( \frac{\partial \bar{\alpha}}{\partial T} \right)_t K' \] (12)
(as graphically demonstrated in Fig. 2). In Eq. (12) both partial derivatives are generally non-zero, and \( (\partial \bar{\alpha}/\partial t)_T \) means the change of \( \bar{\alpha} \) if we replace the process \( K' \) at \( t \) with the process \( K' + dK' \) (\( = T/(t + dt) \)) at \( t + dt \) (see Fig. 3b). Accordingly, \( (\partial \bar{\alpha}/\partial T)_t \) reflects the change of \( \bar{\alpha} \) at \( t \) if we replace the process \( K' \) at \( T/t \) with the process \( K' + dK' \) (where \( dK' = dT/t \)) (see Fig. 3a).

![Diagrammatic representation of the partial derivatives in the system \( \alpha = \bar{\alpha}(t, T) \)](image)

It is important to point out that the partial derivatives \( (\partial \bar{\alpha}/\partial t)_K \) in Eq. (7) and \( (\partial \bar{\alpha}/\partial t)_T \) in Eq. (12) are in general not equal as is indicated by their different physical meanings.* Hence, comparison of isothermal and non-isothermal kinetics is not possible to reduce to the question of the meaning and value of the derivatives \( (\partial \bar{\alpha}/\partial T)_t \), but the difference in the values of \( (\partial \bar{\alpha}/\partial t)_{T=K} \) and \( (\partial \bar{\alpha}/\partial t)_T \) is also significant.

A similar analysis can be applied for any type of process, e.g. quadratic, hyperbolic, etc.

* We can demonstrate a simple example for the special form of Eq. (4) i.e. \( ds/dt = -aT \) [where \( f(s) = -s \) and \( k(T) = T \), compare Eq. (3)]. It is easy to find that \( \bar{\alpha}(t, K) = \exp(-Kt); \)
(\( \bar{\alpha}(t, K') = \exp(-K't^2/2) \) and \( \bar{\alpha}(t, T) = \exp(-T^2/2) \). Hence \( (\partial \bar{\alpha}/\partial t)_K = -K \exp(-Kt) \) and \( (\partial \bar{\alpha}/\partial t)_{T=K} = -K/2 \exp(-Kt/2) \).

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Discussion

We may now consider once more the meaning of Eq. (1) in the light of the preceding rational approach. We may ascribe to it two different meanings:

a) Eq. (1) rewritten as

\[
\frac{dx}{dt} = \left( \frac{\partial G}{\partial t} \right)_T + \left( \frac{\partial G}{\partial T} \right)_t \frac{dT}{dt}.
\]

This is a consequence of the constitutive equation of the type

\[\dot{z} = G(T, t)\]

which, in fact, is implicitly involved in [1, 7]. However, this constitutive equation would physically describe a material controlled by an internal clock, which is not the case for an ordinary chemical reaction.

b) Eq. (1) as understood in the sense of Eqs (7), (10) and (12). It is evident that its meaning then depends critically on the precise definition of the symbol \( C \) on the right-hand side of Eq. (1). This is rather an extension of the idea expressed by Felder and Stehel [4], Hrma and Šatava [6], and Gilles and Tompa [10] that the interpretation of Eq. (1) is necessarily related to the process itself.

As we can see, there is no essential discrepancy between the isothermal and non-isothermal kinetics. In usual practice the function \( k(T) \) is expressed by an exponential type equation [14] and instead of \( f(\dot{a}) \) a particular model relation is used, based upon a physico-geometrical hypothesis [8]. In such a special case the kinetic constants (i.e. parameters defining the analytical form of a particular differential equation [3]) can be determined by either kinetics.* Disagreements sometimes reported [1] between the kinetic data observed under isothermal and non-isothermal conditions are therefore not fundamental and may be caused by:

a) experimental reasons, e.g. inaccurate determination of basic quantities and/or not exact satisfaction of the required and predetermined conditions for a given process;

b) oversimplified separation of \( \dot{a} \) and \( T \) functions in Eq. (4) [as given in Eq. (3)] and/or inaccurate formulation of the particular functions \( k(T) \) and \( f(\dot{a}) \);

c) a more complex constitutive equation.

Considering here only point c), we can continue using the same method as above. Assuming a constitutive equation (4) which involves the higher derivatives of temperature \( T \) (e.g. \( T' \)) we have for instance

\[
\frac{dx}{dt} = F(\dot{a}, T, T').
\]

It then follows for the isothermal kinetics that

\[
\frac{dx}{dt} = F(\dot{a}, K, 0) \rightarrow \dot{x}(t) = \dot{x}(\dot{a}, K)
\]

* For the integration of Eq. (8) [solution Eq. (9)] the temperature-dependence of \( k(T) \) must be kept in mind (for the analytical solution see [15]).

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and for the linear non-isothermal kinetics

$$\frac{dz}{dt} = F(z, K', t, K') \rightarrow z(t) = \tilde{z}(t, K')$$

(17)

and/or

$$z(t) = \tilde{z}(t, T).$$

It can be seen that the resulting isothermal kinetics is equivalent to that described in Eqs (5), (6) and (7), but this linear non-isothermal kinetics is not of the same nature as that discussed in p. 196, Eqs (5)-(12). It gives more information about the process but would be appropriate only for systems exhibiting very fast changes with temperature increase. This is not the case for an ordinary chemical reaction either.

* 

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Résumo — Dans l’optique d’une approche rationnelle, on procède à un classement de la cinétique en régimes isotherme et non-isotherme. On met en évidence le choix judicieux de valeurs fondamentales et d’équations d’état. On étudie la discussion récente concernant la signification des dérivées partielles et l’on éclaire la question en considérant l’équation

$$z = f(T, t)$$

où $z$ est le degré d’avancement de la réaction, $T$ et $t$ la température et le temps, $f$ une fonction. On discute les causes du désaccord quelquefois observé entre les données évaluées en régimes isotherme ou non-isotherme.

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ZUSAMMENFASSUNG — Isotherme und nicht-isotherme Kinetik wurden entsprechend einer rationellen Annäherung klassifiziert. Die geeignete Auswahl der fundamentalen Mengen und konstitutiven Gleichungen wurde betont. Die neuerliche lebhafte Diskussion über die Bedeutung der partiellen Derivativen wurde überprüft und durch die Gleichung geklärt:

\[ x = f(T, t) \]

wobei \( x \) den Reaktionsgrad, \( T \) und \( t \) die Temperatur und die Zeit, \( f \) eine Funktion bedeuten. Es wurde auch die in einigen Fällen beobachtete Nichtübereinstimmung der durch isotherme und nicht-isotherme Kinetik erhaltenen Daten behandelt.

Резюме — С точки зрения рационального подхода классифицированы изотермическая и неизотермическая кинетика. Подчеркнута необходимость соответствующего выбора основных величин и применяемых уравнений. Предмет широкой дискуссии, направляемой в последнее время на значение частных производных, рассмотрен снова и даны разъяснения относительно уравнения

\[ x = f(T, t) \]

gде \( x \) — мера реакции, \( T \) и \( t \) — температура и время, соответственно, и \( f \) — функция. Рассмотрено тоже расхождение, обнаруживаемое иногда между данными, рассчитанными посредством изотермической и неизотермической кинетики.
Kinetics with Regard to the Equilibrium of Processes Studied by Non- Isothermal Techniques

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With 9 figures

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The non-isothermal degree of conversion $\lambda$ and the equilibrium advancement for the process $\lambda_{eq}$ are defined by the relationship $\lambda = \alpha \lambda_{eq}$, where $\alpha$ is the isothermal degree of conversion. The precise meaning of non-isothermal kinetics in relation to basic types of processes studied under dynamic conditions is discussed. For an invariant type of process the correct form of the kinetic equation is investigated. For the universal non-isothermal kinetic equation, a modified rate for the process is given by

$$\frac{d\lambda}{dt} = \left( \frac{d\lambda}{d\tilde{T}} - \frac{d\ln \lambda_{eq}}{dT} \right) \lambda_{eq}$$

(1)

for the temperature $T$, time $t$ and the constant heating rate $\tilde{T}$. Thus in monovariant and permanent processes it becomes necessary to establish the $\lambda_{eq}$ vs. $T$ dependence.

1. Introduction

During the last ten years non-isothermal techniques of investigation have been extensively employed to study various types of processes. These thermal methods of analysis have been used successfully for a considerable time to study physical and/or chemical changes in samples investigated in a temperature regime at a given heating rate. Existence of a comparatively easy experimental technique, which make possible to collect enough thermal data from a single run, have attracted attention for use in kinetic analysis of processes (see ref.


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views). In such a case it is not always clear, what property of the system investigated may best represent its removal from the initial and/or final state. Classical kinetics have been used to establish the concentration of a particular compound that is either created or consumed during the process. A rather abstract quantity, the degree of reaction, has been introduced in the case of condensed systems, for example in heterogeneous reactions and phase transformations. In order to define this degree of reaction it is necessary to take into consideration its true dependence upon the final state.

Despite the non-isothermal character of the investigation all past theories, concerning the relationship between kinetics and rate of conversion, have been based on the normal mathematical formulation for an isothermal process. Furthermore, thermal analysis is often applied to study solid state reactions. This leads to the introduction of an additional problem, namely the choice of an appropriate model for the mechanism of the process. In the literature there is frequent use of a formal mathematical description of the process in the form of the differential equation

\[ \frac{d\chi}{dt} = k(1 - \chi)\eta, \]

where \( \chi \) is the degree of reaction, \( t \) is the time, \( k \) Arrhenius rate constant and \( \eta \) is a semiempirical constant. This equation is chosen by analogy with that used to describe the homogeneous kinetics of gases. Some authors have pointed out the lack of meaning in \( \eta \).

A discussion of the function \( f(\chi) \) in relation to specific mechanisms is not the aim of this article. It was dealt with in the preceding contribution "Study of the kinetics of the mechanism of solid state reactions at increasing temperature" Thermostim. Acts 2 (1971) 1.

The purpose of this article is to discuss in detail a thermodynamic model of the processes being studied under non-isothermal conditions. In addition an attempt will be made to investigate the mathematical description for reaction kinetics applicable to experimental data being collected with rising temperature.

2. Measure of progress achieved in the process during investigation

The process can be defined as the path followed by the system undergoing a change of state. The energy of the process is essentially determined by the initial and final states of the system in question. This applies to both chemical reactions and phase transitions in a more general sense, such as boiling, melting, evaporation etc. The course of the process is usually investigated by detecting the change of a certain property of the system as a function of time and/or temperature. The property chosen must be sufficiently sensitive to represent the change of state. For example it may be the concentration of a reactant in a system in a chemical reaction, it may be the weight of condensed phases in a system during thermogravimetry, it may be the volume of a system in a dilatometric or volumetric experiment, the enthalpy of a system in DTA, DSC and calorimetry, the index of refraction in thermal refractometry or even the intensity of a diffraction peak measured in high temperature diffractometry.

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For isothermal kinetic investigations a degree of conversion is frequently derived from the instantaneous value \( Z_t \) of measured property \( Z \) by \(^8\)
\[
\alpha = \frac{Z_t - Z_0}{Z_{\infty} - Z_0} \quad (T = \text{constant}),
\]
where \( Z_\infty \) is the value of the property \( Z \) achieved after infinite isothermal heating at the temperature \( T \) and \( Z_0 \) is the initial value of \( Z \). The difference between the eqs. (1) and (5) is not merely formal; it is mainly rooted in the unequal character of the quantities \( Z_t \) and \( Z_\infty \). While \( Z_t \) is a constant independent of temperature, \( Z_\infty \) may be a function of temperature. Considering the case when \( Z_\infty \) is a function of temperature the process at any arbitrary moment can be characterised by the value \( Z_t \) achieved and by the instantaneous temperature \( T_t \). At this temperature the maximum achievable value for \( Z \) is given by the equilibrium value \( Z_\infty \). It does not seem logical enough to consider the kinetic behaviour of the system at the given point in connection with the final state characterised by \( Z_t \). A more adequate way can be realised through the instantaneous isothermal degree of conversion \( \alpha \) than through the advancement of the process \( \lambda \), which can be immediately determined from the kinetic trace. If the function dependence \( Z_\infty = f(T) \) is known, the transformation of \( \lambda \) to instantaneous \( \alpha \) is possible through
\[
\alpha = \frac{Z_t - Z_0}{Z_{\infty} - Z_0} \lambda.
\]
The reciprocal quantity of transformation coefficient can be symbolised as \( \lambda_{eq} \) and assigned equilibrium advancement of the process, which depends on the temperature only
\[
\lambda_{eq} = \frac{Z_{\infty} - Z_0}{Z_t - Z_0}.
\]

3. Type of processes

It is evident that the quantity \( \lambda_{eq} \) describes that the equilibrium state is variable with temperature. According to the dependence of \( \lambda_{eq} \) upon temperature the processes can be classified as follows:

- For the linear correlation between \( \alpha \) and \( n \) the expression
  \[
  \alpha = a_n + b
  \]
  can be written according to eqs. (2) and (6), where \( a_n \) and \( b \) are the temperature dependent constants. For such a case the Arrhenius specific rate constant is considered to denote the time dependence of \( \alpha \) [compare eq. (14)].

(i) The equilibrium state of a system is changed by a jump at a particular temperature $T_0$. Below this temperature the value of $Z_{\infty}$, which represents the equilibrium state of a system, is constant and equal to $Z_0$. Above $T_0$ the value of $Z_{\infty}$ is constant and equal to $Z_f$ as is illustrated in Fig. 1. Such a case can be demonstrated by the boiling of water under the constant total pressure of air saturated by water vapour at given temperature of the system or by the decomposition of calcite under a constant pressure of CO$_2$. This type of process includes phase transitions, congruent melting, crystallization and simple decompositions. (The relaxation of metastable states can also be considered here, but in this instance $T_0$ is equal to zero). This type of processes can be designed invariant processes.

