SOME PROBLEMS CONCERNING THE MATHEMATICAL THEORY OF NON-ISOTHERMAL KINETICS. III. THE CLASSICAL NON-ISOTHERMAL CHANGE OF SOME EQUATIONS DERIVED FROM THE RATE EQUATION $d\alpha/dt = f(\alpha)k(T)h(\alpha, T)$ ACCEPTED AS POSTULATED PRIMARY ISOTHERMAL DIFFERENTIAL KINETIC EQUATION

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ABSTRACT

A deeper analysis and development of the ideas from the previous two articles [Urbanovici and Segal, Thermochim. Acta, 111 (1987) 335; 118 (1987) 65] is presented. Special emphasis is given to the classical change, or better, classical non-isothermal change (CNC), of some isothermal kinetic equations. We shall start from the isothermal differential kinetic equation $d\alpha/dt = f(\alpha)k(T)h(\alpha, T)$ axiomatically accepted as postulated primary isothermal differential kinetic equation (P-PIDKE). A critical examination of the correct and incorrect procedures to derive non-isothermal kinetic equations using CNC is presented. The particular isothermal differential kinetic equation $d\alpha/dt = Af(\alpha)e^{-E/RT}$ will be considered as example.

A new formulation of the model of the infinitesimal isothermal portions (MIIP), as well as discussions concerning the difference between non-isothermal kinetics with constant heating rate and non-isothermal kinetics with variable heating rates are presented.

The article concludes with the necessity to use PIDKE or alternatively MIIP for deriving correct non-isothermal kinetic equations.

INTRODUCTION

As previously shown [1,2] non-isothermal kinetic analysis requires the investigation of the change of a property of the system under investigation with simultaneous change of the temperature. In the following we shall assume a uniform space distribution of temperature in all the subsystems of the system, whose temperatures could differ. Thus heat transfer between the subsystems, described by the Newton law could occur [3–7]. The mass transfer phenomena will be considered as fast enough for the occurrence of the chemical reaction in the kinetic regime.

AGAIN ON THE FUNDAMENTAL PROBLEM OF NON-ISOTHERMAL KINETICS

According to the fundamental problem of non-isothermal kinetics as mentioned in ref. 2, in order to derive non-isothermal kinetic equations we shall start from the following isothermal kinetic equation

$$\frac{d\alpha}{dt} = f(\alpha)k(T)h(\alpha, T) \tag{1}$$

where $h(\alpha, T)$ is a function of the inseparable variables degree of conversion α, and temperature T. Equation (1) will be considered axiomatically as postulated primary isothermal differential kinetic equation (P-PIDKE). Its integral form is

$$\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)h(\alpha, T)} = k(T)(t_2 - t_1) \qquad T = \text{const.} \tag{2}$$

or for $\alpha_1 = 0$, $t_1 = 0$, $\alpha_2 = \alpha$, $t_2 = t$, α and t being current values

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)h(\alpha, T)} = k(T)t \qquad T = \text{const.} \tag{3}$$

In the following, we shall use eqn. (3) without important loss in generality for the results.

From eqn. (3) it turns out that in principle

$$\alpha = u(t, T) \tag{4}$$

Introducing relationship (4) in eqn. (1) one obtains

$$\frac{d\alpha}{dt} = f[u(t, T)]k(T)h[u(t, T), T] \equiv v(t, T) \tag{5}$$

The variables t and T in eqns. (1)–(5) are independent. We shall use these isothermal kinetic equations to derive non-isothermal kinetic equations through the classical non-isothermal change (CNC). The classical non-isothermal change of a differential or integral kinetic equation consists in the substitution of T with a function giving its change in time. The CNC will be applied to eqns. (1), (4) and (5). Equally the model of the infinitesimal isothermal portions (MIIP) will be applied considering eqn. (2). The non-isothermal kinetic equations will be derived for heating rates low enough to keep valid the Maxwell–Boltzmann energy distribution. The example of the well known particular form of eqn. (1)

$$\frac{d\alpha}{dt} = Af(\alpha)\, e^{-E/RT} \tag{6}$$

with

$$A = \text{constant} \tag{7}$$

$$E = \text{constant} \tag{8}$$

and generally [6,7,20]

$$f(\alpha) = (1 - \alpha)^n \alpha^m \left[\ln \frac{1}{1 - \alpha}\right]^P \tag{9}$$

will be used.

