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SOME PROBLEMS CONCERNING THE MATHEMATICAL THEORY OF NON-ISOTHERMAL KINETICS. I. REACTIONS DESCRIBED BY RATE EQUATIONS OF THE FORM $\mathrm{d}\alpha/\mathrm{d}t = Ak(T)\mathrm{f}(\alpha)$

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ABSTRACT

The article is dedicated to some critical considerations concerning the kinetic equations used to describe non-isothermal processes.

INTRODUCTION

Non-isothermal kinetic studies require the changes with time to be followed of a certain temperature dependent property of the investigated system as well as its temperature [1]. In non-isothermal kinetics the following dependence between the temperature of the system, T, and time can always be considered:

$$\psi(t, T) = 0 \tag{1}$$

where t and T are dependent variables (see Appendix I). From eqn. (1) it follows that:

$$T = \theta(t) \tag{2}$$

$$t = \varphi(T) \tag{3}$$

By taking the derivative of T with respect to t, from eqn. (2) one obtains the heating rate, $\mathrm{d}T/\mathrm{d}t$, of the system in the general form:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \theta'(t) \tag{4}$$

During a non-isothermal kinetic experiment the heating rate can be either kept at a constant value β,

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta \tag{5}$$

or can be changed according to the following relationships:

$$\frac{dT}{dt} = \theta'(t) = \beta_1(t) \tag{6}$$

$$\frac{dT}{dt} = \frac{1}{\varphi'(T)} = \beta_2(T) \tag{7}$$

For the usual case (eqn. 5) the following integral relationships can be written:

$$T = \theta(t) = T_0 + \beta t \tag{8}$$

$$t = \varphi(T) = \frac{T - T_0}{\beta} \tag{9}$$

where T_0 is the temperature corresponding to $t = t_0$.

THE WAY TO PUT THE PROBLEM

Let x be a property of the system which changes with time according to the following differential equation

$$\frac{dx}{dt} = A\mathrm{f}(x)\mathrm{k}(T) \tag{10}$$

which is valid in isothermal conditons. Other variables on which x could depend will be considered as constants and included in the constant factor A. Equation (10) through variables separation and integration with (x_0, t_0) as initial conditions transforms into:

$$\frac{dx}{\mathrm{f}(x)} = A\mathrm{k}(T)\,dt \tag{11}$$

and

$$\int_{x_0}^{x} \frac{dx}{\mathrm{f}(x)} = \mathrm{k}(T) \int_{t_0}^{t} dt \tag{12}$$

or

$$\int_{x_0}^{x} \frac{dx}{\mathrm{f}(x)} = A\mathrm{k}(T)(t - t_0) \tag{13}$$

In relationship (13) x depends implicitely on the independent variables T and $t(T$ is considered as a variable as at various temperatures, namely $T_1, T_2, \ldots, T_n$, one obtains the corresponding isothermal curves). The integral kinetic equation (13) describes a family of isothermal curves.

Let us consider the function

$$x = \mathrm{g}(t, T) \tag{14}$$

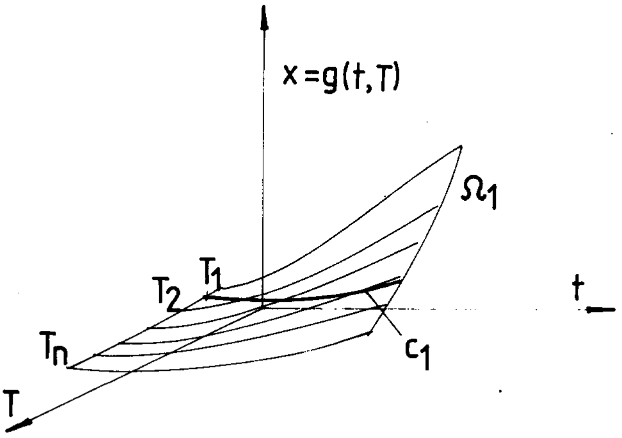

Fig. 1. Tridimensional diagram $x = g(t, T)$.

for isothermal conditions. In a three-dimensional orthogonal system the x values lie on a surface Ω_1 (Fig. 1). The surface Ω_1 which can be obtained from the isothermal curves corresponding to the temperatures $T_1, T_2, \ldots, T_n$, describes the behaviour of the system at various temperatures.