(ii) The equilibrium state of a system is changed in a particular temperature interval from $T_0$ to $T_f$, where $T_0 < T_f$. Below $T_0$ the value of $Z_{\infty}$ is constant and equal to $Z_0$; above $T_f$ the value of $Z_{\infty}$ is constant and equal to $Z_f$. Within the interval $(T_0, T_f)$ the course of $Z_{\infty}$ vs. $T$ should be expressable by a monotonic function. The corresponding plot of $\lambda_{eq}$ vs. $T$ can be seen in Fig. 2. Such a case can be demonstrated by the boiling of a saline solution in water. Namely on weighing an autoclave which contains a saline solution (e.g. 20 w/o CaCl$_2$) and which is provided by a pressure valve (e.g. 1 atm), a weight lost will occur above the boiling temperature (i.e. 105°C). By escaping of water vapour the salt concentration increases raising simultaneously the boiling temperature of the saline solution in water (e.g. 58 w/o CaCl$_2$ — 140°C) until complete drying out is reached. This type of process adequately describes the melting of solid solutions, the shift in equilibrium across multi-phase monovariant regions as, for example occurs in two phase regions in binary systems (see section 8 and Fig. 7 for further description of this phenomena) as well as the dehydration of zeolites. This type of process is designed a monovariant process.

(j) The equilibrium state of a system is changed in a continuous manner with temperature, starting at any temperature. There is no characteristic temperature for the beginning of the process. The final $Z_f$ is not given by the termination of the process but by the conditions of the experiment. This situation is illustrated in Fig. 3. The weighing of liquid water which evaporates below its boiling point into the constant volume of the system (including balance) exemplifies this case. The final temperature of the process is determined by the relationship between the initial amount of water and the initial com-

---

Fig. 1. Diagrammatic representation of an invariant process. $\lambda_{eq}$ = Theoretical dependence of the equilibrium advancement for the process upon temperature. $\lambda(t, T)$ = Probable kinetic curve expressed in the degree of conversion for the process. This curve departs from the theoretical course of $\lambda_{eq}$ owing to kinetic impedance. $T_0$ = Equilibrium temperature of the conversion.

Fig. 2. Diagrammatic representation of a monovariant process. For $\lambda$ and $\lambda_{eq}$ see Fig. 1. $T_0, T_f$ = Temperature interval where the equilibrium state changes.
and boiling of water as illustrated in Fig. 4. Another example of this type of combined process may be the dehydration of hydrates in air.

A further example is afforded by the recombination and decomposition of CaCO₃ which take place during the heating of active CaO in a stream of CO₂ as illustrated in Fig. 5. As another case the heating of palladium can also demonstrate Fig. 5. At lower temperature (about 700°C) palladium oxide is formed in air while at the temperature 875°C the dissociation occurs. Similarly, the oxydation and dissociation of quenched oxides and alloys belong to this group.

Fig. 3. Diagramatic representation of a permanent process. a) The dependence of the equilibrium property measured Zₑq upon temperature T. The final values of the property Zₑq can also be given by the arrangement of experimental conditions (indexes 1, 2, 3). b) The course of the equilibrium advancement for the individual cases of final state chosen in a). For description of λ and λₑq see Fig. 1

Fig. 4. Diagramatic representation of the combined process for evaporation and boiling of water. For λ and λₑq see Fig. 1

Fig. 5. Diagramatic representation of the combined process of the recombination and decomposition of CaO and CaCO₃. For λ and λₑq see Fig. 1.

It is to be emphasized that owing to unsufficient choice and definition of experimental regime during an experiment the most unwanted superposition of processes may be created.

In some cases it is better to separate simple processes by a suitable modification of the experimental conditions. This separation is necessary for the evaluation of the kinetic parameters since these relate only to simple processes.

4. Non-isothermal degree of conversion

From the viewpoint of kinetic studies made with rising temperature the quantity λ is understood as the degree of conversion according to the definition given by eq. (1). It should be emphasized here that the isothermal degree of conversion α (eq. 5) is not always identical
with $\lambda$. Accordingly, the quantity $\lambda$ ought to be called the *non-isothermal degree of conversion*.

According to eq. (6) the quantity $\lambda$ is a function both of the isothermal degree of conversion $\alpha$ and of the equilibrium advancement for the process $\lambda_{eq}$.

Thus

$$\lambda = f \{ \lambda_{eq}(T), \alpha[T, T] \}.$$  \hspace{1cm} (8)

The rate for the process as observed under non-isothermal conditions comprises two terms (i.e. derivation of eq. 6, $\lambda = \lambda_{eq} \alpha$)

$$\frac{d\lambda}{dt} = \alpha \frac{d\lambda_{eq}}{dt} + \lambda_{eq} \frac{d\alpha}{dt}.$$ \hspace{1cm} (9)

By contrast with pure isothermal conditions where $T$ is constant, non-isothermal conditions require that $T$ is a function of $t$. Mathematically if follows that even the isothermal $\alpha$ must also be regarded as being a function of both $t$ and $T$. However, $\lambda_{eq}$ is a function of $T$ only ($d\lambda_{eq}/dt = 0$). According to the rules of partial derivation the following equation can then be obtained:

$$\frac{d\lambda}{dt} = \left( \frac{\partial}{\partial T} \right)_t \frac{dT}{dt} + \left( \frac{\partial}{\partial \alpha} \right)_T \frac{d\alpha}{dt}.$$  \hspace{1cm} (10)

so that

$$\frac{d\lambda}{dt} = \alpha \frac{d\lambda_{eq}}{dT} \frac{dT}{dt} + \lambda_{eq} \left[ \left( \frac{\partial}{\partial T} \right)_t \frac{dT}{dt} + \frac{\partial\lambda}{\partial \alpha} \right]$$ \hspace{1cm} (11)

which should be an equation transforming an isothermal rate to a non-isothermal rate.

5. **Specific rate constant**

The rate of a reaction $r$ investigated at constant temperature is usually expressed\(^3,4\) as

$$[r = k \int (\alpha)^r \mathrm{d}T \mathrm{constant}],$$  \hspace{1cm} (13)

where $k$ is the temperature dependent rate constant for the process

$$k = A T^m \exp(-E/RT).$$ \hspace{1cm} (14)

Here $A$ is the pre-exponential factor which is proportional to the frequency or the probability that the system will overcome the energy barrier separating the initial and final states. The height of this barrier corresponds to the activation energy $E$. Exponential ($-E/RT$) expresses the probability that the energy barrier will be exceeded when only one chance is available. $f(\alpha)$ is a function which represents the hypothetical model for the reaction mechanism, $m$ is a characteristic constant within the interval $[0,1]$ arising out of the different theoretical assumptions, e.g. the semi-empirical Arrhenius equation ($m = 0$), collision theory ($m = 1/2$) and the activated complex theory ($m = 1$).

6. **Non-isothermal kinetic equation for invariant processes**

For this type of process the value of $\lambda_{eq}$ is equal to unity above $T_0$. In this temperature range eq. (12) accordingly reduces to the form of eq. (10), which consists of the isothermal rate ($\alpha/\partial T$)\(_t\) and the isochronous part ($\partial\alpha/\partial T$)\(_t\) multiplied by the heating rate.

Equation (13) corresponds to the isothermal term of eq. (10) and can be viewed in a three-dimensional diagram $\alpha - T - t$, see Fig. 6, which can picture this standpoint. Any individual point on the non-isotherm should thus be achieved either along the path of the instantaneous temperature increase being followed by responsible isotherm or by the time propagation linked up with the given isochron. Such final states ($F$) are independent upon the path of its achievement.

![Fig. 6. Diagrammatic representation of a non-isotherme under the assumption of validity of eq. (10). The circles designate the final points $F$ achievable regardless to the path under which is the system treated. $\alpha = f(t, T)$ non-isotherm, $\alpha = f(T)$ isochron](image)
Apart from the experimental realization this approach would be correct only in the case where \( x \) is a state function. In addition it would imply that the system has a memory of the past. For the illustration of mathematical consequence of this presumption see Appendix.

This is in contradiction with the established physical meaning of the instantaneous rate of reactions which is dependent only upon the present state of the system. Therefore the term \((\partial x/\partial T)\) itself has no logical sense and the rate of the reaction ought to be expressed as the total differential

\[
\left( \frac{d\lambda}{dt} \right) = \frac{d\alpha}{dt} = kj(\alpha) \frac{1}{\lambda_{eq}} = \text{constant}.
\]  

(15)

This also implies for the square brackets of eq. (12).

7. Universal non-isothermal kinetic equation for the remaining simple processes

For other than invariant processes the general eq. (9) must be considered. Substituting eqs. (6, 11 and 15) into (9) the following form is obtained \((\Phi = d\lambda/dT)

\[
\frac{d\lambda}{dt} = \alpha \frac{d\lambda_{eq}}{dT} \Phi + \lambda_{eq} k j(\alpha)
\]

(27)

and after modification, this reduces to

\[
\frac{d\lambda}{dt} = \frac{\lambda_{eq} \frac{d\lambda_{eq}}{dT}}{\lambda_{eq}} = \frac{k j(\alpha)}{\lambda_{eq}}.
\]

(28)

This expression is valid for the case where \( f(\alpha) \) represents a process mechanism, which is independent of temperature.

The expression on the right-hand side of eq. (28) is identical with that on the right-hand side of eq. (13). Accordingly, the fraction on the left-hand side of eq. (28) signifies the modified rate of process \((d\xi/dt)\).

Thus

\[
\frac{d\xi}{dt} = \left( \frac{d\lambda}{dt} - \lambda \Phi \frac{d\lambda_{eq}}{dT} \right) / \lambda_{eq}.
\]

(29)

This rate can be determined from the shape of the kinetic curve by means of the scanned value \( \lambda \), the graphically or numerically evaluated derivative \( d\lambda/dt \) and the conditions of the experiment, \( \Phi \). In addition a known dependence of \( \lambda_{eq} \) upon \( T \) for the given system and the experimental conditions must be established. After plotting \( \lg (d\xi/dt) \) vs \( 1/T \) the activation energy for the process will be determined with the same systematical error, as is found for the invariant process.

For a monovariant process for which the temperature interval \((T_f - T_0)\) is small, the kinetic curve whose onset lies at a temperature above \( T_f \), is preferable for a simple treatment. In such a case, for any point of the kinetic curve, the identity \( d\xi/dt = d\lambda/dt \) is valid; kinetic parameters can therefore be derived in the same manner as those for invariant processes. In all other instances a knowledge of the temperature dependence of \( \lambda_{eq} \) is required.

8. Estimation of the temperature dependence of equilibrium advancement for a process

In the general case where the above function is unknown only the probable form of the function \( \lambda_{eq} vs T \) can be considered. According to eq. (7) \( \lambda_{eq} \) is a linear function of the quantity \( Z_{\infty} \).

Then

\[
\lambda_{eq} = z \cdot Z_{\infty} + y,
\]

(30)

where \( z = 1/(Z_f - Z_0) \) and \( y = -Z_0/(Z_f - Z_0) \) are constants.

The quantity \( Z \) is chosen as being linearly proportional to the number of atoms in the reacting phase. Thus \( Z_{\infty} \) can be written

\[
Z_{\infty} = x' n_\infty + y',
\]

(31)

where \( n_\infty \) refers to the equilibrium number of moles, or possibly atoms, of reactant. This number of moles must obey a general expression for the equilibrium constant \( K \)

\[
K = \exp (-\Delta G^0/RT) = g (n_\infty).
\]

(32)

On inversion

\[
n_\infty = f [\exp (-\Delta G^0/RT)],
\]

(33)

where \( \Delta G^0 \) is the free enthalpy change in the process and \( g \) (and \( f \)) represents an appropriate function.

Thus

\[
\lambda_{eq} = X f [\exp (-\Delta G^0/RT)] + Y,
\]

(34)
where \( X = x x' + x' y + x y' \) and \( Y = x' y + x y' + y y' \). Assuming a simple temperature dependence for \( \Delta G \) in a form of the first approximation

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0,
\]

where \( \Delta H^0 \) and \( \Delta S^0 \) are temperature independent enthalpy and entropy changes, respectively

\[
\lambda_{eq} = X [\exp (-\Delta H^0/RT) \exp (\Delta S^0/R)] + Y = X [B \exp (-\Delta H^0/RT)] + Y. \tag{36}
\]

Fig. 7. Samples of possible processes which can occur in the binary system forming eutectic, a) Typical phase diagram with the compositions chosen, b) The dependence of \( \lambda_{eq} \) vs. \( T \) obtained by means of lever rule from a). Dashed lines correspond the probable kinetic curves of these processes, \( \lambda(t, T) \cdot T \) represents individual temperatures. IA = Invariant process of melting of pure component \( A \), M = Monovariant process of melting of solid solution, C = Combined process of melting of two phase solid, IE = Invariant process of melting of eutectic mixture.

To solve the above equation the approximate analytical form of the function \( f \) and the constants \( X \), \( Y \) and \( B \) must be determined.

For instance, in the most simple case-model, namely that of the melting of an ideal solid solution to yield an ideal liquid mixture it is extremely difficult to calculate the explicit form of the \( \lambda_{eq} \) vs \( T \) function. Clearly this type of function should be a complex function

\[
\lambda_{eq} = g [\exp [(G_A - G_B)/RT]], \tag{37}
\]

where \( G_A \) and \( G_B \) are the Gibbs free energy changes for the melting of the pure components \( A \) and \( B \), respectively. If the first approximation of the temperature dependence of \( G_A \) (and \( G_B \)) is assumed to be \( G_A = H_A (1 - T/T_d) \), a general type of function \( \lambda_{eq} \) vs \( T \) similar to eq. (36) can be obtained. There is, however, a significant difference, namely that function (37) is valid only within the temperature interval \( T_0 < T < T_f \) i.e. for a monovariant process. The calculation can be made only by means of a computer using numerical methods of analysis.

For most practical purpose the analytical form of the \( \lambda_{eq} = f(T) \) function is unnecessary and the plot can be obtained from the established phase diagram using the lever rule. This procedure is shown in Fig. 7.

9. Discussion

The concept of the advancement of equilibrium for the process \( \lambda_{eq} \) can also be usefully applied in isothermal studies where the equilibrium stage alters with temperature. For this reason, the original definition of isothermal \( \alpha \) has been retained as far as possible throughout the present treatment.

An important fact associated with the mathematical bases of these considerations of monovariant processes is that the procedure adopted here assumes a single mechanism to underlie a specific process. This means that the same function \( f(\alpha) \) is maintained throughout the treatment, regardless of changes of equilibrium. The modified rate of the process \( d\xi/dt \) therefore includes changes of equilibrium taking place during the process. It cannot be excluded that a different treatment based on a different model (and different logical approach) for the course of the process may also be successful if a change in the function \( f(\alpha) \), appropriate to the non-isothermal advance of the process, is admitted.