NEW ASPECTS CONCERNING MIIP

MIIP is used for the mathematical treatment of the non-isothermal curves and implies the division of such curves into infinitesimal intervals which are supposed to be described by integral isothermal equations of the form (2) which can be directly derived from the differential equation (1).

The division of the non-isothermal curve can be realised in two ways: (a) division of the t axis in equal infinitesimal intervals Δt, (b) division of the α (N) * axis in equal infinitesimal intervals $\Delta\alpha$ (N). A division of the T axis could be also performed, but this is not significant as T and t are dependent variables in non-isothermal conditions.

A new variant of MIIP with respect to these given in our previous articles [1,2] consists in considering the temperature in relationships of the form (2) as corresponding to the middle of the infinitesimal interval. This allows the replacement of the sums s and S by a unique sum σ (see Appendix 1).

In some cases when the results obtained by applying MIIP cannot be changed into non-isothermal integral kinetic equations through summation, due to the inseparability of variables, we shall express them as non-isothermal differential kinetic equations. As will be shown in the following, the use of MIIP based on the integral isothermal kinetic equation (2) is equivalent to the CNC of the isothermal differential kinetic equation (1).

Accepting the idea according to which the non-isothermal kinetic equations can be derived from the isothermal ones through CNC, one has to accept the equality between the values of the non-isothermal kinetic parameters and the isothermal ones.

THE DIRECT PROBLEM (DP) AND INVERSE PROBLEM (IP) OF ISOTHERMAL KINETICS AND NON-ISOTHERMAL KINETICS

Direct problem

From known kinetic parameters [f(α), k(T) and h(α, T) or particularly n, A and E] to determine the $\alpha(t)$ and $\dot{\alpha}(t)$ curves for isothermal and non-isothermal conditions. For the non-isothermal case the heating programme should be known.

Inverse problem

From the experimentally known $\alpha(t)$, $\dot{\alpha}(t)$ and $T(t)$ non-isothermal curves to determine the kinetic parameters of the process.

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* (N) after a variable (usually α) or before a mathematical relationship means non-isothermal; in the following this notation will be preferred instead of N as subscript.

This article deals mainly with the derivation through CNC of some non-isothermal kinetic equations as starting point for solving the DP. The finding of some non-isothermal equations for the DP will help us to find the solution of IP which requires the same equations.

To solve the problems of non-isothermal kinetics one has to consider several possibilities for the variation of the temperature.

THE TEMPERATURE OF THE SYSTEM IS GIVEN BY AN EXTERNAL PROGRAMME

This is the most usual case in non-isothermal kinetics. Neglecting the thermal effects inside the system (actually inside the subsystem where the process being investigated occurs) one can consider that its temperature equals the programmed one. In such conditions

$$\psi(t, T) = 0 \tag{10}$$

or explicitly

$$T = \theta(t) \tag{11}$$

$$t = \rho(T) \tag{12}$$

The initial condition

$$T_0 = \theta \qquad (t = 0) \tag{13}$$

is obvious. The heating rates $\beta_1(t)$ and $\beta_2(T)$ are given by [1,2]

$$\frac{dT}{dt} = \theta'(t) \equiv \beta_1(t) \tag{14}$$

$$\frac{dT}{dt} = \frac{1}{\rho'(T)} \equiv \beta_2(T) \tag{15}$$

For

$$\frac{dT}{dt} = \beta = \text{const.} \tag{16}$$

$$T = T_0 + \beta t \tag{17}$$

Relationships (16) and (17) are characteristic for linear non-isothermal kinetics.