Now, the problem is to derive the differential and integral kinetic equations describing adequately a non-isothermal process from the corresponding isothermal kinetic equations.

In order to do that, it is necessary to assume that the functions $f(x)$ and $k(T)$ do not change their form in non-isothermal conditions. We should equally suppose that the heating rate is small enough to keep the validity of the Maxwell–Boltzmann distribution in the system submitted to non-isothermal kinetic analysis.

THE DERIVATION OF SOME DIFFERENTIAL EQUATIONS AND THEIR INTEGRATED FORMS WHICH DESCRIBE NON-ISOTHERMAL PROCESSES. SOME INADEQUATE EQUATIONS FOR NON-ISOTHERMAL KINETICS

Case I. Derivation of equations valid in nonisothermal kinetics from the isothermal differential equation taking into account that in nonisothermal conditions t *and* T *are dependent variables*

From equation (10) and relationships (2), (3) and (7) one obtains:

$$\frac{dx}{dt} = A f(x) k(\theta(t)) \tag{15}$$

$$\frac{dx}{dT} = \frac{A}{\beta_2(T)} f(x) k(T) \tag{16}$$

The differential equations (15) and (16) which are equivalent from the standpoint of the information about x (t and T being dependent variables) can be considered as adequately describing non-isothermal processes.

From eqns. (15) and (16) through variable separation and integration one obtains:

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A \int_{t_0}^{t} \mathrm{k}(\theta(t))\, \mathrm{d}t \tag{17}$$

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A \int_{T_0}^{T} \frac{\mathrm{k}(T)}{\beta_2(T)}\, \mathrm{d}T \tag{18}$$

For constant heating rate, eqns. (17) and (18) transform into:

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A \int_{t_0}^{t} \mathrm{k}(T_0 + \beta t)\, \mathrm{d}t \tag{19}$$

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = \frac{A}{\beta} \int_{T_0}^{T} \mathrm{k}(T)\, \mathrm{d}T \tag{20}$$

Equations (17–20) also describe adequately non-isothermal processes.

Case II. Model of the infinitesimal-isothermal portions (MIIP)

Let us divide the time interval between t_0 and t on the time axis in small equal intervals Δt, within which the non-isothermal process investigated can be considered as described by integral equations for isothermal conditions (Fig. 2). The following two possibilities (eqns. 21 and 23) can be considered:

(A)

$$\left.\begin{array}{l} \displaystyle\int_{x_0}^{x_1} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t_0))\, \Delta t \\ \displaystyle\int_{x_1}^{x_2} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t_0 + \Delta t))\, \Delta t \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \displaystyle\int_{x_{n-1}}^{x_n} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t_0 + (n-1)\, \Delta t))\, \Delta t \end{array}\right\} \tag{21}$$

From eqn. (21) by summation one obtains:

$$\int_{x_0}^{x_n} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A \sum_{i=1}^{n} \mathrm{k}(\theta(t_0 + (i-1)\, \Delta t))\, \Delta t = s: \tag{22}$$

(B)

$$\left.\begin{array}{l} \displaystyle\int_{x_0}^{x_1} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t_0 + \Delta t))\, \Delta t \\ \displaystyle\int_{x_1}^{x_2} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t_0 + 2\, \Delta t))\, \Delta t \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \displaystyle\int_{x_{n-1}}^{x_n} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t_0 + n\, \Delta t))\, \Delta t \end{array}\right\} \tag{23}$$