A vital question, which now arises, concerns the true meaning of the activation energy as calculated for monovariant processes. Information is missing with regard to the basic model for the path along which the system crosses the various energy barriers. The assumption that \( E = f(T) \) cannot therefore be justified.

The general form of the non-isothermal equation indicates a possibility for obtaining approximate values of equilibrium data by comparing kinetic curves obtained with different heating rates.

The authors firmly believe that this theory will serve, as an important first approach to a classification on a unified level of experimental data obtained from dynamic studies, especially for variant processes.

The authors wish to acknowledge the assistance of Dr. A. Brown (Aktiebolaget Atomenergi, Studsvik, Sweden) in the task of formulating the definitions used in this treatment and kind comments of Professor V. Šátava (University of Chemical Technology in Prague) as well as of the colleagues at the Department of Magnetic Oxides, The Institute of Solid State Physics.

Appendix

The term \( \frac{\partial \alpha}{\partial T} \) is commonly assumed to be zero because of difficulty to imagine a real change of \( \alpha \) at constant time. But let us analyze this term as a slope of the isochronous curve \(^{15}\) (see Fig. 6). No general expression for such isochronous slope has been derived yet in relation to the known kinetic terms as \( k(T) \) and \( f(\alpha) \). The simplest approach is to start from a consideration of the formal dependence of \( \alpha \) upon \( t \) in order to investigate the effect of the first term on the right-hand side of eq. (10). For the particular case where \( f(\alpha) = 1 - \alpha \) using a kinetic equation in the form \( g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = k(T)t \),

\[
\alpha = 1 - \exp \left( - k(T)t \right) \tag{A16}
\]

the following relationship can be written after differentiation

\[
T = \text{const.} \quad \left( \frac{\partial \alpha}{\partial T} \right)_T = k(T) \left( 1 - \alpha \right) \tag{A17}
\]

\[
t = \text{const.} \quad \left( \frac{\partial \alpha}{\partial t} \right)_t = \frac{dk(T)}{dT} \cdot t(1 - \alpha) = k_0 e(1 - \alpha) \tag{A18}
\]

Despite the lack of physical basis for the defining of a “time” rate constant \( k_0 \), eq. (18) may well serve for the purpose of showing possible mathematical consequences arising out from the consideration \( \alpha \) as a state function. On substituting eqs. (17) and (18) into eq. (10) can then be obtained

\[
\frac{d\alpha}{dt} = \left[ k(T) + \frac{dk(T)}{dT} \frac{dT}{dt} t \right] (1 - \alpha) \tag{A19}
\]

For a non-isothermal system the meaningful relationship between \( T \) and \( t \) is given by the linear expression \(^{12}\) \( dT/dt = \Phi \), corresponding to a constant rate of heating. Integration of this equation within the temperature interval corresponding to the duration of the process gives

\[
t = (T - T_0)/\Phi \tag{A20}
\]

where \( T_0 \) indicates the equilibrium temperature for conversion. Below this temperature the process and its investigation are beyond realization \(^{13}\). On combining eqs. (19) and (20) and after the modification

\[
\frac{d\alpha}{dt} = k(T) \left[ 1 + (m + E/RT)(1 - T_0/T) \right] (1 - \alpha) \tag{A21}
\]

the value of \( m \), always less than unity, can be neglected with respect to the values of the term \( E/RT \) which is usually greater than 10; thus

\[
\frac{d\alpha}{dt} = k(T) \left[ 1 + \frac{T - T_0}{T^2} \frac{E}{R} \right] (1 - \alpha) \tag{A22}
\]

Equation (22) should then be considered here as formal kinetic equation which complies with eq. (10). The effect of the equilibrium temperature \( T_0 \) on the apparent activation energy might have ex-
plained here the discrepancy observed in the vicinity of the on-set temperature of the process frequently accounted for on the basis of a reverse reaction.

Introducing eq. (14) into (21)

\[
\frac{dx}{dt} = A T^m \exp \left( -\frac{E}{RT} \right) \left[ 1 + (m + E/RT) \left( 1 - T_0/T \right) \right] (1 - \alpha) \tag{A23}
\]

this can serve for a normal evaluation of the activation energy from the plot of \( \log (dx/dt) \) vs \( 1/T^2 \). The slope of this line, assuming thermally independent values of \( E, A, m \) and \( f(\alpha) \), will then be represented by

\[
\frac{d \log \left( [dx/dt]/(1 - \alpha) \right)}{d(1/T)} = m \frac{T - E/R + \left( E/R \right) \left( 1 - T_0/T \right) - T_0(m + E/RT)} {1 + (m - E/RT) \left( 1 - T_0/T \right)}.
\tag{A24}
\]

In order to simplify the last equation, \( Tm \) can be neglected having regard to the magnitude of \( E/R \) so that

\[
\frac{d \log \left( [dx/dt]/(1 - \alpha) \right)}{d(1/T)} = -\frac{E}{R} \left[ 1 + \frac{2(T_0/T - 1)}{1 + (E/RT) \left( T - T_0 \right)} \right]

= -\frac{E}{R} \left[ T_0/T \left( 2 - E/RT \right) + E/RT \right]. \tag{A25}
\]

Fig. 8. Plot of the relative error in the value of activation energy \( E \) with regard to temperature \( T \). \( T_0 \) = Equilibrium temperature of the conversion. The higher the magnitude of the activation energy and temperature are, the lower the relative error is yielded.

Fig. 9. Graphical comparison of the rate for the unimolecular process obtained on the basis of eqs. (16) and/or (22).

\[
\left[ \frac{dx}{dt} \right]_{eq. (16)} = Z \exp \left( -\frac{E}{RT} \right) (1 - \alpha)
\]

\[
\left[ \frac{dx}{dt} \right]_{eq. (22)} = \frac{\left[ \frac{dx}{dt} \right]_{eq. (16)}}{g(T)} + \frac{\left[ \frac{dx}{dt} \right]_{eq. (15)}}{g(T)}
\]

\[
g(T) = \frac{T - T_0}{T_0} - \frac{E}{R}
\]

as calculated by means of TESLA computer using \( Z = 1 \cdot 10^{13}, E = 2.7 \cdot 10^4, \phi = 0.1, T_0 = 300 \) in temperature interval from 310 to 460 K and employing series.\(^3,9,14\).

\[
\left[ \frac{dx}{dt} \right]_{exp} = \text{experimentally obtained rate of the decomposition of } \alpha-\text{calcium sulphate hemihydrate under comparable conditions.}^{14}
\]

Similarly, proceeding further by conceivably neglecting the integers 1 and 2 with respect to the magnitude of \( (E/RT) \), a step which yields an approximate deviation of about 10\% for \( E = 2 \cdot 10^4, T = 10^3 \) and \( T > T_0 \)

\[
\frac{d \log \left( [dx/dt]/(1 - \alpha) \right)}{d(1/T)} = -\frac{E}{R} \left[ \frac{E}{RT} - T_0/T \left( E/RT \right) \right] = -\frac{E}{R}. \tag{A26}
\]
Perfurverbindungen als Lösungsmittel in der Photokinetik

Van

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Mit 3 Abbildungen

(Eingegangen am 28. Juli 1971)

Photokatalytische Verfahren haben als isolierte Derivate von Photokatalytischen Modellorganismen eine besondere Rolle in der Photokatalyse. Die von ihnen erzielten Ergebnisse können als wichtige Vorstufen für die Entwicklung von Photokatalysatoren angesehen werden.

Summary

Perfurverbindungen sind keine Lösungsmittel. Die photochemischen Reaktionen in Perfurverbindungen verlaufen jedoch in Lösungsmitteln, die nicht mehr elektronenaufnehmend sind.

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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

* 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. 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, 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. 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 as thermospectrometry, thermoluminiscence, thermorefractometry, thermocouacoustmetry, 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 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 multi-component 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., \[ Y = \hat{Y}(X_1, X_2, \ldots) \] where the state quantity \( Y \) is a function \( \hat{Y} \) of variables \( X_1, X_2, \ldots \).

* We are not concerned with the magnitude of the system 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 as ordering of crystallographic sites, distribution of species (and vacancies) on, for example, cation regular and interstitial sites, nor with their thermodynamic potentials which were dealt with in detail elsewhere.
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 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, 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; 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, 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 \( Z = \tanh(T^q) \). 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.*

---

* 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.
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, $\dot{Q}$ ($= dQ/dt$), 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, $\dot{T}$ ($= dT/dt$), 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* as recently summarized by Kratochvíl. 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 $A$ ) of time, $t$, or

$$
\begin{align*}
T &= \tilde{T}(t) \\
V &= \tilde{V}(t) \\
P &= \tilde{P}(t) \\
S &= \tilde{S}(t) \\
U &= \tilde{U}(t) \\
\dot{T} &= \tilde{Q}(t)
\end{align*}
$$

(1)

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

$$
\dot{U} = \dot{Q} - PV
$$

(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

$$
\begin{align*}
G &= \tilde{G}(P, T, \dot{T}) \\
V &= \tilde{V}(P, T, \dot{T}) \\
S &= \tilde{S}(P, T, \dot{T})
\end{align*}
$$

(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, $S$, or

$$
\dot{S} \geq \frac{\dot{Q}}{T}
$$

(4)

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

$$
G = U - TS + PV
$$

(5)

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

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

(6)

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

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

(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 \( (\partial G/\partial \dot{T})\dot{T} \leq 0 \), which can be identified for all possible values of \( \dot{T} \) 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 \( G = G(P, T) \), i.e. Gibbs free energy obtains the form known from ordinary thermodynamics.

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

\[
\left| \frac{\partial G(P, T)}{\partial P} \right|_{P, T} = V(P, T)
\]

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

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

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 \( [b(\dot{T})] \leq 0 \), or

\[
\left| \frac{\partial G(P, T)}{\partial T} \right|_{P, T} = - S_{eq}(P, T)
\]

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

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 (\( \dot{T} > 0, \dot{T} = 0 \)), 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 system's 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 $\partial G/\partial \dot{T} \neq 0$ 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 $U = \bar{U}(S, V)$ and $dU = TdS - PdV$ into the form of Gibbs free energy $G = \hat{G}(T, P)$ and $dG = -SdT + VdP$ 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 $V = \bar{V}(P, T)$ and/or

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

$$dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$

and

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

$$= V dP + T \left[ -\left( \frac{\partial V}{\partial T} \right)_P dP + \left( \frac{\partial S}{\partial T} \right)_P dT \right]$$

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

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

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

and

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

$$dV = \alpha_T V dT - \beta V dP$$

$$dH = V(1 - \alpha_T) dP + c_P dT$$

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 and optical properties, and will affect the rate of chemical reactions, 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
EXTERNALLY APPLIED FIELDS

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Partly open, quasistationary thermodynamic system suitable for the portrayal of TA methods as calloric, thermodilatometric, weight, evolved gas, magnetic, dielectric and thermomechanical measurements (symbols see text).}
\end{figure}

controlled are \( \mu, \mathcal{H}, E \) and \( F \) called the chemical potential, magnetic and electric fields and mechanical tension, respectively. Corresponding extensive parameters representing the state of the sample are \( n, M, \varphi \) and \( \tau \), 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 \( \Phi \) depending exclusively on the intensive parameters as independent parameters of our TA experiment

\[ \Phi = \Phi(T, P, \mu, \mathcal{H}, E, F) \] (16)

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

\[ d\Phi = -SdT + VdP - nd\mu - Md\mathcal{H} - \varphi dE - \tau dF \] (17)

* For a more rigorous analysis of electromagnetic and mechanic measurements it is more convenient to replace the term \( PdV \) by the term \( p\varphi dP \) which indicates the energy change in a unit volume of the sample as a result of a mass change for given \( E, \mathcal{H} \) and \( F \). The symbol \( p \) is density and \( \varphi \) 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 \( \Phi = \sum \gamma \delta X \)

<table>
<thead>
<tr>
<th>Experimentally controlled intensive parameter</th>
<th>Corresponding extensive parameter to be detected ( Y' = \partial \Phi/\partial X )</th>
<th>( \partial^2 \Phi )</th>
<th>( \partial Y )</th>
<th>( \partial S )</th>
<th>( \partial X )</th>
<th>( \partial X \partial T )</th>
<th>( \partial Y )</th>
<th>( \partial S )</th>
<th>( \partial X )</th>
<th>( \partial T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure ( P )</td>
<td>Volume ( V )</td>
<td>(- \frac{1}{V} \frac{\partial V}{\partial P} = \beta ) thermal compressibility</td>
<td>( \frac{1}{V} \frac{\partial V}{\partial T} = a_V ) thermal expansion</td>
<td>( \frac{\partial P}{\partial T} = a_V ) thermal expansivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical potential ( \mu )</td>
<td>Mole number ( n )</td>
<td>( \frac{\partial n}{\partial \mu} \approx ) (logarithm of activity)</td>
<td>( \frac{\partial n}{\partial T} = k_{nT} ) thermal solubility</td>
<td>( \frac{\partial \mu}{\partial T} = S ) partial molar entropy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic field ( \mathcal{H} )</td>
<td>Magnetization ( M )</td>
<td>( \frac{\partial M}{\partial \mathcal{H}} = \chi ) magnetic susceptibility</td>
<td>( \frac{\partial M}{\partial T} = a_M ) magnetocaloric effect</td>
<td>( \frac{\partial \mathcal{H}}{\partial T} = \frac{a_M}{\chi} ) thermal susceptibilities</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric field ( E )</td>
<td>Polarization ( \mathbf{P} )</td>
<td>( \frac{\partial \mathbf{P}}{\partial E} = \gamma ) dial. susceptibility</td>
<td>( \frac{\partial \mathbf{P}}{\partial T} = \gamma_p ) pyroelectric effect</td>
<td>( \frac{\partial E}{\partial T} = \frac{\gamma_p}{\chi_p} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanic tension ( F )</td>
<td>Deformation ( \tau )</td>
<td>( \frac{\partial \tau}{\partial F} = C_T ) elastic stiffness coeff.</td>
<td>( \frac{\partial \tau}{\partial T} = \alpha_T ) thermal strains coefficient</td>
<td>( \frac{\partial F}{\partial T} = K_{F_T} ) thermal stress coefficient</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ( T )</td>
<td>Entropy (enthalpy) ( S (H) )</td>
<td>( T \frac{\partial S}{\partial T} = \frac{\partial H}{\partial T} ) ( \gamma ) thermal capacity, essential term in TA</td>
<td></td>
<td></td>
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</tbody>
</table>