The CNC of eqn. (1)

From eqn. (1) through CNC one obtains

$$\text{(N)} \qquad \frac{d\alpha}{dt} = f(\alpha)k[\theta(t)]h[\alpha, \theta(t)] \tag{18}$$

or taking into account eqn. (15)

$$\text{(N)} \qquad \frac{d\alpha}{dT} = \frac{1}{\beta_2(T)}f(\alpha)k(T)h(\alpha, T) \tag{19}$$

Equations (18) and (19) are equivalent from the standpoint of the information they contain about the system, due to the dependence between t and T in non-isothermal kinetics. This is the reason that we will consider in the following only the change of α with time. Equations (18) and (19) cannot be directly integrated, thus to solve the DP one has to use numerical methods of integration. For the particular case of eqn. (6), one obtains

(N) $\qquad \dfrac{d\alpha}{dt} = A f(\alpha)\, e^{-E/R\theta(t)}$ (20)

which can be integrated as follows

(N) $\qquad \displaystyle\int_0^\alpha \dfrac{d\alpha}{f(\alpha)} = A \int_0^t e^{-E/R\theta(t)}\, dt$ (21)

We consider that eqns. (18)–(21) give a correct description of non-isothermal processes.

The use of MIIP

MIIP (Δt)

Through division of the non-isothermal curve $\alpha(t)$ into infinitesimal intervals corresponding to the above-mentioned division of the t axis, for the n-th interval

$$T = \theta\left(\frac{(n-1)\Delta t + n\Delta t}{2}\right) = \theta\left(\frac{2n-1}{2}\Delta t\right)$$ (22)

and according to eqn. (2)

(N) $\qquad \displaystyle\int_{\alpha_{n-1}}^{\alpha_n} \dfrac{d\alpha}{f(\alpha)h\left(\alpha,\, \theta\left(\dfrac{2n-1}{2}\Delta t\right)\right)} = k\left(\theta\left(\dfrac{2n-1}{2}\right)\Delta t\right)\Delta t$ (23)

If

$h(\alpha, T) \equiv 1$ (24)

by summing the n relationships of the form (23) ($\alpha_0 = 0$), and considering the limits for $n \to \infty$ and $\Delta t \to 0$ (see Appendix 1)

(N) $\qquad \displaystyle\lim_{\substack{n\to\infty \\ \Delta t\to 0}} n\,\Delta t = t$ (25)

(N) $\qquad \displaystyle\lim_{n\to\infty} \alpha_n = \alpha$ (26)

α and t being current values, one obtains

(N) $\qquad \displaystyle\int_0^\alpha \dfrac{d\alpha}{f(\alpha)} = \int_0^t k[\theta(t)]\, dt$ (27)

i.e. the integral equation which can be obtained from the differential equation (18), taking into account eqn. (24). If relationship (24) is not valid,

it is not possible to obtain from eqn. (23) an integral equation (the variables cannot be separated). In such a case we shall bring relationship (23) to a differential form.

Using the theorem given in Appendix 2, from eqn. (23) with Δt infinitesimal one obtains

(N)
$$\frac{\alpha_n - \alpha_{n-1}}{f\left(\frac{\alpha_n + \alpha_{n-1}}{2}\right) h\left(\left(\frac{\alpha_n + \alpha_{n-1}}{2}\right), \theta\left(\frac{2n-1}{2}\Delta t\right)\right)}$$

$$= k\left(\theta\left(\frac{2n-1}{2}\Delta t\right)\right) \Delta t \tag{28}$$

where $(\alpha_n - \alpha_{n-1})$ is an infinitesimal quantity too. Equation (28), for $n \to \infty$ and $\Delta t \to 0$, when

(N)
$$\lim_{n \to \infty} \frac{\alpha_n + \alpha_{n-1}}{2} = \alpha \tag{29}$$

(N)
$$\lim_{\substack{n \to \infty \\ \Delta t \to 0}} \frac{2n-1}{2}\Delta t = t \tag{30}$$

(N)
$$\lim_{\substack{n \to \infty \\ \Delta t \to 0}} \frac{\alpha_n - \alpha_{n-1}}{\Delta t} = \frac{d\alpha}{dt} \tag{31}$$

α and t being current values, leads after rearrangement to the non-isothermal differential kinetic equation (18) obtained through CNC in the isothermal kinetic differential equation (1).

