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RATIONAL APPROACH TO THERMODYNAMIC RROCESSES 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 α 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 Tannei [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

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \left(\frac{\partial C}{\partial t}\right)_T + \left(\frac{\partial C}{\partial T}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t}. \tag{1}$$

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 equation. By assuming that the degree of reaction*, α, 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 α 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:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \left(\frac{\partial C}{\partial t}\right)_V + \left(\frac{\partial C}{\partial V}\right)_t \frac{\mathrm{d}V}{\mathrm{d}t} \tag{2}$$

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, $\mathrm{d}\alpha/\mathrm{d}t$, is proportional to the product of two separate functions; the first, $k(T)$, is temperature-dependent, and the second, $f(\alpha)$, is related to α only:

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha)\,. \tag{3}$$

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 α 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 α, as the solution of a special form of the differential equation (3), $\mathrm{d}\alpha/\mathrm{d}t = k(T)\alpha$, 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.

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* 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 α, by the equation

$$\alpha(t) = [C(t) - C_0]/[C_\infty - C_0]$$

where subscripts indicate the value of C at the initial time ($t = 0$) and at $t \rightarrow \infty$. The case where C_∞ 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 al 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 α, 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 α, 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 $T(t) = K =$ 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

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* 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.

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.

$$\mathrm{d}\alpha/\mathrm{d}t = F(\alpha, T) \tag{4}$$

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

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

$$\mathrm{d}\alpha/\mathrm{d}t = F(\alpha, K)\,. \tag{5}$$

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

$$\alpha(t) = \hat{\alpha}(t, K)\text{*}\,. \tag{6}$$

We may write formally

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\hat{\alpha}}{\partial t}\right)_{\mathrm{K}} + \left(\frac{\partial\hat{\alpha}}{\partial K}\right)_{\mathrm{t}} \frac{\mathrm{d}K}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_{\mathrm{K}}\,. \tag{7}$$

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

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

$$(\mathrm{d}\alpha/\mathrm{d}t) = F(t, K't)\,. \tag{8}$$

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

$$\alpha(t) = \tilde{\alpha}(t, K') \tag{9}$$

and we may proceed

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\tilde{\alpha}}{\partial t}\right)_{\mathrm{K'}} + \left(\frac{\partial\tilde{\alpha}}{\partial K'}\right)_{\mathrm{t}} \frac{\mathrm{d}K'}{\mathrm{d}t} = \left(\frac{\partial\tilde{\alpha}}{\partial t}\right)_{\mathrm{K'}}. \tag{10}$$

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* Note that the superposed caret in α serves to distinguish this function from its value.

(the illustration of which is given in Fig. 1). Similarly to Eq. (7) $\mathrm{d}K'/\mathrm{d}t = 0$ according to the assumption that K' is a constant for a linear process and $(\partial\tilde{\alpha}/\partial K')_t$ indicates the change in α in two infinitesimally close processes differing by $\mathrm{d}K'$ (see Fig. 1).

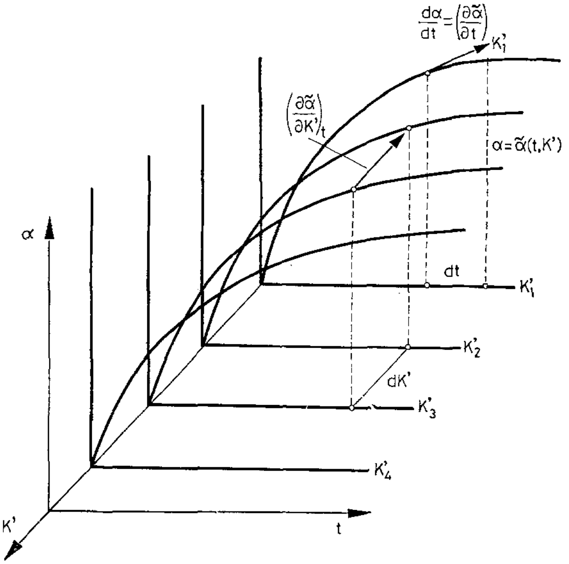

Fig. 1. Diagrammatic representation of the system $\alpha = \tilde{\alpha}(t, K')$

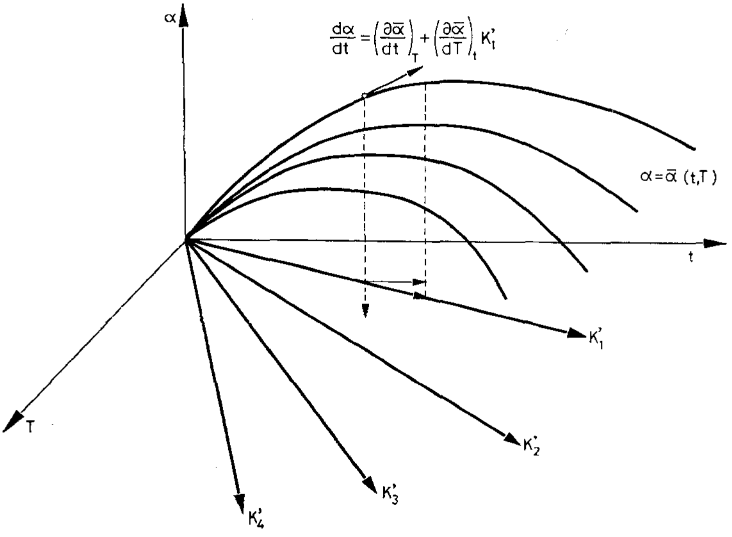

Fig. 2. Diagrammatic representation of the system $\alpha = \bar{\alpha}(t, T)$

However, the solution of Eq. (8) may also be obtained in the form

$$\alpha(t) = \tilde{\alpha}(t, T/t) \ \mathit{def.} = \ \bar{\alpha}(t, T) \tag{11}$$