\( \gamma \) 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 \(c_{\nu}, \alpha_{\nu}\) and \(K_{FT}\). Some interesting coefficients can also be obtained on the basis of interactions between non-thermal properties only, e.g. electromagnetic field with mechanical tension (piezoelectric coefficient \(d\tau = \partial \mathcal{P}/\partial F\) or \(= \partial \tau/\partial E^{22}\), magnetoelastic coefficient \(C_{M} = \partial M/\partial F = \partial \tau/\partial \mathcal{H}\)) and/or pressure with mole number (molar volume \(V = \partial n/\partial P\) or \(= \partial V/\partial n\), change of concentration with pressure \(V K_{np} \approx \partial n/\partial P\) 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 \((dV = 0)\). 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

\[
\begin{align*}
n &= n(\mu, T) & dn &= (\partial n/\partial \mu)_T\ d\mu + K_{nT} \ dT \\
M &= M(\mathcal{H}, T) & dM &= \chi d\mathcal{H} + \sigma_M \ dT \\
\mathcal{P} &= \mathcal{P}(E, T) & d\mathcal{P} &= \chi_p dE + p_p \ dT \\
\tau &= \tau(F, T) & d\tau &= C_\tau dF + \alpha_\tau \ dT
\end{align*}
\]

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

\[
dS = \alpha_p V \ dP - c_p/T \ dT
\]

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

\[
\begin{align*}
dY &= 0 & \text{isolated (thermally closed) system} & \text{(e.g. } dS = 0 \text{ adiabatic or for eqn. (14) } dV = 0 \text{ isochoric)} \\
dX &= 0 & \text{system under constant external field} & \text{(e.g. } dP = 0 \text{ isobaric)} \\
dT &= 0 & \text{system at constant temperature} & \text{(e.g. } dT = 0 \text{ isothermal)} \\
dT &= \text{const.} & \text{system under constant heating (TA)} & \text{(e.g. } dT = \phi \text{ non-isothermal)}
\end{align*}
\]
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).

$$H = \hat{H}(\mu, \dot{S}(\mu, T)) \quad dH = (\mu - T K_n) d\mu + c_\mu dT$$

$$H = \hat{H}(\mathcal{H}, \dot{S}(\mathcal{H}, T)) \quad dH = (M - T \alpha_M) d\mathcal{H} + c_\mathcal{H} dT$$

$$H = \hat{H}(E, \dot{S}(E, T)) \quad dH = (\mathcal{P} - T \alpha_P) dE + c_E dT$$

$$H = \hat{H}(F, \dot{S}(F, T)) \quad dH = (\tau - T \alpha_\tau) dF + c_F dT$$
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, $\mu-T$ for solid solutions, $H-T$ for ferromagnetics, $E-T$ for dielectrics and $F-T$ for mechanically stressed systems.$^5$

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
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 $\Phi$. This yields the discontinuity in entropy $\Delta S$, 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 $\Phi$ 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 $\Delta C_X$. 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.\textsuperscript{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 Ehrnfist Relations**

<table>
<thead>
<tr>
<th>Term</th>
<th>First-order transformation</th>
<th>Second-order transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Y_b - Y_a) , dX$</td>
<td>$(S_b - S_a) , dT$</td>
<td>$\lim_{T \to T_{eq}} \left( \frac{\Delta Y}{\Delta H} \right) \rightarrow 0 \equiv - \left( \frac{\partial \Delta Y}{\partial T} \right)_X \equiv - \left( \frac{\partial \Delta Y}{\partial T} \right)_X \equiv$ change of thermal capacity, $\Delta C_x$</td>
</tr>
<tr>
<td>$(V_b - V_a) , dP$</td>
<td>$\frac{dT}{dP} = \frac{\Delta V}{\Delta H} , T_{eq}$</td>
<td>$\frac{dT}{dP} = \nu \frac{\Delta u}{\Delta C_p} , T_{eq}$</td>
</tr>
<tr>
<td>$(n_b - n_a) , d\mu$</td>
<td>$\frac{d\mu}{d\mu} = \frac{\Delta n}{\Delta H} , T_{eq}$</td>
<td>$\frac{d\mu}{d\mu} = \frac{\Delta K_n}{\Delta C_{\mu}} , T_{eq}$</td>
</tr>
<tr>
<td>$(M_b - M_a) , d\mathcal{H}$</td>
<td>$\frac{d\mathcal{H}}{dH} = \frac{\Delta M}{\Delta H} , T_{eq}$</td>
<td>$\frac{d\mathcal{H}}{dH} = \frac{\Delta a_M}{\Delta C_x} , T_{eq}$</td>
</tr>
<tr>
<td>$(\mathcal{P}_b - \mathcal{P}_a) , dE$</td>
<td>$\frac{dE}{dE} = \frac{\Delta \mathcal{P}}{\Delta H} , T_{eq}$</td>
<td>$\frac{dE}{dE} = \frac{\Delta p \mu}{\Delta C_{\mathcal{P}}} , T_{eq}$</td>
</tr>
<tr>
<td>$(\tau_b - \tau_a) , dF$</td>
<td>$\frac{dF}{dF} = \frac{\Delta \tau}{\Delta H} , T_{eq}$</td>
<td>$\frac{dF}{dF} = \frac{\Delta \tau}{\Delta C_{\tau}} , T_{eq}$</td>
</tr>
</tbody>
</table>
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 $\Delta H$ including the simultaneous effect of the second intensive parameter $X$, i.e. $\Delta H = \Delta\hat{H}(X, \Delta\hat{S}(X, T))$. Making partial derivatives we can proceed according to eqn. (13) to obtain

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

(29)

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

$$\frac{d\Delta H}{dT} = \Delta c_X + \frac{\Delta H^*}{T} - \frac{\partial \ln \Delta Y}{\partial T} \Delta H$$

(30)

where $\Delta Y$ equals respective $\Delta V, \Delta n, \Delta M, \Delta P$ 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 $\Delta H$ 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 ($X = P, \Delta Y = \Delta V > 0$), where the second and the last term of the right-hand side of eqn. (30) cancel each other yielding $d\Delta H/dT \approx \Delta c_P$. 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 $\Delta Y$.

According to the preceding scheme, we can derive the required increase of any non-thermal property $dX_1$ to balance the equilibrium of transformation if the other non-thermal property is changed by $dX_2$, i.e. $dX_1/dX_2 = X_{eq} \Delta Y_2/\Delta Y_1$ (compare Table 2), as well as to find out the non-thermal dependence of any $\Delta Y$ in analogy with eqns. (29) and (30) [$\Delta F = \Delta\hat{F}(X_1, \Delta\hat{Y}(X_1, X_2))$] 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

\[ n_A = n_A(t) \quad \text{(or} \quad -n_B = n_B(t) \text{)} \]

\[ T = T(t) \]

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 \( \xi \), called the true degree of transformation\(^{28} \) (or generally conversion)

\[ \xi = \frac{n_A}{n_A + n_B} \quad \text{or} \quad (1 - \xi) = \frac{n_B}{n_B + n_A} \]

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, \( \lambda \), defined on the basis of an experimentally measured property \( Z \) by the equation\(^ {28,29} \)

\[ \lambda = \frac{Z - Z_0}{Z_F - Z_0} \]

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 \( \xi \) and \( \lambda \) which is usually accepted without proofs as proportionality

\[ \xi = K_\lambda \lambda \]

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 \( (n_A + n_B) = \text{const.} \) we have by eqns. (31)–(33)

\[ \frac{d\xi}{dT} = \frac{dn_A}{dT} \left( \frac{1}{n_A + n_B} \right) = K_\lambda \frac{d\lambda}{dT} = K_\lambda \frac{dY}{dT} \left( \frac{1}{Y_F - Y_0} \right) \]
For the total change \( \Delta Y = Y_F - Y_0 \) the proportionality coefficient \( K_\lambda \) keeps a certain value in accordance with the corresponding thermal coefficients in Table 1, e.g.

\[
K_\lambda = \frac{K_{nAT}}{(\partial Y/\partial T)} \frac{\Delta Y}{(n_A + n_B)}
\]

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

\[
Z = Z_{\text{meas.}} K_{\text{app.}}
\]

where \( K_{\text{app.}} \) is known as \emph{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

\[
Z = \hat{Z}(Z_{\text{meas.}}, \dot{Z}_{\text{meas.}}, T, \dot{T}, P, \ddot{P}, K_{\text{app.}}, \cdots)
\]

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

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

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**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 \(^{33, 34}\)

\[
\begin{align*}
\lambda &= \hat{\lambda}(\lambda, T) \\
\dot{T} &= \hat{T}(\lambda, T)
\end{align*}
\]  
(38)

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

(i) **isothermal kinetics** assuming

\[
\begin{align*}
T &= \text{constant (and } \dot{T} = 0) \\
\dot{\lambda} &= f(\lambda) k(T)
\end{align*}
\]  
(39)

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

(ii) **linear non-isothermal kinetics** assuming \(^{35}\)

\[
\begin{align*}
\dot{T} &= \phi = \text{constant (i.e. } T = T_{t=0} + \phi t) \\
\dot{\lambda} &= f'(\lambda, T) k'(T, \phi) \cong f(\lambda) k(T) \phi
\end{align*}
\]  
(40)

where \(\phi\) 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 \(T_A - T_F\), 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 \(\lambda_{eq}\) defined as

\[
\lambda_{eq} = \frac{Z_F - Z_0}{Z_{TF} - Z_0}
\]
(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 \(^{28}\)

\[
\lambda = \lambda_{eq} \frac{Z - Z_0}{Z_T - Z_0} = \lambda_{eq} \alpha
\]
(42)
where \( \alpha \) is the \textit{isothermal degree of transformation} defined in accordance with ordinary isothermal studies. It follows that \( \lambda \) can be understood as the \textit{non-isothermal degree of transformation} containing all complex information about the process normally provided by a set of \( \alpha \) determined for a series of \( T(Z_{TF}) \) within the interval \( T_0(Z_0) \) to \( T_r(Z_r) \) (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 \( T_\circ \)), \textit{variant} (temperature interval \( T_0-T_r \)) and \textit{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\(^\text{29}\).

(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 \( T_r \), 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 \( \Phi \) 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-

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**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\textsuperscript{\textsuperscript{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 $\dot{n}^v$ (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\textsuperscript{4-6}

$$\dot{U} = \dot{Q} - P \dot{V} + \mu_\alpha \dot{n}^v$$

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

$$\dot{H} = \dot{Q} + V \dot{P} + \mu_\alpha \dot{n}^v$$

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. $H = \tilde{H}(P, n, \tilde{S}(P, n, T))$, so that

$$\dot{H}_A = V_A \dot{P} + \overline{H}_A \dot{n}^A + T \left[ - \frac{\partial V_A}{\partial T} \dot{P} - \frac{\partial \mu_A}{\partial T} \dot{n}^A + \frac{\partial S}{\partial T} \dot{T} \right]$$

where the superposed strip describes molar values for the given extensive property ($\tilde{F}$). By combining with $\dot{H}_B$ we get

$$\dot{H} = (V_A + V_B) \dot{P} + (\overline{H}_A - T \overline{S}_A) \dot{n} + (\overline{H}_B - T \overline{S}_B) \dot{n} - T(\alpha_{vA} + \alpha_{vB}) \dot{P} + (c_{pA} + c_{pB}) \dot{T}$$

if $(V_A + V_B) = V$, $\overline{H}_A - T \overline{S}_A = \overline{G}_A = \mu_A$ and $P_0 = P = \text{const.}$, i.e. $\dot{P} = 0$, we have by eqn. (44)

$$\dot{Q} = (c_{pA} + c_{pB}) \dot{T} + \mu_A \dot{n}^A + \mu_B \dot{n}^B - \mu_\alpha \dot{n}^v$$

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\textsuperscript{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. Hence assuming the transformation of the type

\[ \text{ijv}(A) \rightarrow \text{ij}(B) + v \uparrow (*) \]

where i and j are two conservative components of phases A and B and v is the volatile component (superscript v). For \( n^c = \sum n^i = n^1 + n^j \) we have for example \( c^m_p(A) = c^m_{pA}/n^c_A, N^i_A = n^i_A/n^c_A, N^1_A = n^1_A/n^c_A \), etc. These parameters are stable regardless of the mass lost during dissociation except for the volatile part. Introducing the degree of transformation \( \xi \) 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

\[ Y^m = Y^m_A(1 - \xi) + Y^m_B \xi \]

where

\[ \xi = \frac{n_B}{n^c} = 1 - \frac{n_A}{n^c} \]

Assuming, for example, the fluxes in the form of \( \dot{\mu}^i = \sum \dot{N}^i_A \dot{n}^r_A + \sum \dot{N}^i_A \dot{n}^r_B \) (c.g. \( \dot{n}^r_A = N^r_A n^c_A + N^r_A n^c_B \)) together with eqns. (49) and (50), we obtain after some algebraic manipulation

\[ \frac{\dot{Q}}{n^c} = c^m_p(1 - \xi) \dot{T} + c^m_p \xi \dot{T} + (1 - \xi) \sum \mu_A \dot{N}_A^i + \xi \sum \mu_B \dot{N}_B^i + \\
+ (1 - \xi) \mu_\text{ incr}^i N_\text{ incr}^i + \xi \mu_\text{ incr}^r N_\text{ incr}^r \]

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.

\[ [K^e(T_s - T) + K^r(T_s^4 - T^4)]/n^c = \]

\[ = (c^m_p + \Delta c^m_p \xi) \dot{T} + \]

\[ + (1 - \xi)(\mu_A^r - \mu_B^r) N_A^r + \xi(\mu_B^r - \mu_A^r) N_B^r + \]

\[ + (\Delta H_\text{ef} + \Delta N^r \mu_r) \xi + \]

\[ + (\Delta \mu^i - \Delta \mu^r) \xi \]

where the individual lines describe the heat consumption due to:

(a) specific heat flux between the surroundings and the sample, where \( K^e_s \) and \( K^r_s \) are the sample heat transfer coefficients for conduction and radiation;

(b) the change of the system temperature, where \( \Delta c_p \) 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 $\Delta H_{\text{eff}}$ is the effective enthalpy change) including the specific loss of the volatile component ($\Delta N^v$) by dissociation taking place during $A \rightarrow B$ transformation;

(e) the redistribution of conservative components between the phases often called phase separation, where $\Delta \mu^i = \mu^i_B - \mu^i_A$ and $\delta$ is a new parameter called extent of phase separation (normalized $0-\delta-0$) by equation $\xi (N^i_A - N^i_B) = (1 - \xi) (N^i_A - N^i) = \delta$.