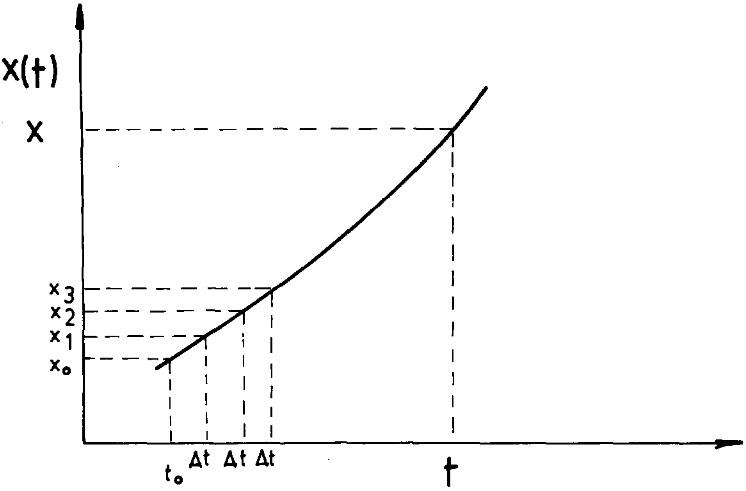

Fig. 2. Infinitesimal isothermal portions on the non-isothermal dependence $x(t)$.

$$\int_{x_0}^{x_n} \frac{dx}{f(x)} = A \sum_{j=1}^{n} k(\theta(t_0 + j\,\Delta t))\,\Delta t = S \tag{24}$$

For $n \to \infty$ and $\Delta t \to 0$

$$\lim_{n \to \infty} x_n = x \tag{25}$$

$$\lim_{\substack{n \to \infty \\ \Delta t \to 0}} n\,\Delta t = t - t_0 \tag{26}$$

and the sums s and S (Darboux's sums) have the same finite limit which equals the integral of $Ak(\theta(t))$ on the closed interval (t_0, t), thus $Ak(\theta(t))$ is the Riemann integrable [2].

$$\lim_{n \to \infty} s = \lim_{n \to \infty} S = A \int_{t_0}^{t} k(\theta(t))\,dt \tag{27}$$

Taking into account this result, relationships (22) and (24) for $n \to \infty$ transform into:

$$\int_{x_0}^{x} \frac{dx}{f(x)} = A \int_{t_0}^{t} k(\theta(t))\,dt \tag{28}$$

i.e. relationship (17). Equation (28) with the change of variable $t \to T$ transforms into relationship (18).

Case III. Derivation of inadequate equation from the integrated isothermal equation (13)

Taking into account that in eqn. (13) t and T are independent variables as well as that the function $x = g(t, T)$ included implicitely in eqn. (13)

fulfils Schwarz's theorem [2] one can write the total differential of eqn. (13) (see Appendix II)

$$\frac{\mathrm{d}x}{\mathrm{f}(x)} = A\left[\mathrm{k}'(T)(t-t_0)\,\mathrm{d}T + \mathrm{k}(T)\,\mathrm{d}t\right] \tag{29}$$

Contradictory to the assumption, that T is constant, used to derive eqn. (13) from eqn. (11) one assumes that t and T, supposed to be independent variables in deriving eqn. (13), are connected by relationships such as eqn. (1). With this erroneous supposition, relationship (29) is divided by $\mathrm{d}t$ (although this operation was considered as impossible at the derivation of eqn. (29)) thus giving:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\mathrm{f}(x)\left[\mathrm{k}'(T)(t-t_0)\frac{\mathrm{d}T}{\mathrm{d}t} + \mathrm{k}(T)\right] \tag{30}$$

The error made in deriving eqn. (30) consists in transforming a differential relationship with t and T as independent variables into another differential relationship where t and T are dependent. Taking into account relationships (1)–(7) one can derive from eqn. (30) the following two differential equations:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\mathrm{f}(x)\left[\mathrm{k}'(\theta(t))(t-t_0)\beta_1(t) + \mathrm{k}(\theta(t))\right] \tag{31}$$

$$\frac{\mathrm{d}x}{\mathrm{d}T} = A\mathrm{f}(x)\left[\mathrm{k}'(T)(\varphi(T)-\varphi(T_0)) + \frac{\mathrm{k}(T)}{\beta_2(T)}\right] \tag{32}$$

eroneously treated as differential equations adequately describing non-isothermal processes.

Let us now analyse the integrated forms of eqns. (31) and (32).