MIIP ($\Delta\alpha$)

As previously, in this case one has to divide the non-isothermal curve $\alpha(t)$ into small infinitesimal intervals. For the n-th interval

$$T = \theta\left(\frac{t_n + t_{n-1}}{2}\right) \tag{32}$$

(N)
$$\int_{(n-1)\Delta\alpha}^{n\Delta\alpha} \frac{d\alpha}{f(\alpha)h\left(\alpha, \theta\left(\frac{t_n + t_{n-1}}{2}\right)\right)} = k\left(\theta\left(\frac{t_n + t_{n-1}}{2}\right)\right)(t_n - t_{n-1})$$

$$\tag{33}$$

If relationship (24) is valid by summing the n relationships of the form (33) (see Appendix 1), and taking the limits when

(N)
$$\lim_{\substack{n \to \infty \\ \Delta\alpha \to 0}} n \Delta\alpha = \alpha \tag{34}$$

(N)
$$\lim_{n \to \infty} t_n = t \tag{35}$$

α and t being current values, one obtains relationship (27). For the general

case corresponding to $h(\alpha, T) \ne 1$, using in eqn. (33) the theorem from Appendix 2, it turns out that

$$(N) \quad \frac{\Delta\alpha}{f\left(\frac{2n-1}{2}\Delta\alpha\right), h\left(\left(\frac{2n-1}{2}\Delta\alpha\right), \theta\left(\frac{t_n + t_{n-1}}{2}\right)\right)}$$

$$= k\left(\theta\left(\frac{t_n + t_{n-1}}{2}\right)\right)(t_n - t_{n-1}) \qquad (36)$$

Considering the limits for $n \to \infty$ and $\Delta\alpha \to 0$

$$(N) \qquad \lim_{n \to \infty} \frac{t_n + t_{n-1}}{2} = t \qquad (37)$$

$$(N) \qquad \lim_{\substack{n \to \infty \\ \Delta\alpha \to 0}} \frac{2n-1}{2}\Delta\alpha = \alpha \qquad (38)$$

$$(N) \qquad \lim_{\substack{n \to \infty \\ \Delta\alpha \to 0}} \frac{\Delta\alpha}{t_n - t_{n-1}} = \frac{d\alpha}{dt} \qquad (39)$$

α and t being current values, eqn. (36) after rearrangement leads to eqn. (18).

From the analysed cases one can conclude that the CNC is equivalent to the use of MIIP.

CNC of eqn. (5)

This procedure is incorrect, as for deriving eqn. (5) the non-isothermal nature of the system was not taken into account.

Applying the CNC to eqn. (5) one gets

$$(N) \qquad \frac{d\alpha}{dt} = f(u[t, \theta(t)])k[\theta(t)]h(u[t, \theta(t)], \theta(t)) \equiv v[t, \theta(t)] \qquad (40)$$

It is easy to see that eqn. (40) is not equivalent to eqn. (18) considered by us as correct. Concerning the physical meaning of the CNC of eqn. (5), as shown in Appendix 3, using this equation one can draw a surface Ω_1, representing the isothermal curves $d\alpha/dt = v(t, T)$ for various temperatures (in this case T and t are independent variables). The shift on the surface Ω_1 when T and t are related by eqn. (11) is equivalent to the CNC of relationship (5). Thus one can conclude that the shift on a surface Ω_1 obtained from several isothermal curves $(d\alpha/dt)(t)$ at various temperatures (shift which corresponds to a relationship of the form (11) between t and T) is not a true non-isothermal shift.

Equation (5) can be integrated in isothermal conditions as follows

$$\int_{\alpha_1}^{\alpha_2} d\alpha = \int_{t_1}^{t_2} v(t, T)\, dt \qquad T = \text{const.} \qquad (41)$$

which for isothermal conditions is equivalent to eqn. (2).

When applying MIIP using eqn. (41), through very simple calculations one obtains the non-valid non-isothermal differential kinetic equation (40). One can conclude the MIIP cannot be applied to any isothermal integral kinetic equation but to the isothermal kinetic equation derived directly from eqn. (1), i.e. to an equation of the form (2). Although eqns. (1) and (5) are equivalent in isothermal conditions, they are not equivalent with respect to the CNC, as for deriving eqn. (5) integrations in isothermal conditions were carried out.