This analysis shows that this system must also be described by help of $\delta$ besides the previously introduced $\xi$. Furthermore, it is worth noting that each mass flux is diffusion controlled, 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

\[ \begin{align*}
\dot{\xi} &= \dot{\xi}_n(\xi, \delta, I, T) \\
\dot{\delta} &= \dot{\delta}_n(\delta, I, T) \\
\dot{I} &= \dot{I}_n(\xi, \delta, I, T) \\
\dot{T} &= \dot{T}_n(\xi, \delta, I, T),
\end{align*} \]  

where $\dot{I}$ is bounded with $\xi$, $\delta$ and $T$ by nucleation-growth equation which is usually indicated in the form

\[ \dot{I} = \dot{I}_n(\xi, \delta, I, T) \dot{F}_{\text{grow}}(\xi, \delta, T) \]  

Equation (54) is well known in the simplified shape of Kolgomorov–Johnson–Mehl–Avrami–Yerofeev equation, where the parameter $\delta$ 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 ($\Delta N^v$); compensation calorimetry (DSC) and enthalpiometry ($\Delta H_{\text{eff}}$, $\dot{T} = \phi = \text{const.}$), Calvet microcalorimetry (DCC) and other spontaneous heat flux measurements ($\dot{Q}$, $\dot{T} \neq \text{const.}$), direct TA ($T$) and its derived techniques as DTA measuring the temperature difference $\Delta T = (T - T_{\text{reference}})$ or even possibly high-temperature X-ray diffraction ($\delta$). This approach also yields the virtually new parameter $\delta$ as an entire property of a multi-component heterogeneous system which, for advanced kinetic studies, ought to be incorporated into the calculation. Consequently, for variant processes proceeding in two-phase region the values of $\xi$ and $\delta$ again contain the equilibrium parts, $\xi_{\text{eq}}$ and $\delta_{\text{eq}}$, compare eqn. (41).

For the actual interpretation of TA curves, Holba 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 $\zeta$ [eqn. (50)], temperature $T$, pressure $P$, partial pressure of volatile components $p_v^*$, total chemical composition $N^i = n^i/n^e$ and composition of product condensed phase B, $N_B^i$, i.e. $Z = \mathcal{Z}(T, P, p_v^*, N^i, N_B^i)$. Using eqn. (49) for $N^i$ and the derived derivative for $N_B^i$ we can write for the rate of the change of a measured extensive property $\mathcal{Z}$

$$\mathcal{Z} = n^e \left\{ \left[ \Delta Z^e + \sum \frac{\partial Z_A^i}{\partial N_A^i} \frac{N^i - N_B^i}{1 - \xi} \right] \xi + \xi \sum \left( \frac{\partial Z_A^e}{\partial N_B^i} - \frac{\partial Z_A^e}{\partial N_A^i} \right) \right\} n^e +$$

$$+ \frac{\partial Z^e}{\partial T} \frac{\partial \mathcal{Z}}{\partial T} + \frac{\partial Z^e}{\partial P} \frac{\partial \mathcal{Z}}{\partial P} + \frac{\partial Z^e}{\partial p_v^*} \frac{\partial \mathcal{Z}}{\partial p_v^*} + \cdots + \frac{\partial Z^e}{\partial X} \mathcal{X} \right\} n^e$$

(55)

where $Z^e = Z/n^e$ and $X$ mean, in accordance with the above symbolic, any additional intensive parameter varied from the surroundings. The term $\Delta Z^e = Z_A^e - Z_B^e$ is the integral change of $Z^e$ due to the transformation. The following term which is also multiplied by $\xi$ is of similar meaning as the extent of phase separation in eqn. (52e). The primitive proportionality $\bar{N}^e = n^e \Delta n^e \xi$, 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 $\Delta Z^e$ 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, e.g. $T = T_* + \Delta T$, $p_v^* = p_* + \Delta p^*$, etc., where $\Delta T$ and $\Delta p^*$ 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. 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 $H = \widetilde{H}(P, X, \mathcal{S}(T, P, X))$.

$$dH = V(1 - T\alpha)\frac{d}{dP} + (Y - T\alpha)\frac{d}{dX} + C_pdT$$

(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 $\mu$, $\mathcal{H}$, $E$ 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, $a_x = a_x + b_x T$ and the heat capacity as $C_p = a_c + b_c T + c_c T^2$, and after substitution and integration we obtain

$$
\Delta H = \Delta H_0 + \Delta V(1 - \Delta a_x T^2/\mathcal{2} - \Delta b_x T^3/\mathcal{3})(P - P_0) + \\
+ (\Delta Y - \Delta a_x T^2/\mathcal{2} - \Delta b_x T^3/\mathcal{3})(X - X_0) + \\
+ [\Delta a_c T - \Delta b_c T^2/\mathcal{2} - \Delta c_c/T]_T^T \delta_0
$$

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

$$
[\Delta a_c T(1 - \ln T) + \Delta b_c T - \Delta c_c/2 T^2]_T^T \delta_0.
$$

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 mechanoelectric system, cf. eqn. (28). Moreover, the partial derivative of $\Phi$ with respect to $n$ does not provide the convenient parameter $\mu$, so useful in the standard description of equilibria**. Hence, let us restrict our attention to the ordinary $\Delta H$ and $\Delta G$ 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

---

* 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. $\Delta H$ (cal mole\(^{-1}\)), $\Delta C_p$ (cal K\(^{-1}\) mole\(^{-1}\)), $\Delta S$ (e.u.), $\Delta V$ (cal bar\(^{-1}\) = cm\(^3\)/4184), etc.

** This, of course, can be helped by introducing an additional parameter $n$ into eqn. (16) thus yielding the desired term $\mu dn$ (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 $\Phi$. 

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

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

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

(58)

where $T_A$ and $T$ are the temperature of fusion and of the system, respectively, and $\Delta H_A$ is the change of standard enthalpy at $T_A$. Practical applicability and common simplifications were surveyed by, for example, Adams and Cohen. 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 $\Delta H_A$. On the other hand, if $\Delta H_A$ 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 Kirchhoff 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, Iin). The possible distortion of its rectangularity (λ-shaped and/or diffuse-like phase transformations) 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 $\phi_1$ and $\phi_2$, $\phi_3$, 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\textsuperscript{30, 31} [cf. eqn. (37)] in ordinary dynamic calorimetry\textsuperscript{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\textsuperscript{44–46}. This was quantitatively estimated by Proks\textsuperscript{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\textsuperscript{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\textsuperscript{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\textsuperscript{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\textsuperscript{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.\textsuperscript{49}. Such new, actually non-isothermal approaches to non-isothermal kinetics\textsuperscript{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.\textsuperscript{4* 5} and matured in stating the fundamental equation of TA in the form (cf. Chapter 7)\textsuperscript{1, 6}.

\begin{equation}
\dot{Q} = \dot{U} + PV - \mu i - \mathcal{H}M - E\dot{\phi} - F\dot{t} + \gamma A + \varphi C \quad (59)
\end{equation}

heat interaction with = response change of the state of TA system the surroundings (according to type of TA method)

The additional work terms, such as \(\gamma A\) and \(\varphi C\), can be chosen according to the type of TA in question, e.g. emanation TA, where \(A\), \(\gamma\), \(C\) and \(\varphi\) 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 \(\beta\), compressibility \(\mathcal{E}\), deformation \(\varepsilon\), stress \(\sigma\) or \(\tau\), force \(F\), etc.

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Irreversible thermodynamics and true thermal state dynamics in view of generalised solid-state reaction kinetics

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Abstract

Reaction dynamics of processes involving solids are extensively studied by thermal analysis methods. They are often solved almost naively by analogy with apparently gradientless homogeneous reactions. Other oversimplified approximations involve the regular shape of reacting particles that are assumed to be circles or spheres regardless of their true texture (stereology). This model never matches the results of traditional morphology observations. This article points the direction where a more rigorous solution should go by introducing a more actual state of the sample but, unfortunately, is yet unable to show the practical way how to actually bring in the challenge of entire introducing fluxes incorporation which solution makes difficult mathematical problem but it enables wide options of state of the system. Practical examples are illustrated on the flux-dependent growth of dendrites. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemical reaction; Diffusion; Solid-state; Gradients; Fluxes; Temperature fluctuation; Unstable interface; Dissipations; Irreversibility; Stereology; Bifurcations; Solidification; Undercooling; Non-equilibrium growth; Dendrites

1. Introduction

Motto: “reading literature on kinetics of solid-state processes and, in particular, the papers on non-isothermal kinetics, one cannot help noticing the similarities between Science and Religion” Brown [1].

Reaction dynamics of processes involving solids are extensively studied by thermal analysis methods [1,2], i.e. under conditions where the heat flow is supplied to or absorbed from the investigated sample by means of a surrounding thermostat which is under temperature control (regulated at constant or under spontaneous heating/cooling). There is a vast amount of data published on such “non-isothermal” kinetics of solid-state processes frequently treated on the basis of oversimplified (and customarily isothermal) modelling [3–7]. It became a subject of criticism and discussion, e.g. [1,6–11], which we do not want to repeat, other than stressing that real solid-state reactions are often too complex to be described in terms of single pairs of Arrhenius parameters and a traditional set of simple reaction orders, i.e. rational exponents representing our models of the reaction mechanism under study [4–7]. Even the participation of the most evident flux-diffusion is seldom recognised, other than by the appearance of overall (characteristic) time-dependent terms [10].

However, the modern tools of thermal physics make available powerful mathematical models associated with the reality of natural processes that are never at

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equilibrium nor without gradients by appreciating the decisive role of thermal fluxes. In the scientific intent (publications) of non-isothermal kinetics it, however, has not been applied yet but in the more urgent technological processing, such as industrially significant arc melting or welding, its solution became a real necessity to overcome feasible manufacturing difficulties. In particular, we can generally assume that at some distance from the reaction zone where the solidification is taking place, the molten material undergoes irregular (turbulent) motion. It creates a mushy zone consisting of cascade of branches and side branches of crystals and interspacial melts that remains lying between the original reactant (fluid) and the product (fully solidified region). Some chemical admixtures of the alloy solution are concentrated in the interspacial regions and ultimately segregated in the resulting microtexture pattern. Such a highly irregular microstructure of the final solid can become responsible for alternative properties, e.g. reduced mechanical strength that is a costly factor thus worthy for an active search as to resolve the intricacy of the processes involved. It follows that small changes in the surface tension, microscopic temperature fluctuations or non-steady diffusion may determine whether the growing solid looks like a snowflake or like seaweed. The subtle way in which tiny perturbations at the reacting interface are amplified then become important research topics bringing necessarily into play a higher mathematics. The challenge of theorists turns out to be the prediction of spacing of the final crystalline array which requires computations how the initially stationary flat interface accelerates in response to the moving temperature gradient, how local concentrations (e.g. impurities) adjust to this motion, how the flat interface destabilise and became branched, how the resulting crystalline twigs interact with each other and how the branched array coarseness and ultimately finds a steady-state configuration. In every details it is not an easy task at all.

A real solid-state reaction under thermoanalytical investigation, even those most ideal one, is intrinsically more complicated than most of us would like to believe. As emphasised above, we will have to deal with these complications, usually caused by actual localisation of generated heat, liquids and gases (or other freely moving products) if we are to achieve new levels of performance. The conceptual underpinnings for much of our more advanced perception of phase transformations have thus to use complicated mathematics that is curiously employed to describe both the pattern formation in crystal growth and the so called symmetry breaking (the origin and distribution of elementary particles in the early Universe). Therefore, such an intricate approach is not too welcome in the ordinary practice of chemical kinetics and its further application to daily kinetic evaluations has not been assumed as yet. Our contribution tries to point the direction where we should go but, unfortunately, is yet unable to show the practical way how to actually bring in the challenge of entire fluxes incorporation which solution thus sustains the imminent task for both the advanced research to take part during this new century and the newly educated generation of young thermodynamists to undertake it.

2. Current approach

Our originally proposed theory, based on generalised (near-equilibrium) thermodynamics applicable to thermal treatment and analysis, employed conditions of constant heating [4,11,12] (i.e. constant first derivatives, particularly those regarding the change of temperature, dT/dr, assuming that d²T/dr² = 0) supposing only the straightforward heat interaction between the sample and regulated thermostat. It does not involve the actual effect of heat liberated and/or absorbed by the reacting sample itself so that it is herewith extended to areas so far not commonly applied in the traditional domain of thermal analysis, although it is most pertinent to its feature of “real heating and/or cooling” phenomena (where the second derivatives can often be non-zero, in general notation d²x/dr² ≠ 0). Moreover, classical sphere of thermodynamic definitions of stability are inapplicable to the determination of the morphology of growing interfaces, and current extensions have not yet furnished a fully acceptable alternative. The simplest assumption made is that the morphology which appears is the one which has the maximum growth rate and/or minimum undercooling (or less commonly overheating). This assumption can be justified on the basis of minimum (non-equilibrium) entropy production. In contrast to aspects of the classical thermodynamics, these new
“true flow” features, which should be taken into account in all actually studied thermal processes are the subject of the thermodynamics of irreversible processes [12–23] and are thus the issues worthy of discussion.

Classical kinetics of solid-state reactions is mostly performed by assuming physical–geometrical model functions reflecting chemical changes at the flat reaction interface in its systematic advance into the unchanged reactant. These models are derived on the basis of a formal description of geometrically well-defined sample bodies [3–9]. It is assumed that it is possible to transfer concepts from the convenient, simple geometry of homogeneous-like kinetic models (represented by non-dimensional concentration) to idealised heterogeneous (dimension-like geometry) models [6,24,25] (represented by the surface versus volume ratio between the reactant and product phases and based on the derived representation by a dimensionless fractional degree of conversion). Space dimensionality is factually introduced through the formation of a reaction interface and the consequent possibility of multi-dimensional interfacial forward movement—called growth. However, the more adequate aspects of fractal geometry [24,26] and/or integral geometry (stereology) [27,29] have not been put into wider use as yet.