In eqn. (31) after variable separation and integration by parts one obtains:

$$\int_{x_0}^{x}\frac{\mathrm{d}x}{\mathrm{f}(x)} = A\left[\int_{t_0}^{t}\mathrm{k}'(\theta(t))(t-t_0)\beta_1(t)\,\mathrm{d}t + \int_{t_0}^{t}\mathrm{k}(\theta(t))\,\mathrm{d}t\right] \tag{33}$$

where $\mathrm{k}'(\theta(t))$ is the derivative of k with respect to θ.

The first integral from the right member of eqn. (33) can be solved through integration by parts.

$$I_1 = \int_{t_0}^{t}\mathrm{k}'(\theta(t))(t-t_0)\beta_1(t)\,\mathrm{d}t = \mathrm{k}(\theta(t))(t-t_0)\Big|_{t_0}^{t_1} - \int_{t_0}^{t}\mathrm{k}(\theta(t))\,\mathrm{d}t \tag{34}$$

or

$$I_1 = \mathrm{k}(\theta(t))(t-t_0) - \int_{t_0}^{t}\mathrm{k}(\theta(t))\,\mathrm{d}t \tag{35}$$

Introducing this result in eqn. (33) it turns out that:

$$\int_{x_0}^{x}\frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(\theta(t))(t-t_0) \tag{36}$$

or taking into account relationship (2)

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(T)(t - t_0) \tag{37}$$

i.e. the isothermal eqn. (13). This result confirms the non-validity of eqn. (31). Actually this result could have been expected as the integral of a function with a total differential does not depend on the integration path.

Applying the same method to integrate eqn. (32) one obtains successively:

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\left[\int_{T_0}^{T} \mathrm{k}'(T)(\varphi(T) - \varphi(T_0))\,\mathrm{d}T + \int_{T_0}^{T} \frac{\mathrm{k}(T)}{\beta_2(T)}\,\mathrm{d}T\right] \tag{38}$$

$$I_2 = \int_{T_0}^{T} \mathrm{k}'(T)(\varphi(T) - \varphi(T_0))\,\mathrm{d}T = \mathrm{k}(T)(\varphi(T) - \varphi(T_0))\,\Big|_{T_0}^{T} - \int_{T_0}^{T} \mathrm{k}(T)\varphi'(T)\,\mathrm{d}T \tag{39}$$

$$I_2 = \mathrm{k}(T)(\varphi(T) - \varphi(T_0)) - \int_{T_0}^{T} \frac{\mathrm{k}(T)}{\beta_2(T)}\,\mathrm{d}T \tag{40}$$

Thus

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(T)(\varphi(T) - \varphi(T_0)) \tag{41}$$

and taking into account relationship (3) one obtains:

$$\int_{x_0}^{x} \frac{\mathrm{d}x}{\mathrm{f}(x)} = A\mathrm{k}(T)(t - t_0) \tag{42}$$

As expected, relationship (13) is again obtained thus confirming the non-validity of eqn. (32).

A shift on the surface Ω_1, t and T being connected by eqn. (1) does not lead to a true non-isothermal curve as this shift is determined by relationship (13). In Fig. 1 the curve C_1 on the surface Ω_1 is not a true non-isothermal curve.

The three analysed cases impose the following conclusions.

(i) The derivation of equations describing non-isothermal processes should be always performed either starting from the isothermal differential equation with t and T as dependent variables or from the model MIIP. The use of the isothermal integrated equation leads to erroneous results.

(ii) The shift on a surface obtained from isothermal curves does not lead to a true nonisothermal curve.

If a continuous function $\mathrm{k}^*(T)$ for which conclusions (i) and (ii) are not valid exists, then, the right member of relationships (17) and (36) should be equal

$$A\int_{t_0}^{t} \mathrm{k}^*(\theta(t))\,\mathrm{d}t = A\mathrm{k}^*(\theta(t))(t - t_0) \tag{43}$$

for every value of t which fulfils the condition $t > t_0$.