The only common and insignificant case when the CNC of eqn. (5) could be equivalent to the CNC of eqn. (1) can be realised for

$$f(\alpha)h(\alpha, T) \equiv 1 \tag{42}$$

and consequently

$$\frac{d\alpha}{dt} = k(T) \tag{43}$$

For the particular case of eqn. (6) through integration one obtains

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \, e^{-E/RT}t \qquad T = \text{const.} \tag{44}$$

From eqn. (44), in principle

$$\alpha = \mu(A \, e^{-E/RT}t) \tag{45}$$

Equation (6) with α given by eqn. (45) takes the form

$$\frac{d\alpha}{dt} = Af(\mu(A \, e^{-E/RT}t)) \, e^{-E/RT} \tag{46}$$

By applying the CNC in eqn. (46) one obtains

$$\text{(N)} \qquad \frac{d\alpha}{dt} = Af(\mu(A \, e^{-E/R\theta(t)}t)) \, e^{-E/R\theta(t)} \tag{47}$$

which is not equivalent to eqn. (20). The integral form of eqn. (47) is

$$\text{(N)} \qquad \alpha = A \int_0^t f(\mu_1(A \, e^{-E/R\theta(t)}t)) \, e^{-E/R\theta(t)} \, dt \tag{48}$$

which is not equivalent to eqn. (21).

The material presented in this paragraph imposes the following conclusions: (1) the CNC of a kinetic differential equation of the form (5) obtained from eqn. (1) is not valid; (2) the shift on a surface Ω_1 (see Appendix 3) obtained from various isothermal curves $\dot{\alpha}(t)$ at various temperatures does not lead to a true non-isothermal curve; (3) in order to apply MIIP one has to start from isothermal integral equations of the form (2) derived directly from eqn. (1) and not from isothermal integral equations of the form (41).

CNC of eqns. (3) or (4)

The CNC of eqn. (3) leads to

(N) $\qquad \displaystyle\int_0^\alpha \frac{d\alpha}{f(\alpha)h[\alpha,\,\theta(t)]} = k[\theta(t)]\,t$ (49)

In order to integrate the left member of eqn. (49), $\theta(t)$ is considered formally as a constant.

From eqn. (4) through CNC one obtains

(N) $\qquad \alpha = u[t,\,\theta(t)]$ (50)

It is known that eqn. (50) is the solution of eqn. (49). In the following we will demonstrate that these CNC are incorrect. In order to do that let us consider a function $w(\alpha,\,T)$ such that

$$\frac{dw(\alpha,\,T)}{d\alpha} = \frac{1}{f(\alpha)h(\alpha,\,T)} \qquad T = \text{const.}$$ (51)

i.e. isothermal conditions.

By introducing eqn. (51) in eqn. (3) one gets

$$\int_0^\alpha \frac{dw(\alpha,\,T)}{d\alpha}\,d\alpha = k(T)t \qquad T = \text{const.}$$ (52)

or performing the integration

$$w(\alpha,\,T) - w(0,\,T) = k(T)t$$ (53)

Relationship (4) is a solution of eqn. (53). On the other hand one can see that taking into account eqn. (51), actually eqn. (53) is another form of eqn. (3). Thus the CNC applied to eqns. (3) and (4) is equivalent to the CNC applied to eqn. (53), i.e.