Disregarding the initial process of new phase formation (nucleation) the kinetic models are described in terms of the overall atom attachments to the reaction interface due to either chemical reaction (bond redistribution steps) or interfacial diffusion (reactant supply). A stabilised (steady) state is taken for granted neglecting, however, directional changes (fluctuations). The models also neglect other important factors such as interfacial energy (immediate curvature, capillarity) and particularly, internal/external transport of heat and mass to and from the localised reaction boundary which may result in the breakdown of planar reacting interface, which anyhow, at the end of process, often exhibits complex topology (resulting microstructure). Various activated disturbances are often amplified until a marked difference in the progress of the tips and depressions of the perturbed reacting interface occurs, making the image of resultant structures irregular (unrefinable), see Fig. 1. This creates difficulty in correlating traditional morphology observations with anticipated structures that are

Fig. 1. Initial evolution of an unstable and stable interface. Let us imagine a planar section of a reacting interface (left). During its propagation, any such interfaces will become a subject to random (spatially regular) disturbances caused by temperature fluctuations, variations of grain boundaries, curvature, insoluble subdivisions, concentration fluctuations, energy irregularities, etc. An unstable interface (upper) is distinguished from a stable interface (lower, assumed in all physical–geometrical modelling such as a contracting sphere, left) by its response to such disturbances. Projections may find themselves in a more advantageous situation for growth and therefore increase in prominence. Shadow area of the left magpie can represent either the traditionally, plainly projected and homogeneously layered product or, in our view, perturbation favoured, heterogeneous and thus morphologically vastly structured growth outcome. This is usually the best manifested during the casting of alloys, and/or rapid quenching in general, where a stable interface is only obtained in special cases, such as at the columnar solidification of pure metals or directional solidification during pulling single crystals by the stabilised methods by the Bridgeman or Czochralsk. It seems to operate for all transformations carried out at high rates of cooling/heating, or latent heat extraction/production, where the cooperative outcome of heat, mass (including decomposition products) and viscous (tension) flux initiates local instabilities. We can also meet it in everyday events of snowflakes formation.
usually very different from the originally presupposed (simple, planar) geometry. Depending on the directional growth conditions, so-called dendrites (from the Greek ‘dendros’ = tree) develop, their arms being of various orders and trunks of different spacing due to the local uneven conditions of heat supply. This process [28–34] is well known in metallurgy (quenching and casting of alloys), water and weather precipitates [35–37] (snow flakes formation, crystallisation of water in plants) but also for less frequent types of other precipitation, crystallisation and decomposition processes associated with dissipation of heat, fluids, etc.

It is always interesting to see how far the use of classical methods can be extended in this non-equilibrium situation. Growth rates, undercoolings and supersaturations are closely related by functions whose forms depend upon the process controlling growth [28,29] (the chemical reaction involved in the atomic attachment, heat and electrical conduction, or mass and viscous flow). In each case, the growth rate increases with increasing degree of undercooling and the perturbation on the reaction interface can be imagined to experience a driving force for such an accelerated growth usually expressed by the negative value of the first derivative of the Gibbs (free) energy change, $\Delta G$, with respect to distance, $r$. For small undercoolings, we can still adopt the above-mentioned concept of the constancy of the first derivatives [4,12], so that $d\Delta G$ equals to the product of the entropy change, $\Delta S$, and the temperature gradient, $\Delta T$, which is the difference between the thermodynamic temperature gradient (associated with transformation) and the heat-imposed gradient at the reaction interface as a consequence of external and internal heat fluxes. Because $\Delta S$ is often negative, a positive driving force will exist to allow perturbations to grow, only if $\Delta T$ is positive. This pseudo-thermodynamic approach gives the same result as that deduced from the concept of zone constitutional undercooling [32] and its analysis is important for the manufacturing of advanced materials (fine-metals, nano-composed assets, growth of quantum-low dimensional possessions, composites and whiskers, tailored textured configurations, growth of biological structures, processes involving water freeze-out in, e.g. cryopreservations, etc.) and thus, it is worth further and more detailed examination.

### 3. Impact of non-equilibrium thermodynamics

Any treatment of classical thermodynamics begins with some sort of statement of the principle of conservation of energy, $E$, (1st law) defining the mechanical concept of work and introducing temperature, $T$, as an integrating factor of a certain differential equations (which apparently eliminates heat from thermodynamics). If we could identify heat, $q$, with entropy, $S$, the mysterious 2nd law becomes quite intuitive and very easy to understand when imagining that heat cannot be annihilated in any real physical process. In classical thermodynamics (understood in the yet substandard notation as “thermostatics”) we generally accept for processes the non-equality $dS \geq dq/T$ accompanied by a statement to the effect that, although $dS$ is a total differential, being completely determined by the states of system, $dq$ is not. It has the very important consequence that in an isolated system $dq = 0$ and entropy has to increase. Because in isolated systems processes move forwards equilibrium, the equilibrium state corresponds to maximum entropy. In true non-equilibrium thermodynamics, the local entropy follows the formalism of extended thermodynamics [13–22] where gradients are included and small corrections to the local entropy appear due to flows making $(dS/dt) \geq (dq/dt)(1/T)$. The local increase of entropy in continuous systems can be then defined by using the local production of entropy density, $\sigma(r,t)$. For the total entropy change $dS$, consisting of internal changes and contributions due to interaction with surroundings, $i$ and $e$, we can define the local production of entropy as $\sigma(r,t)\equiv dS/dt \geq 0$. The irreversible processes obey the Prigogine evolution theorem about the minimum of the entropy production [22].

Traditionally, the phenomenological description of macroscopic systems is based on a selected number of observables accessible by macroscopic measurements. These may be intensive, $I$ (temperature $T$, pressure $P$, magnetic field $H$, etc.) or extensive, $X$ (energy $E$, entropy $S$, volume $V$, mass $m$, momentum $u$, dimensionless extent of reaction $x$, etc.). Classical thermodynamic systems at (infinitesimal $dI$ and $dX$) or near equilibrium including its extension to constant heating [4,11] (assuming real $\Delta I$ and $\Delta X$) cannot depict the often disturbing role of heat fluxes, $dq/dt$. In most real situations, we can assume local equilibrium, where thermodynamic relations remain valid.
for the thermodynamic variables assigned to an elementary volume \( \Delta V \) [14,15]. With each extensive quantity, \( X \), we can associate a density (quantity per unit volume) through the function \( x(r, t) \) dependent on position, \( r \), and time, \( t \),

\[
x(r, t) = \lim_{\Delta V \to 0} \frac{X(r, t)}{\Delta V}
\]  

(1)

For the total value of the extensive quality

\[
X(t) = \int_V x(r, t) \, dV
\]

(2)

where the space integral, \( \int_V \), extends over the volume, \( V \), occupied by the system under study.

4. Introducing fluxes

By manipulating various factors that influence the rate of change of \( X(t) \) in a non-equilibrium system, we can obtain a balance equation for the density \( x(r, t) \) by specifying hydrodynamic derivatives (d/dt a total time derivative) thus maintaining the view of continuum mechanics. The general balance of \( x(r, t) \) has the form:

\[
\frac{dx}{dt} = -\text{div} \, j_x + \sigma_x
\]

(3)

where \( \sigma_x \) is density of the source of value \( x \), and \( j_x \) is the non-convective (dissipative) part of the flux of a particular \( x \) (e.g. diffusive flux, thermal flux, viscosity flux, etc. i.e. fluxes responsible for the actual condition of a given region of the reacting interface). In the case of a mass balance or an energy balance, we have

\[
\frac{d\rho_i}{dt} = -\text{div} \, \rho_i u_i + v_i \quad \text{(mass balance)}
\]

(4)

and

\[
\rho \frac{dE}{dt} = -\text{div} \, j_E + \rho q \quad \text{(energy balance as a local form of the first law of thermodynamics)}
\]

(5)

where \( \rho \) is the total mass density and \( \rho_i \) is the partial mass density of the \( i \)th subsystem. Some other appropriate fluxes like the momentum density, \( \rho_i u_i \) (for individual velocities \( u_i \) which principally also include diffusion) or the heat flux \( j_E \), and those expressing the presence of sources or sinks, like rates of chemical reactions \( v_i \) or density of supplied heat, \( q \) may also be included. In this generalised thermodynamic view the notion of irreversibility is of the utmost importance and a local field derived from entropy must again obey the Clausius inequality. The temporal change of the total entropy \( S \) in some subsystem is due to both the interaction of the system with its surroundings (the entropy flux \( d_s S \)) and the internally produced entropy \( \langle d_s S \rangle \). Moreover, \( dS - d_s S = d_s S > 0 \). In a like manner to Eq. (3) we may write

\[
\frac{\rho dS}{dt} = -\text{div} \, j_s + \sigma (\text{local form of the second law of thermodynamics})
\]

(6)

where \( j_s \) and \( \sigma \) are the entropy flux and the entropy production per unit volume, respectively.

Let us consider the extension into the range of non-linear phenomenological laws where the balance Eqs. (3)–(6) have a general form

\[
\frac{d\Phi_i}{dt} = f_i(\{\Phi_i\}, \Psi)
\]

(7)

where \( \Phi_i \) and \( f_i \) are shorthand notations for the state variables and the rates respectively. In general, \( f_i \) are functionals of \( \{\Phi_i\} \) because they contain the effect of space derivatives. The symbol \( \Psi \) stands for a set of parameters that may enter in the description to define the process. Within the framework of linear non-equilibrium thermodynamics, the mass and entropy balance Eqs. (4) and (6) would give certain forms for \( f_i \) as summarised in Table 1 which illustrates the various type of fluxes, that can be involved.

The entropy flux \( j_s = j_E/T - \sum_i j_i u_i / T \) and the entropy production take a remarkable bilinear form

\[
\sigma = \sum_a J_a X_a,
\]

where \( J_a \) and \( X_a \) are conjugate variables known as generalised fluxes and forces associated with the various irreversible processes, see also Table 1. **Generalised forces can be viewed as the driving forces for irreversible phenomena which are manifested through the fluxes (e.g. a temperature gradient is associated with a heat flow).** Such gradients may arise transiently, or be maintained systematically, by appropriate boundary conditions (constraints) applied on the surface of the system studied. For the local formulation of irreversible processes, it is necessary to see how the fluxes \( J_a \) (which in principle are unknown quantities) are related (if at all) to the forces \( X_a \) which, according to Table 1, are known functions of the state variables.
and their gradients (we should note that the above mentioned classical equilibrium is characterised by the absence of both the macroscopic constraints, $X_{u}^\text{eq} = 0$ and travelling fluxes $J_{u}^\text{eq} = 0$).

In the linearity range of irreversible processes, the phenomenological Onsager coefficients, $L_{ab}$ [19,21], are determined by the internal structure of the system, independently of the applied constraints (but dependent on the state variables $X(t) = T, P, \ldots$) yielding $J_{a} = \sum_{b}L_{ab}X_{b}$ where $L_{ab} = (dJ_{a}/dX_{b})_{0}$, fulfilling $\sigma = \sum_{ab}L_{ab}X_{a}X_{b} > 0$. An important issue of dynamic equations is the stationary solution which describes the state of the system that is independent of time. The answer to the question of how this state remains stable during the action of small fluctuations of physical values (fluctuations are usually damped with time), lies in the criteria of stability. Linearised stability asserts asymptotic stability around its reference state, e.g. $X_{i} = X_{i,\text{ref}} + \Delta X_{i}$ (for $\Delta X_{i}/X_{i} \ll 1$) and expanded for small $\Delta X_{i}$ we obtain, in abstract notation, $d(\Delta x)/dt = L\Delta x$, where $L$ is a linear operator and the problem is solved by determining so called eigenfunctions and eigenvalues of $L$ and the unseen characteristic parameters $m$. The reference state is asymptotically stable for most $m$ but, for some $m$, the solution of such a thermodynamic branch is unstable and, for critical values of $\Psi_{\text{crit}}$, bifurcation appears, in other words, several quite different evolutions of the system are possible and that which is realised depends on $\Psi$ in a non-analytical fashion (a special domain of non-linear mathematics).

5. Stereology aspects

In the special case of non-isothermal reaction kinetics, which regularly involves solid-state processes, the rate equations are often solved almost naively by analogy with apparently gradientless homogeneous reactions. Other oversimplified approximations (as mentioned above where reacting particles are often assumed to be regular circles or spheres regardless of their true morphology) are introduced that never match the results of traditional morphology measurements by, e.g. light or electron microscopy. This is worth of similar attention, being related to the above discussed case of disregarded temperature and concentration gradients. This simplification aspect is often neglected, although very important, because we have to keep in mind that all possible images (postulated geometrical models or real structures seen on a screen, or otherwise observed) are only two-dimensional representations of the real three-dimensional structures. For a more objective evaluation of the numerical characteristics of real geometrical bodies we, therefore, have to employ so called stereology, understood here as integral geometry.

Invariant measures of the internal configuration of a multiphase body (where individual phases $A, B, \ldots$, internally form three-dimensional structures must fulfil three basic criteria: invariance of motion, additivity and monotony which corresponds to a mathematical hypothesis based on the four Minkowski functionals [29] (quermass integrals or measures) abbreviated as $W_{i}$. These measures have, for each $i$, a definite practical meaning, i.e. volume of $A$, $W_{0}$, mean area (surface), $W_{1}$, length, $W_{2}$ and number of disjunctive features of $A$ (e.g. number of opened against closed structural holes), $W_{3}$, needed for a global geometrical characterisation $M$. It follows that $M_{i}^{j}(A) = \sum c_{i}W_{i}^{j}(A)$ where each $W_{i}^{j}(A)$ is a homogeneous functional of the root $(3 - i)$ and $M_{i}^{j}(A)$ is then a monotonous functional ($c_{i} > 1$). For actual calculations, the two-dimensionally screened images
can be used bearing in mind, however, that these evaluations are only statistical. The solution is based on the utilisation of so-called symmetrical functions of curvature, $C^i_{i=1,2,3}$, providing the relations for mean curvature ($C^0_0 = 1$), Gaussian curvature ($C^0_i = (k_1 + k_2)/2$) and fundamental curvature ($C^2_i = 1/(k_1 k_2)$), where $k_1 = 1/\rho_{\text{min}}$ and $k_2 = 1/\rho_{\text{max}}$ are the main curvatures for minimal and maximal radius of the oscillation circles in a given infinitesimal element of the measured phase surface $\partial A$. Objective proofs of stereological relations are difficult, but the resultant relations reveal surprising simplicity. A convenient universal relation is based on the so-called Kubota’s recurrent formula [28] showing that $W^0_0(A) \Rightarrow V(A)$ (i.e. approaches the $n$-dimensional volume of $A$ in the sample space $E$) which is the mean value of the $W^{n-1}_{i-1}$ for all projections of the phase $A$ onto the linear subspace with a lower dimension $(n-i)$, providing more generalised values of coefficients $\sigma_{0,1,2,3} = 2\pi$, $4\pi$ and $2\pi^2$. From measurements in a random section (planar or linear probes or random points) of the investigated structure, we can obtain concrete values of the quantities introduced in Table 2 and illustrated in Fig. 2.