The result of such an analysis is given in Appendix III. One obtains:

$$k^*(\theta(t)) = \text{const} \tag{44}$$

i.e. such temperature dependent function does not exist.

APPLICATIONS IN CLASSIC NON-ISOTHERMAL KINETICS

The basic rate equation used in classic non-isothermal kinetics is [1,3]

$$\frac{d\alpha}{dt} = A_r T^r f(\alpha)^{-E/RT} \tag{45}$$

where in the most general case the conversion function f(α) is given by [4,5]:

$$f(\alpha) = (1-\alpha)^n \alpha^m \left(\ln \frac{1}{1-\alpha}\right)^p \tag{46}$$

$A_r T^r$ is the temperature dependent pre-exponential factor and E is the activation energy.

The classical conditions are the following: A_r is constant; r is constant; E is constant; f(α)—does not change its form. An important particular form of relationship (45) for $r = 0$ and $A_0 = A$ is:

$$\frac{d\alpha}{dt} = A f(\alpha) e^{-E/RT} \tag{47}$$

In the following we shall use eqn. (45), which for $r = 0$ transforms into (47).

For

$$f(x) = f(\alpha) \tag{48}$$

$$k(T) = T^r \, e^{-E/RT} \tag{49}$$

$$A = A_{\mathrm{r}} \tag{50}$$

all the results obtained in the previous sections can be adequately particularized. Thus from relationship (13) one obtains:

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = A_r T^r \, e^{-E/RT}(t - t_0) \tag{51}$$

Taking into account that most frequently $\alpha_0 = 0$ and $t_0 = 0$, eqn. (51) transforms into

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A_r T^r \, e^{-E/RT} \, t \tag{52}$$

Similarly eqns. (15)–(18) taking into account eqns. (48)–(50) turn into:

$$\frac{d\alpha}{dt} = A_r f(\alpha) \theta^r(t) \, e^{-E/R\theta(t)} \tag{53}$$

$$\frac{d\alpha}{dT} = \frac{A_r}{\beta_2(T)} f(\alpha) T^r \, e^{-E/RT} \tag{54}$$

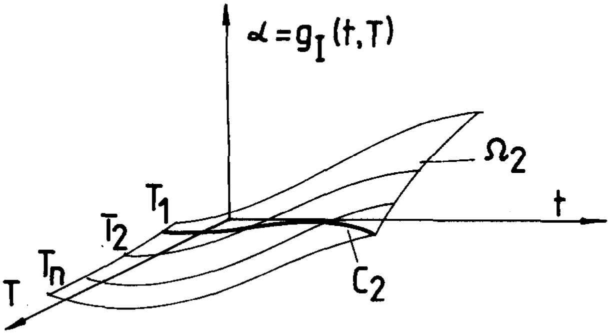

Fig. 3. Plot of α vs. t and T.

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A_r \int_0^t \theta'(t)\ \mathrm{e}^{-E/R\theta(t)}\ \mathrm{d}t \tag{55}$$

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A_r \int_{T_0}^T \frac{T^r\ \mathrm{e}^{-E/RT}}{\beta_2(T)}\ \mathrm{d}T \tag{56}$$

Taking into account that eqn. (52) valid for isothermal conditions contains α implicitely as function of T and t considered independent variables, a general relationship with the form:

$$\alpha = \mathrm{g}_\mathrm{I}(t, T) \tag{57}$$

can be inferred. In eqn. (57) the subscript I stands for isothermal. The representative tridimensional plot of α versus t and T in an orthogonal system of axes is given in Fig. 3. The total differential of eqn. (57) is:

$$\mathrm{d}\alpha = \left(\frac{\partial \mathrm{g}_\mathrm{I}}{\partial T}\right)_t \mathrm{d}T + \left(\frac{\partial \mathrm{g}_\mathrm{I}}{\partial t}\right)_T \mathrm{d}t \tag{58}$$

Taking into account that T and t are independent variables relationship (58) cannot be divided by dt.