(N) $\qquad w[\alpha,\,\theta(t)] - w[0,\,\theta(t)] = k[\theta(t)]\,t$ (54)

To demonstrate the incorrectness of relationship (54) one has to take its derivative with respect to t

(N) $\qquad \displaystyle\frac{1}{f(\alpha)h[\alpha,\,\theta(t)]}\frac{d\alpha}{dt} + \frac{\partial w[\alpha,\,\theta(t)]}{\partial\theta(t)}\frac{d\theta(t)}{dt} - \frac{\partial w[0,\,\theta(t)]}{\partial\theta(t)}\frac{d\theta(t)}{dt}$

$$= \frac{dk[\theta(t)]}{d\theta(t)}\frac{d\theta(t)}{dt}\,t + k[\theta(t)]$$ (55)

Expressing $d\alpha/dt$ from eqn. (55) one obtains

(N) $\qquad \displaystyle\frac{d\alpha}{dt} = f(\alpha)h[\alpha,\,\theta(t)]\left[k[\theta(t)] + \frac{d\theta(t)}{dt}\left(\frac{dk[\theta(t)]}{d\theta(t)}\,t\right.\right.$

$$\left.\left. - \frac{\partial w[\alpha,\,\theta(t)]}{\partial\theta(t)} + \frac{\partial w[0,\,\theta(t)]}{\partial\theta(t)}\right)\right]$$ (56)

It is obvious that, eqn. (56) differs from non-isothermal differential kinetic equation (18), which is considered as valid.

Concerning the physical meaning of the CNC leading the equations like (49), (50) or (54) one has to notice that a shift on a surface Ω_2 (drawn from various isothermal curves $\alpha(t)$ for various temperatures) for T and t related by eqn. (11) is equivalent to the CNC. The CNC of eqn. (44) leads to

(N) $\qquad \int_0^\alpha \dfrac{d\alpha}{f(\alpha)} = A\, e^{-E/R\theta(t)}t$ $\qquad\qquad$ (57)

From eqn. (56) by particularization, or taking the derivative of eqn (57) with respect to t, one obtains

(N) $\qquad \dfrac{d\alpha}{dt} = Af(\alpha)\, e^{-E/R\theta(t)}\left[1 + \dfrac{E}{R\theta^2(t)}\cdot \dfrac{d\theta(t)}{dt}t\right]$ $\qquad$ (58)

which is not equivalent to eqn. (20), and thus incorrect. For a linear heating programme taking into account eqn. (17), eqn. (58) becomes

$\dfrac{d\alpha}{dt} = Af(\alpha)\, e^{-E/R(T_0 + \beta t)}\left[1 + \dfrac{E}{R(T_0 + \beta t)^2}\beta t\right]$ $\qquad\qquad$ (59)

inadequately considered as valid for non-isothermal kinetics [12–15,20].

Finally concerning the CNC of eqns. (3) or (4) one can conclude that: (1) the CNC of eqns. (3) or (4) does not lead to correct non-isothermal integral kinetic equations; (2) the shift on a surface Ω_2 obtained from various isothermal curves $\alpha(t)$ and various temperatures does not lead to a true non-isothermal curve.

On the existence of the total differential $d\alpha = (\partial\alpha/\partial t)_T dt + (\partial\alpha/\partial T)_t dT$ in non-isothermal kinetics

The discussion on this subject has been initiated by McCallum and Tanner [11] who suppose that in non-isothermal kinetics, relationship (60) and its total differential (61) are valid

(N) $\qquad \alpha = u^\star(t, T)$ $\qquad\qquad$ (60)

(N) $\qquad d\alpha = \left(\dfrac{\partial u^\star}{\partial t}\right)_T dt + \left(\dfrac{\partial u^\star}{\partial T}\right)_t dT$ $\qquad\qquad$ (61)

As shown in ref. 1 as well as in Appendix 3 of this paper, relationship (61) has no meaning, as in non-isothermal kinetics T and t are dependent variables. Thus eqn. (60) should be written as

(N) $\qquad \alpha = u^\star[t, \theta(t)]$ $\qquad\qquad$ (62)

whose differential can be written according to relationship (29) from Appendix 3 in the form

$d\alpha = \dfrac{\partial u^\star}{\partial t}dt + \dfrac{\partial u^\star}{\partial \theta}\cdot \dfrac{d\theta(t)}{dt}dt$ $\qquad\qquad$ (63)

where $\partial u^\star/\partial\theta$ does not imply t = constant.