It is clear that introduction of the actual state of the system, either real body structures or imposed gradients, is not easy. The introduction of legitimate non-equilibrium phenomena in the non-linear range leads to new regimes differing quantitatively from the “reference” stationary states of regular equilibrium or near-equilibrium descriptions.

6. Dissipative structures

The question that arises is, therefore, whether the move away from a standard configuration can lead to states displaying spatial or temporal order. We call these regimes dissipative structures to show that they can only exist in conjunction with their environment and if influence constraints are relaxed and the system is allowed to approach equilibrium, the entire organisation will collapse. They can form only in open systems far from equilibrium and dynamic equations have to be non-linear. The best example comes from fluid dynamics when a horizontal fluid layer is heated from below. When the temperature gradient remains small with respect to some characteristic values, heat passes through the fluid by conduction. As the heating is intensified, however, at a certain well-defined critical temperature the gradient pattern (regular due to convention) changes spontaneously, being organised in a cell-like fashion. This high degree of molecular/cell organisation becomes possible through transfer of

![Fig. 2](image-url) Stereology view. Left, internal structure of a three-dimensional sample; right, graphical connotation of the stereological quantities for planar $L_i^3$ and linear $L_i^1$ probes (cf. Table 2).
energy from thermal motion to macroscopic convection currents. A similar situation can occur at a reaction interface under the cooperative action of thermal and concentration gradients, within yet unreacted layer of reactants (solidification). Other examples are the Belousov–Zhabotinsky reaction [39] or the variety of biophysical signals emitted by living cells to control a number of key processes.

Let us analyse the simplest cases of bifurcation. Higher-order non-linearities, by involving two or more variables in connection with spatially inhomogeneous systems, give rise to more complex phenomena. The best examples are systems controlled by simultaneous chemical reactions and mass diffusion. Their evaluation is given by Eq. (3), with the additional assumption that the diffusion flux $j_i$ is approximated by Fick’s law, a special form of the linear phenomenological laws given in Table 1, that is

$$j_i = -D_i \nabla \rho_i$$

(8)

where $\nabla$ is the above mentioned space derivative and $D_i$ are the diffusion coefficients which are in the first approximation, assumed constant. The reactions rates, $w_{\rho_i}$, are (generally non-linear) functions of the concentrations (often in a cubic manner). This gives rise to the following evolution equation

$$\frac{d\rho_i}{dt} = \nu_i \left( \sum_j \rho_j, \Psi \right) + D_i \nabla^2 \rho_i$$

(9)

where $\Psi$ denotes again a set of parameters descriptive of the system (e.g. initial composition, cooling rate, undercooling, characteristic lengths, etc.). When $\Psi = \Psi_{\text{crit}}$, the state of the system may change dramatically causing the symmetry breaking in space and time. From the mathematical point of view, the system becomes localised at the thermodynamic branch and the initially stable solution of the appropriate balance equation bifurcates. New stable solutions suddenly appear and may overlap. One possibility is time-symmetry breaking, associated with the merging of time-periodic solutions known as limit cycles whose period and amplitude are stable and independent of the initial conditions. Their importance lies in the fact that they can constitute models of rhythmic phenomena observed in nature, particularly biological or chemical clocks. Cascading bifurcations are also possible. This opens the way to a gradual increase of complexity by a mechanism of successive transitions, leading either to the loss of stability of a primary branch and the subsequent evolution to a secondary solution displaying asymmetry in space similar to stable rotating waves as observed in the classical Belousov–Zhabotinsky reaction [38,39]. Such transitions are sometimes accompanied by some remarkable trends, e.g. certain classes of reaction-diffusion systems under zero-flux boundary conditions, may exhibit no net entropy production change when the system switches from the thermodynamic branch to a dissipative structure. On the other hand, there is a systematic decrease in entropy in the vicinity of bifurcation points. Associated fields are the theory of chaos [40–43], fractals [44] and some aspects of the prediction of weather [35].

7. The chaotic case of dendritic growth

One of the most practical applications is the highly non-equilibrium crystallisation of highly supersaturated solutions or, as mentioned above, any solidification of rapidly quenched alloys. They exhibit a free dendritic growth, i.e. unconstrained development of curious shapes of crystals precipitating within concentration or temperature gradients (mostly in undercooled melt). This phenomenon has long been known in the technology of the crystal growth and is exemplified in the formation of cellular structures [27]. Explanation of this complex phenomena is usually done in terms of constitutional undercooling, $\Delta T$, and its thermodynamic meaning is associated with the local equilibrium temperature of the melt solidification in an arbitrary point near the solidification front. It corresponds to a local concentration in the melt which is higher than that for the actual temperature in the same point. Consequently, the disturbance of the solidification front spontaneously increases and the phase interface become unstable, see Fig. 3.

The formation of a dendrite begins with the breakdown of an unstable planar solid/liquid interface, cf. Fig. 1. Perturbations are amplified until a marked difference in growth of the tips and depressions occurs. The temperature gradient must be deformed in the liquid at the tip increases, while that in the solid decreases. Therefore, more heat will flow into the tip and less will flow out of it. Meanwhile, the reverse
Fig. 3. The conditions of dendritic growth. The right diagrams illustrate the reacting front geometry (upper), temperature (bottom) and concentration (middle) fields resulting in dendrite growth. $T_a$ is the temperature field in the system, $T_e$ the equilibrium temperature of solidification; $T^*$ the growth temperature, $T_l$ the temperature of liquidus, $C_0$ the concentration in the liquid phase, $\Delta C^*$ the supersaturation (as a length of the tie-line at the temperature tip), $G$ the temperature gradient and $mG_0$ the gradient of liquidus (1). In pure substances with the plane ($C_0 = 0$ and $G > 0$) or equiaxed ($C_0 = 0$ and $G < 0$) front dendrites can grow in an undercooled melt only. The necessary condition of dendritic growth in binary systems is a constitutional undercooling, illustrated for both the columnar (dashed, $C_0 > 0$ and $mG_0 > G > 0$) and equiaxed ($C_0 > 0$ and $G < 0$) conditions. When a positive gradient of temperature ($G > 0$) is imposed (such as directional columnar solidification) the latent heat is transported together with unidirectional heat flux into the solid(s). When heat is extracted through the solid the solute diffusion will be the limiting factor only. $\Delta T_e$ see phase diagram left, factually provides the degree of supersaturation, $\Delta C/\Delta C^*$, but its determination is also a function of other parameters and requires its evaluation by a set of differential equations. The simplest solution is obtained when the tip morphology is supposed to be hemispherical, instead, the real form of the dendrite tip is best represented by a paraboloid of revolution. Due to the anisotropy the dendrite will grow in the preferred crystallographic direction which is closest to the heat flow, $J_B$, whereas cells grow with their axes parallel to the heat flow direction without regard to the crystal orientation (e.g. marked [0 0 1]). In the opposite case of one component system the heat is rejected at the interface of a tip into the liquid phase. Consequently, the equiaxial dendrites emerge in solid phase.

situation occurs in the depressions forcing perturbations to be damped out. Moreover, the equilibrium temperature at the interface, determined mainly by composition, is changed as a consequence of the local interface curvature. Because the tip can also reject solute in the lateral direction, it will tend to grow more rapidly than a depression, which tends to accumulate the excess solute rejected by the tips. Therefore, the form of the perturbation is no longer (initially) sinusoidal but adopts the form of cells which are ellipsoid-like crystals growing anti-parallel to the net flux direction. If the growth conditions continue close to the limit of constitutional undercooling of the corresponding planar interface, tree-like formation occurs and the cells rapidly change to dendrites, which then exhibit secondary arms and crystallographically governed growth directions. If the heat extraction is isotropic, dendritic growth is equiaxial. For a single dendrite, a short parabolic tip region can be observed which often constitutes less than 1% of the length of the whole dendrite and perturbation appear on the initially smooth needle as in the case of the breakdown of the originally discussed planar interface. If the primary spacing is sufficiently great, these cell-like secondary branches will develop into dendrite-type branches and thus leads to the formation of tertiary and higher-order arms. When the tips of the branches encounter the diffusion field of the arms of neighboring dendrite, they will stop growing and begin to ripen and thicken. Beside the normal temperature gradients discussed above, the radial temperature gradient can also be accounted through convention usually originating by the non-homogeneous distribution of the mass density throughout the fluid (Rayleigh–Bernard instability [29,34]) or by variation of the surface tension of free surfaces (Marangoni convection [29,34]) for the densities differences between phases or by electromagnetic forces (electrophoresis). Numerical computations provided both a long-wave convective instability or short-wave bifurcations.
These diffusion processes are driven by gradients in the liquid which are in turn due to temperature on the interface. The interface temperature is related to the interface composition, the surface curvature and the departure of interface from local equilibrium. The last contributions are curvature undercooling, composition and kinetic undercoolings. The ratio of the change in concentration at the tip to the equilibrium concentration difference is known as supersaturation and represents the driving force for the diffusion. The form of the tip is affected by the distribution of the rejected heat or solute and interactions makes the development of an exact theory extremely complex, usually involving an exponential integral (known from nonisothermal evaluation procedures [4]). The methods of the perturbation analysis were introduced into crystal growth theory by Mullins and Sekerka [33] who expressed the deviations from the spherical form in terms of spatial functions $Y_{im}(\Theta, \phi)$

$$R = r_0(t) + \delta(t)Y_{lm}(\Theta, \phi)$$  \hspace{1cm} (10)

where $r_0$ is the radius of the unperturbed sphere, $\delta(t)$ the time-dependent amplitude of the perturbation and $R$ is the distance of the perturbed surface from sphere centre. It was assumed that the principle of local thermodynamic equilibrium is satisfied. Relationships describing the rate of change of the perturbation amplitude were derived. This quantity determines the stability conditions of the growing interface: when $d\delta/dt > 0$, than the perturbations are amplified and the growth process is unstable.

More complex equations of perturbation balance of the discontinuity interface were derived within the framework of the linear approach. Generalised conditions for the heat transport at a curved interface have the form

$$v_N[\rho c_T + (\rho c_T)_S]$$

$$= D_S \frac{\partial T_S}{\partial n} - D_L \frac{\partial T_L}{\partial n} v_N[Q + CM(f_S - f)]$$  \hspace{1cm} (11)

where $C_M$ is twice the mean curvature of the solidification front, $v_N$ is the normal component of the growth rate, $(f_S - f)$ is the difference between Gibbs and surface energy, $D_{1,s}$ is the diffusion coefficients in the liquid (L) and solid (S) phases, $T_{1,s}$ is appropriate temperatures on interface, $\rho$ is density and $c$ is heat capacity. All the derivatives are taken with respect to the direction normal to the interface. Since the surface energy can be expressed in terms of interface entropy, the last term on the right hand side of Eq. (11) destabilizes the system for negative values of the surface entropy (and vice versa).

The applications of linear and also non-linear morphological stability theory to diverse areas of crystal growth are developing rapidly. Any steady-state description of dendritic growth ignores the rather obvious fact that dendrites are inherently time-dependent structures. The dendritic side branches also appear to be oscillatory in time and space. These important morphological and dynamical properties of dendrites suggest that a dendrite might be better treated as a dynamical phase transformation displaying time-dependent behaviour. So, dendritic growth may represent an example of self-organising formation phenomena, which is a deeply researched subject within the broader field of nonlinear dynamics and dissipative phase formation [29,39]. The effect of temperature flow can affect the degree of ordering of certain directionally solidified eutectics to produce a characteristic growth of well-organised lamellae [27,28] and can be found in directionally grown composites, layered products of decompositions, etc.

8. Conclusion

It is clear that above-mentioned, single-value characterisation of non-equilibrium processes [11,40,44] is not fully agreeable and thus needs to undergo modifications to match another style of presentation adequate to the modern level of scientific treatments available. Some progress was achieved in the determination of activation energy $E_A$ of reaction in theories, in which the temperature gradient, temperature dependence of $E_A$ or competitive processes were assumed [45–47]. But it should be brought into concurrence with the description of fluxes, in particular, with the ever-participating heat flux that is involved in all thermophysical measurements that employ higher rates of temperature changes. During such a non-equilibrium (or even “thermodynamically near-equilibrium”) processing the resulting overall reaction rate is determined not only by kinetic processes taking place at the phase interface (usually characterizable by some set of constants) but also by the nearby mass and energy transport. Both features combine their course
of action in a complex manner, because the transport properties determine the conditions on the entire phase interface and, vice versa, the depletion of interfacial reactants controls the strength of the fluxes. The kinetics of phase transformations is thus influenced by the neighbouring temperature, stress, concentration and similar distribution gradients both across and along the reaction interface. Thus, it is necessary to bring all processes together in one model, which is capable of describing the evolution of the system as a whole. Such a model of the total process needs to be described by a set of functions of time and space coordinates yet inconvenient in our, so far common, kinetic language.

As an example of such functions resulting from non-linear theories of diffusion or heat conduction we can mention the following relations [48,49]:

\[
\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left[ D_1(x) \frac{\partial \rho}{\partial x} + D_2(x) \left( \frac{\partial \rho}{\partial x} \right)^2 \right]
\] (12)

\[
\tau \frac{\partial^2 \rho}{\partial t^2} + \frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}
\] (13)

\[
\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left( \int_0^{t'} dt' \int_{-\infty}^{x'} dx' D(t - t', x - x') \frac{\partial \rho}{\partial x} \right)
\] (14)

Eq. (12) reflects the dependence of the fluxes on the quadrature of the density gradient (by coefficient \(D_2\)). During the derivation of the next Eq. (13), the relaxation of fluctuated fluxes to the value given by the Fick law was supposed. The relaxation time of this process is \(\tau\). The Eq. (14) introduces the generalised diffusion coefficient \(D(t,x)\) which described non-local dependence of fluxes on the density gradients and on history of the density profiles. It would be also interesting to see this classical diffusion process in relation to quantum mechanics [39,50–52] which would be the subject of our next communication.