In the literature connected with relationship (58) there is much discussion initiated by MacCallum et al. [6–21] concerning its validity and interpretations. In our opinions some of these standpoints are inconsistent because in one way or another they are based on the assumption that relationships such as (57) and (58) are also valid in non-isothermal kinetics; in non-isothermal kinetics t and T are dependent variables. Even if we meet a relationship of the form:

$$\alpha = \mathrm{g}_\mathrm{N}(t, T) \tag{59}$$

where the subscript N stands for non-isothermal, this should be written in one of the following equivalent forms with α as a function of only one variable:

$$\alpha = \mathrm{g}_\mathrm{N}(t, \theta(t)) = \mathrm{g}_\mathrm{N1}(t) \tag{60}$$

$$\alpha = \mathrm{g}_\mathrm{N}(\varphi(T), T) = \mathrm{g}_\mathrm{N2}(T) \tag{61}$$

The differentiation of eqns. (60) and (61) leads to:

$$\mathrm{d}\alpha = \frac{\partial g_{\mathrm{N}}}{\partial \theta}\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\,\mathrm{d}t + \frac{\partial g_{\mathrm{N}}}{\partial t}\,\mathrm{d}t = \frac{\mathrm{d}g_{\mathrm{N1}}}{\mathrm{d}t}\,\mathrm{d}t \tag{62}$$

$$\mathrm{d}\alpha = \frac{\partial g_{\mathrm{N}}}{\partial \varphi}\frac{\mathrm{d}\varphi(T)}{\mathrm{d}T}\,\mathrm{d}T + \frac{\partial g_{\mathrm{N}}}{\partial T}\,\mathrm{d}T = \frac{\mathrm{d}g_{\mathrm{N2}}}{\mathrm{d}T}\,\mathrm{d}T \tag{63}$$

In relationships (62) and (63) the partial derivatives have a different meaning than in eqn. (58), as $\theta(t)$ and $\varphi(T)$ are dependent functions of t and T.

The term $(\partial g_{\mathrm{I}}/\partial T)_t$ from eqn. (58) was considered without physical meaning as one cannot change the temperature at a constant value of time. Of course, this is not possible in non-isothermal kinetics working with eqns. (60) and (61) but is possible on the surface Ω_2 constructed from several isothermal curves. The term $(\partial g_{\mathrm{I}}/\partial T)_t$ should be interpreted as a mathematical shirt on surface Ω_2 parallel to the temperature axis. The only shifts on Ω_2 with physical meaning are those parallel with the time axis which correspond to the isothermal curves.

Concerning relationship (58) we cannot agree with Felder and Stahel [8] who claim that this is not a total differential (see the considerations connected with case III).

Other authors [5,17,19,20] derive non-isothermal kinetic equations using the method described in case III. In this way, for $\mathrm{d}T/\mathrm{d}t = \beta = \text{const.}$, the particular form of eqns. (30)–(32) with $r = 0$, $\alpha_0 = 0$, $t_0 = 0$, is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{f}(\alpha)\,\mathrm{e}^{-E/RT}\left[\frac{E}{RT^2}\beta t + 1\right] \tag{64}$$

where taking into account eqns. (8) and (9)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{f}(\alpha)\,\mathrm{e}^{-E/RT}\left[\frac{E}{RT}\left(1 - \frac{T_0}{T}\right) + 1\right] \tag{65}$$

i.e. a differential equation valid for isothermal kinetics. This is the reason why we agree with the critical standpoints of Criado concerning these equations [21]. For $r \neq 0$ the following equation was obtained:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A_{\mathrm{r}}T^r\mathrm{f}(\alpha)\,\mathrm{e}^{-E/RT}\left[1 + \left(\frac{r}{T} + \frac{E}{RT^2}\right)(T - T_0)\right] \tag{66}$$

This questionable equation can be obtained also from eqn. (30) taking into account relationships (48)–(50).

From (65) and (66) through integration one obtains:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A\,\mathrm{e}^{-E/RT}t = A\frac{T - T_0}{\beta}\,\mathrm{e}^{-E/RT} \tag{67}$$

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A_rT^r\,\mathrm{e}^{-E/RT}t = A_r\frac{T - T_0}{\beta}T^r\,\mathrm{e}^{-E/RT} \tag{68}$$

which are particular forms of eqns. (36) and (41), valid for isothermal kinetics i.e. inconsistent.