One has to mention the formal connection between the procedure presented in the last section to derive non-isothermal kinetic equations and the acceptance of a equation of the form (61). Some authors calculated the partial derivative $(\partial u^\star / \partial T)_t$ starting from a relationship of the form (57). In this way they found that $\partial u / \partial \theta$ equals $(\partial u^\star / \partial T)_t$; thus from a relationship of the form (61) they derived the non-isothermal differential kinetic equation obtained by us in the previous section [12–15].

Some problems concerning non-isothermal kinetics with constant heating rate and with variable heating rate

For constant heating rate, eqn. (1) taking into account eqn. (17) leads to

(N) $$\frac{d\alpha}{dt} = f(\alpha)k(T_0 + \beta t)h(\alpha, T_0 + \beta t) \tag{64}$$

which is a particular form of eqn. (18). In principle through integration of eqn. (64) one obtains

(N) $$\alpha = p_1(t, \beta) \tag{65}$$

which introduced in eqn. (64) gives

(N) $$\frac{d\alpha}{dt} = p_2(t, \beta) \tag{66}$$

In relationships (65) and (66), t and β can be considered as independent variables so that various curves $\alpha(t)$ and $\dot{\alpha}(t)$ for various constant heating rates $\beta_1, \beta_2, \ldots$ can be considered; thus the surfaces Ω_3 and Ω_4 corresponding to eqns. (65) and (66) can be drawn.

Also, in principle from eqn (18) we could derive for the general case (11)

(N) $$\alpha = p_3[t, \beta_1(t)] \tag{67}$$

or introducing this result in eqn. (18)

(N) $$\frac{d\alpha}{dt} = p_4[t, \beta_1(t)] \tag{68}$$

Through differentiation from eqns. (65) and (67) one obtains

(N) $$d\alpha = \left(\frac{\partial p_1}{\partial t}\right)_\beta dt + \left(\frac{\partial p_2}{\partial \beta}\right)_t d\beta \tag{69}$$

(N) $$d\alpha = \left(\frac{\partial p_3}{\partial t}\right) dt + \left(\frac{\partial p_3}{\partial \beta_1}\right)\left(\frac{d\beta_1(t)}{dt}\right) dt \tag{70}$$

Equation (70) can be divided by dt, while in eqn. (69) such an operation is not possible as β and t are independent variables (see Appendix 3).

Let us suppose that we operate changes which consist in the substitution of β with $\beta_1(t)$ in eqns. (65) and (66). These changes correspond to shifts on

the surfaces Ω_3 and Ω_4 when β and t are connected through the relationship.

$$\beta = \beta_1(t) \tag{71}$$

Thus through the change of β with $\beta_1(t)$ in eqns. (65) and (66) one gets

(N) $$\alpha = p_1[t, \beta_1(t)] \tag{72}$$

(N) $$\frac{d\alpha}{dt} = p_2[t, \beta_1(t)] \tag{73}$$

Without getting into detailed calculations we have to mention that α given by eqn. (72) is not a solution of the differential equation (18), and $d\alpha/dt$ given by eqn. (73) is not equivalent to eqn. (18), i.e.

(N) $$p_1[t, \beta_1(t)] \neq p_3[t, \beta_1(t)] \tag{74}$$

(N) $$p_2[t, \beta_1(t)] \neq p_4[t, \beta_1(t)] \tag{75}$$

As an application we will consider eqn. (21) for T given by eqn. (17)

(N) $$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t e^{-E/R(T_0 + \beta t)} \, dt \tag{76}$$

Considering thus the change $\beta \to \beta_1(t)$ we could obtain

(N) $$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t e^{-E/R[T_0 + \beta_1(t)\cdot t]} \, dt \tag{77}$$

which is not equivalent to eqn. (21).

Formally the integration of the right member of eqn. (77) is performed considering that $\beta_1(t) =$ constant. The conclusions of this section are: (1) it is not possible to obtain correct non-isothermal kinetic equations with variable heating rates from non-isothermal equations for constant heating rates through the change $\beta \to \beta_1(t)$; (2) the shifts on the surfaces Ω_3 and Ω_4 obtained from curves $\alpha(t)$ and $\dot{\alpha}(t)$ for various constant heating rates does not lead to a true non-isothermal curve with variable heating rates.