using $K' = T/t$. The function $\bar{\alpha}$ for given values of t and T yields the value of α at t in the linear process characterised by $K' = T/t$. In terms of $\bar{\alpha}$ we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\bar{\alpha}}{\partial t}\right)_{\mathrm{T}} + \left(\frac{\partial\bar{\alpha}}{\partial T}\right)_{\mathrm{t}} \frac{\mathrm{d}T}{\mathrm{d}t} = \left(\frac{\partial\bar{\alpha}}{\partial t}\right)_{\mathrm{T}} + \left(\frac{\partial\bar{\alpha}}{\partial T}\right)_{\mathrm{t}} K' \tag{12}$$

(as graphically demonstrated in Fig. 2). In Eq. (12) both partial derivatives are generally non-zero, and $(\partial\bar{\alpha}/\partial t)_{\mathrm{T}}$ means the change of α if we replace the process K' at t with the process $K' + \mathrm{d}K' \left(= T/(t + \mathrm{d}t)\right)$ at $t + \mathrm{d}t$ (see Fig. 3b). Accordingly, $(\partial\bar{\alpha}/\partial T)_{\mathrm{t}}$ reflects the change of α at t if we replace the process K' at T/t with the process $K' + \mathrm{d}K'$ (where $\mathrm{d}K' = \mathrm{d}T/t$) (see Fig. 3a).

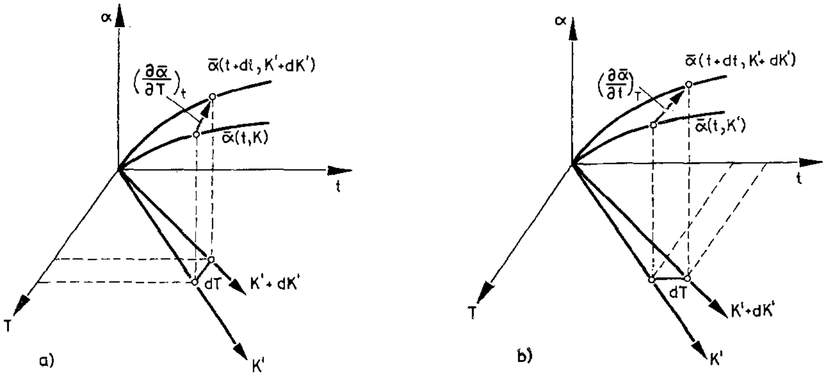

Fig. 3. Diagrammatic representation of the partial derivatives in the system $\alpha = \bar{\alpha}(t, T)$

It is important to point out that the partial derivatives $(\partial\hat{\alpha}/\partial t)_{\mathrm{K}}$ in Eq. (7) and $(\partial\bar{\alpha}/\partial t)_{\mathrm{T}}$ 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 $(\partial\alpha/\partial T)_{\mathrm{t}}$, but the difference in the values of $(\partial\acute{\alpha}/\partial t)_{\mathrm{T=K}}$ and $(\partial\bar{\alpha}/\partial t_{\mathrm{T}})$ is also significant.

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

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

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

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial G}{\partial t}\right)_{\mathrm{T}} + \left(\frac{\partial G}{\partial T}\right)_{\mathrm{t}} \frac{\mathrm{d}T}{\mathrm{d}t}\,. \tag{13}$$

This is a consequence of the constitutive equation of the type

$$\alpha = G(T, t) \tag{14}$$

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 $f(\alpha)$ 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 α and T functions in Eq. (4) [as given in Eq. (3)] and/or inaccurate formulation of the particular functions $k(T)$ and $f(\alpha)$;

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. $\dot{T}$) we have for instance

$$\mathrm{d}\alpha/\mathrm{d}t = F(\alpha, T, \dot{T})\,. \tag{15}$$

It then follows for the isothermal kinetics that

$$\mathrm{d}\alpha/\mathrm{d}t = F(\alpha, K, 0) \rightarrow \alpha(t) = \mathring{\alpha}(\alpha, K) \tag{16}$$

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* 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]).

and for the linear non-isothermal kinetics

$$\mathrm{d}\alpha/\mathrm{d}t = F(\alpha, K't, K') \rightarrow \alpha(t) = \breve{\breve{\alpha}}(t, K') \tag{17}$$

and/or

$$\alpha(t) = \bar{\bar{\alpha}}(t, T).$$

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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Résumé — 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 éclaircit la question en considérant l'équation

$$\alpha = f(T, t)$$

où α 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.

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:

$$\alpha = f(T, t)$$

wobei α 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

$$\alpha = f(T, t)$$

где α — 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.