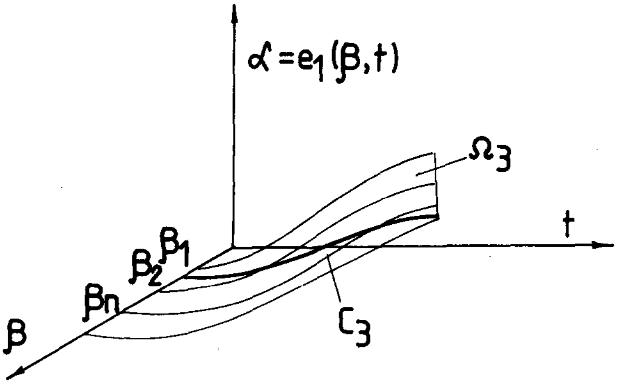

Fig. 4. Plot of α vs. β and t.

Thus while eqns. (53)–(56) correctly describe non-isothermal kinetic data equations (64)–(68) are inadequate for being used in non-isothermal kinetics.

Taking into account conclusion (i) a relatively recent non-isothermal differential kinetic equation derived by MacCallum [22] from an integrated isothermal relationship should, in our opinion, be reviewed. This applies equally to the considerations according to which, from several isothermal experiments, one can obtain at least one non-isothermal description of the process [1,14].

Similar problems appear when considering several non-isothermal experimental curves obtained at constant values of the heating rate β_1, $\beta_2, \ldots, \beta_n$. In this case taking into account that t and T are connected through relationship (8), surfaces Ω_3 and Ω_4 can be drawn up (see Figs. 4 and 5). In order to do that, one has to consider eqns. (55) and (56) taking into account

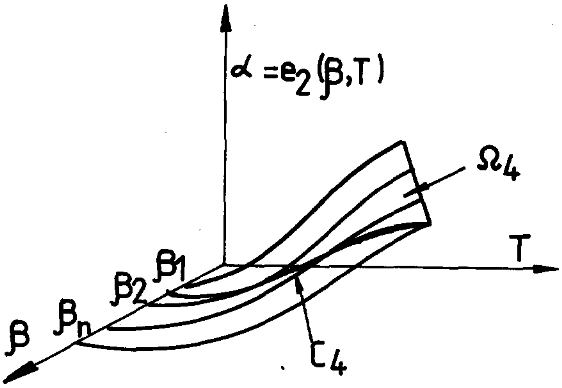

Fig. 5. Plot of α vs. β and T.

eqn. (8). Thus, in principle, one can derive:

$$\alpha = e_1(\beta, t) \tag{69}$$

$$\alpha = e_2(\beta, T) \tag{70}$$

with the functions (60) and (61) as particular cases. By plotting these functions in an adequate system of axes one obtains the surfaces Ω_3 and Ω_4. The differentials of the functions (69) and (70) are:

$$\mathrm{d}\alpha = \left(\frac{\partial e_1}{\partial \beta}\right)_t \mathrm{d}\beta + \left(\frac{\partial e_1}{\partial t}\right)_\beta \mathrm{d}t \tag{71}$$

$$\mathrm{d}\alpha = \left(\frac{\partial e_2}{\partial \beta}\right)_T \mathrm{d}\beta + \left(\frac{\partial e_2}{\partial T}\right)_\beta \mathrm{d}T \tag{72}$$

Contrary to the premise according to which β and t are independent, Gorbachev [23] considered that the differential (71) can be divided by dt and introduces the term dβ/dt which is meaningful only if relationship (6) is valid, but this last relationship is valid if β and t are independent variables.

The shifts on surfaces Ω_3 and Ω_4 do not lead to a non-isothermal curve with $\beta_1(t)$ and $\beta_2(T)$ (C_3 and C_4 are not true curves).

APPENDIX I

Dependent and independent variables

From a set of real variables $x_1, x_2, \ldots, x_n$, one is dependent on the others if a relationship of the form:

$$F(x_1, x_2, \ldots, x_n) = 0 \tag{A1}$$

is valid.