In the view of our thermoanalytical practice, the expected results in terms of functions instead of the traditional constants would, however, be quit unfamiliar but we need to get acquainted with them when facing the new prospects of the 21st century. It, in fact, would be better to match the real thermal state dynamics than to use the old representation in terms of customary and almost “religious” constants [1] mostly linked with the activation energy that never express the ease of reaction (desirably to be related to the reactivity “tolerance” and mechanism “annexion”). High values of activation energies are often misleading when determining the character of the process investigated, because high values do not mean difficult reactivity (e.g. spontaneous and rapid exothermic crystallisation) and low values do not imply easy reactivity (e.g. for habitually slow diffusional processes). The interpretation is exactly the other, example is the repeatedly studied case of the reversible CaCO\(_3\) decomposition, which is strongly mass and heat flow dependent (CO\(_2\) partial pressure and diffusion as well as its due concentration gradients created within the solid).

The related classical kinetic analysis is thus generating the numberless figures of almost insignificant values of activation energies [3,4] strongly dependent on the experimental conditions applied.

From the experimental point of view it means that we must complete our thermal analysis by the methods describing more details about the resulting material. We often require to determine chemical composition of phases and their distribution in sample (by energy dispersive analysis of X-rays, or wave dispersive analysis of X-rays, by X-ray microanalysis or electron probe microanalysis). Important information is given by the geometrical relations between all phases present in the system as well as geometrical properties of any individual phase. In this respect the best results can be obtained by image processing and stereology of images obtained by electron microscopy or STM, AFM, etc. The structure and texture of resulting phase depend on conditions of phase transformation process, on its stability and the particular course. The analysis of relations between these conditions (actual temperature, cooling rates, volume and geometry of sample, variable external fields, etc.) and changes of resulting phase properties contribute to the real description of reaction kinetics. As an example of the dependence of solid phase transitions on the thermal conditions is the transformation amorphous—microcrystalline or polycrystalline silicon [55].

The flux approach discussed above was assumed to be important as early as during the 1974 NATAS/Mettler award lecture “Rational approach to the study of processes by thermal analysis” [44] and expanded upon our review [28] and book [29] by introducing a new discipline entitled “kinetic phase diagrams”. The concept of heat allocation may also be recognised as an integrating element in the pathway of ordering not
only matter, but also society [53,54] supporting our better understanding of both our environment and the science of nature in general.

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References

A theoretical analysis of the formation of materials with metastable microstructures under non-ideal and highly non-equilibrium conditions is presented.

The most important processes in material engineering include crystal growth or dissolution from multicomponent (usually high-temperature) solutions. Selection of the most suitable conditions for obtaining a controlled type of crystalline (or even non-crystalline) materials requires a good knowledge of the heterogeneous equilibria between the solid and liquid phases, conveniently collected graphically in the form of phase diagrams. The most widespread are those diagrams describing the equilibrium dependence of the composition upon the temperature, but this is not easy to achieve experimentally [1]. In technology we can practically control or present (or often leave undefined) many parameters as follows:

— Chemical and physical properties of the sample (composition, compactness, homogeneity, impurity, diffusivity, viscosity or even prenuclei sites or mechanical tensions).

— External forces (temperature, pressure, partial pressure, or electromagnetic, hydrostatic or gravitational force fields) and their changes (heating or cooling, convection, atmospheric composition and hydrodynamics and associated flows).

— Sample geometry, including the factors affecting the heat exchange, sink and generation, the extent of volatile component exchange, the interactions between interfaces and/or with the surroundings or with the measuring head.

Furthermore, the classical approach to the study of phase equilibria by long annealing at increased temperature is generally found to be tedious and experimentally demanding. Therefore, dynamic techniques are often preferred as more convenient, in which the tempered sample is investigated in the freeze—in state after a suitable rapid quenching and/or during the entire programmed cooling. A detailed consideration of all the peculiarities involved in such a non-equilibrium procedure is definitely required. It can be verified that for fast enough processes,
occurring, for instance, in metals and alloys, near-equilibrium conditions can be assumed even at the relatively high cooling rate of $10^2$ degree $s^{-1}$, whereas for the very slow diffusional or viscous processes in silicate systems the cooling rate must be as low as $10^{-4}$ degree $s^{-1}$, and to avoid undercooling (or even limiting glass-formation) equilibration of the order of weeks may be required.

To look for materials with desired (specific) properties, we certainly have to use phase diagrams which correspond to non-equilibrium conditions of their preparation, which provide us with the necessary information of possible thermodynamic stability, metastability and even instability under the assumed standard (equilibrium) conditions. There is increased interest in the mathematical analysis and synthesis of such "kinetic" phase diagrams. Besides the classical requirements if the minima and equality of the Gibbs energies of the individual components of the coexisting stable phases, we have to assume the same for the metastable phases occurring at higher energy levels (and different compositions) than for the stable phases, the latter not being achieved due to the kinetic hindrance of new phase formation (nucleation). For the sake of practical use, metastable boundaries can be predicted by a simple extrapolation of the coexistence lines for the stable states into non-equilibrium regions, usually down to lower temperatures. Alternatively, the preliminary shapes of metastable lines can be estimated from a superposition of two corresponding (e.g. simple eutectic) phase diagrams [2]. This is of considerable importance for all dynamic methods (from thermal analysis to sample quenching) for the correct interpretation of the phases observed.

For a system which cannot follow the experimentally enforced (strong) changes, even by establishing the previously discussed metastable equilibria, the boundary lines shift freely along both the concentration and temperature axes, forming thereby the regions of unstable phases to be described in terms of the kinetics of the physico-chemical processes. Such a truly kinetic phase diagram is fully dependent upon the experimental conditions applied (cooling rate, sample geometry and measuring conditions) and can be best treated mathematically in the case of a stationary process conditioning. Paper [6] summarizes the results attained in this field by using the solution of the kinetic equations (Focker-Planck equation) or the Monte-Carlo method. The new method for the description of kinetic phase diagrams based on the stochastic process theory [7, 10] enables us to describe non-stationary processes too. These include such phenomena as "coring" and "surrounding" (see (1)), known long ago in metallurgical engineering, explaining the concentration-dependences across the grains precipitated in the vicinity of hypoeutectic points, respectively.

The kinetic phase diagrams can be used for the description of the processes connected with the preparation of metallic glasses ($10^3$–$10^7$ degree $s^{-1}$) or with the photon, electron or ion beam processing of the surfaces of many materials. The

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cooling rates reached during, for example the laser glassing of metals, can be as fast as of the order of $10^{10}$ degree s$^{-1}$, yielding associated processes of phase formation that are very highly non-equilibrium.

In the case of the non-stationary processes, the composition of the solid phase changes with time as well as the local cooling rate and degree of undercooling at the phase interfaces. Mathematical treatment is then extremely difficult, requiring a joint solution of the equations for heat and mass transfer under given boundary conditions, and the kinetic equations describing the kinetics of the phase transformation on the solidification front. Evaluations under the stochastic theory yield interesting dependences between the undercooling, concentration, linear growth rate and cooling rate (see [5, 8, 10]). The results for Cu—Ni alloy and similar systems are demonstrated in Table 1. For instance, if the cooling rate $R$ increases, the difference in the concentrations of the solid and the liquid phase decreases and tends to zero. This result can simulate the creation of the amorphous phase during rapid cooling.

Not less important in the theoretical treatment is the thermochemistry of mixtures and solid solutions. For example, with regular solutions ($\Delta H^\text{ex} \gg T \Delta S^\text{ex}$), interactions decisive for the system behaviour take place between spherical species

<table>
<thead>
<tr>
<th>Change of values</th>
<th>Temperature on the solidification front, $T$</th>
<th>Undercooling, $\Delta T$</th>
<th>Concentration of the liquid phase, $C_{\text{liq}}$</th>
<th>Concentration difference on the solidification front, $C_{\text{liq}} - C_{\text{sol}}$</th>
<th>Growth rate of solid phase formation, $G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase values</td>
<td>Increase to equilibrium value</td>
<td>Intensive decreases</td>
<td>Decreases</td>
<td>Decreases</td>
<td>Nonlinear increases</td>
</tr>
<tr>
<td>Cooling rate, $R$</td>
<td>$(10^3 \rightarrow 10^6$ Ks$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient, $D$</td>
<td>$(10^{-7} \rightarrow 10^{-3}$ m$^2$ s$^{-1}$)</td>
<td>Decreases</td>
<td>Increases</td>
<td>Increases</td>
<td>Increases</td>
</tr>
<tr>
<td>Kinetic coefficient, $k$</td>
<td>$(10^6 \rightarrow 10^{17}$ s$^{-1}$)</td>
<td>Increases to equilibrium</td>
<td>Decreases</td>
<td>Decreases</td>
<td>Increases</td>
</tr>
</tbody>
</table>

* i.e. rate constant of the front solidification including thermal vibration of molecules, probability of molecules incorporation into solid phase dependent on temperature, interface energy barrier and the difference of Gibbs energy of both phases.
Table 2 Gibbs energy $\Delta G_{\text{mix}} (= \Delta H^{\text{id}} + \Delta S^{\text{id}} + \Delta H^{\text{ex}} + \Delta S^{\text{ex}})$ for binary mixture $(A + B)$ assuming different models of the system nonideality

<table>
<thead>
<tr>
<th>Name</th>
<th>$\Delta H^{\text{ex}}$</th>
<th>$\Delta S^{\text{ex}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ideal</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>athermal</td>
<td>$x_A \ln (x_A + \Omega_A x_B) + x_B \ln (x_B + \Omega_B x_A)$</td>
<td></td>
</tr>
<tr>
<td>regular</td>
<td>$\Omega_R$</td>
<td>0</td>
</tr>
<tr>
<td>subregular</td>
<td>$\Omega_R \cdot \Omega_S$</td>
<td>0</td>
</tr>
<tr>
<td>pseudoregular</td>
<td>$\Omega_R / \Omega_S$</td>
<td>0</td>
</tr>
<tr>
<td>quaziregular</td>
<td>$\Omega_R \cdot \Omega_S$</td>
<td>0</td>
</tr>
<tr>
<td>quazisubregular</td>
<td>$\Omega_R \cdot \Omega_S \cdot \Omega_T$</td>
<td></td>
</tr>
<tr>
<td>quazipseudosubregular</td>
<td>$\Omega_R \cdot \Omega_S / \Omega_T$</td>
<td></td>
</tr>
</tbody>
</table>

Where $T$, $\Delta H$, $\Delta S$, $\Omega$ and $x$ are temperature, enthalpy and entropy change, interaction parameter and mole fraction, respectively, for ideal (id) and excess (ex) quantities. Read $\Delta H^{\text{id}} = 0$, $\Delta S^{\text{id}} = x_A \ln x_A + x_B \ln x_B$, $\Omega_A = \Omega x_A x_B$, $\Omega_S = (1 + \Omega x_A x_B)$, and $\Omega_T = (1 - \Omega x_A x_B)$.

of (molecular) mixtures of metals (see Table 2), whereas for the decisive effect of the mutual arrangement of usually geometrically complicated species of polymers and silicates we have to take up athermal solutions ($\Delta H^{\text{ex}} \ll T\Delta S^{\text{ex}}$). A specific case of ionic (Temkin) solutions requires the incorporation of energetically unequal sites in the solid-state network into the above concept of regular solutions. This is usually true for oxides where, for example, energetically unequal (disparate) tetrahedral $(i)$ and octahedral $(j)$ sites are occupied on different levels of the species $A$ and $B$, so that the ordinary term $x_A \ln x_A$ must be read as the term $\sum x_{Aij} \ln x_{Aij}$, etc.

For the sake of practical applicability, a graphical form of the above effects is shown for the case of a hypothetical phase diagram of a binary mixture of $A$ and $B$. Under the conditions of ultrafast cooling, the phase boundary is depressed to lower temperatures (see Fig. 1b), to be observed experimentally later in a position not associated with that normally called the equilibrium phase boundary (Fig. 1a). If the chemical phases of the system (in Fig. 1a) change in such a way that the mixing of components $A$ and $B$ is accompanied by a large enthalpy change due to strong interactions between $A$ and $B$ solutions (see Table 2), a eutectic point [1] emerges. For still intensive interactions, a more complicated form may occur, exhibiting peritectic compound $C$. Such a type of phase diagram (see Fig. 1c) is illustrative to show possible consequences of phase metastability represented by dashed lines. If the solidified compositions of this system are reheated, phase boundaries corresponding to metastable phases are often observed, making correct interpretation of the experimental data difficult; this is particularly true for thermoanalytical measurements [9] (e.g. DTA).

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Possible shifts and extrapolations in a hypothetical phase diagram of binary mixture $A$ and $B$.

- a - near-ideal behaviour of solid-liquid curves with solid-solid phase separation at bottom;
- b - shift of original (solid) phase boundaries to nonequilibrium (dashed) ones due to the effect of ultrafast cooling (cf. Table 1) exhibiting the consequences of preparation technology;
- c - possible change of the structure of phase boundaries when accounting chemical effect of strong interactions (cf. Table 2) between two components $A$ and $B$ to exhibit eutectic and peritectic points and incongruently melting compound $C$. It results from the system nonideality;
- d - inclusion of metastable phase boundaries (dashed lines) by extrapolation of equilibrium (solid) lines. It shows all possible stable and metastable states available at the system to occur as combined effect of system nonideality and experimental conditions of its treatment; e - possible experimental result while studying such a system (d) by thermal analysis upon heating. By fitting hypothetical experimental points (dots) the lines can assume a form of two separated, eutectic-type diagrams of the $A$ component with $B$ superposed to that of $A$ with $C$. It is worth noting that the both experimentally detected horizontal lines must not necessarily represent stable phase boundary being often a source of false interpretation. Whatmore any of metastable boundary lines may appear as a potential source of an effect detectable by a given thermoanalytical technique in a more or less pronounced (or negligible) form depending on the sample history.

References


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Zusammenfassung — Es wird eine theoretische Untersuchung der Bildung von Stoffen mit metastabilen Mikrostrukturen unter nichtidealen Bedingungen weitab vom Gleichgewicht dargelegt.

Резюме — Представлен теоретический анализ образования веществ с метастабильными микроструктурами в неидеальных и сильно неравновесных условиях.