If such a relationship does not exist, all the n variables are independent.

From an equation like (A1) one obtains:

$$x_k = F_k(x_1, x_2, \ldots, x_{k-1}, x_{k+1}, \ldots, x_n) \tag{A2}$$

By substituting (A2) in (A1) the number of independent variables decreases to unity.

APPENDIX II

The differential of many variables functions. The derivative and the differential of a composed function [2]

The differential of a real function on n independent variables $f(x_1, x_2, \ldots, x_n)$ is:

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x_1}\right)_{x_2,x_3\ldots x_n} \mathrm{d}x_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1,x_3\ldots x_n} \mathrm{d}x_2 \ldots + \left(\frac{\partial f}{\partial x_n}\right)_{x_1,x_2,\ldots x_{n-1}} \mathrm{d}x_n \tag{A3}$$

A composed function of one variable has the form:

$$G(x) = g[U_1(x), U_2(x), \dots U_m(x)] \tag{A4}$$

Its differential is:

$$dG(x) = G'(x)\,dx = \frac{\partial g}{\partial U_1}\frac{dU_1}{dx}\,dx + \dots + \frac{\partial g}{\partial U_m}\frac{dU_m}{dx}\,dx \tag{A5}$$

the partial derivatives $\partial g/\partial U_i$ ($i = 1, \dots m$) having different physical meanings than $\partial f/\partial x_j$ ($j = 1, \dots n$) in (A3).

The derivative of G(x) is:

$$G'(x) = \frac{\partial g}{\partial U_1}\frac{dU_1}{dx} + \dots + \frac{\partial g}{\partial U_m}\frac{dU_m}{dx} \tag{A6}$$

For the particular case:

$$G_1(x) = g_1[U(x), x] \tag{A7}$$

$$dG_1(x) = \frac{\partial g_1}{\partial U}\frac{dU}{dx}\,dx + \frac{\partial g_1}{\partial x}\,dx \tag{A8}$$

$$G_1'(x) = \frac{\partial g_1}{\partial U}\frac{dU}{dx} + \frac{\partial g_1}{\partial x} \tag{A9}$$

APPENDIX III

Derivation of relationship (44)

Let us suppose that

$$k^*(\theta(t)) = h(t) \tag{A10}$$

where h(t) has the form:

$$h(t) = a_0 + 2a_1 t + 3a_2 t^2 + \dots + (n+1)a_n t^n + \dots \tag{A11}$$

Introducing (A11) into (43) with $t_0 = 0$, one obtains:

$$a_0 t + a_1 t^2 + \dots + a_n t^{n+1} + \dots = a_0 t + 2a_1 t^2 + \dots + (n+1)a_n t^{n+1} + \dots \tag{A12}$$

or after performing the calculations:

$$a_1 + 2a_2 t + \dots + na_n t^{n-1} + \dots = 0 \tag{A13}$$

Considering the times $t_1, t_2, \dots t_n, \dots$ the systems of equations obtained from (A13) can be solved to obtain the unknowns $a_1, 2a_2, \dots na_n$. The system admits solutions which differ from the trivial one only if the determinant of the coefficients, equals zero [24]

$$D = \begin{vmatrix} 1 & t_1 & t_1^2 & \dots & t_1^{n-1} & \dots \\ 1 & t_2 & t_2^2 & \dots & t_2^{n-1} & \dots \\ \hline 1 & t_n & t_n^2 & \dots & t_n^{n-1} & \dots \end{vmatrix} = 0 \qquad \text{(A14)}$$

This is a Vandermonde type determinant [24], thus

$$D = \prod_{j>i} (t_j - t_i) \qquad \text{(A15)}$$

where i, $j = 1, 2, \dots n$ and if $t_j \neq t_i$ $(i \neq j)$ then $D \neq 0$. Then the system admits only the trivial solution i.e.,

$$\mathrm{h}(t) = a_0 = \text{const} = \mathrm{k}^*(\theta(t)) \qquad \text{(A16)}$$

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