Let us now consider Gorbachev's article [16] in which he tries to demonstrate the existence of a difference between non-isothermal kinetics with constant heating rate and non-isothermal kinetics with variable heating rate. His mistake consists in transforming a relationship of the form (69) (relationship (2) in [16]) in an improper way (dividing by dt), i.e. in transforming a relationship with β and t independent into an incorrect relationship with β and t dependent. Thus in principle there is no difference between the two kinds of non-isothermal kinetics; the general equation for treating non-isothermal phenomena is eqn. (18) with its particular form eqn. (64).

AUTONOMOUS NON-ISOTHERMAL SYSTEMS ADIABATICALLY ISOLATED

We call these systems autonomous non-isothermal as their non-isothermal character is due only to the heat evolved (exo) or absorbed (endo) in the process investigated. In such cases the temperature of the system depends on the conversion, i.e.

$$T = q(\alpha) \tag{78}$$

with the obvious condition

$$T_0 = q(\alpha = 0) \tag{79}$$

The form of $q(\alpha)$ depends on many factors such as reaction enthalpy, heat capacities of reactants and products, etc. The most usual particular case of relationship (78) is

$$T = T_0 + q_0\alpha \qquad q_0 = \text{const.} \tag{80}$$

As will be demonstrated in the following by using MIIP in a more general case, the CNC can be applied to such systems too. Thus eqn. (1) with the CNC (78) becomes

$$(\text{N}) \qquad \frac{d\alpha}{dt} = f(\alpha)k[q(\alpha)]h[\alpha, q(\alpha)] \tag{81}$$

Through variable separation in eqn. (81) followed by integration one obtains

$$(\text{N}) \qquad \int_0^\alpha \frac{d\alpha}{f(\alpha)k[q(\alpha)]h[\alpha, q(\alpha)]} = t \tag{82}$$

In the particular case of eqn. (6) the CNC gives

$$(\text{N}) \qquad \frac{d\alpha}{dt} = Af(\alpha)\, e^{-E/Rq(\alpha)} \tag{83}$$

$$(\text{N}) \qquad \int_0^\alpha \frac{d\alpha}{f(\alpha)\, e^{-E/Rq(\alpha)}} = At \tag{84}$$

A surface Ω_5 can be drawn from the points T, α and $d\alpha/dt$ given by eqn. (1). The surface can be obtained from various isotherms $(d\alpha/dt)(\alpha)$ at various temperatures. On the surface Ω_5 a shift with T and α connected through eqn. (78) is equivalent to CNC of eqn. (1), i.e. to eqn. (81). For a given process there is only one true way because there is only one function $q(\alpha)$.

MIXED NON-ISOTHERMAL SYSTEMS

In such systems, temperature changes due both to an external programme (usually heating) and to the thermal effect of the process being is investigated.

Let us suppose that no supplementary heat changes occur between the subsystem in which the process is being investigated and the heating subsystem. In such conditions

$$T = T_0 + \theta_1(t) + q_1(\alpha) \tag{85}$$

where $\theta_1(t)$ is the variation due to the thermal change with the heating subsystem; $q_1(\alpha)$ is the variation due to the thermal effect of the process being investigated.

One has to consider two limiting cases

$$\theta_1(t) \equiv 0; \quad T_0 + q_1(\alpha) \equiv q(\alpha) \tag{86}$$

$$q_1(\alpha) \equiv 0; \quad T_0 + \theta_1(t) \equiv \theta(t) \tag{87}$$

To derive the correct non-isothermal differential kinetic equations one has to apply the CNC and MIIP in eqn. (1) using eqn. (85).

The CNC leads to

$$(N) \qquad \frac{d\alpha}{dt} = f(\alpha)k[T_0 + \theta_1(t) + q_1(\alpha)]h[\alpha, T_0 + \theta_1(t) + q_1(\alpha)] \tag{88}$$

The differential equation (88) cannot be directly integrated due to the inseparability of α and t, but numeric methods are available for integration.

Application of MIIP lead us to the following results:

MIIP (Δt)

For the n-th infinitesimal interval

$$(N) \qquad \int_{\alpha_{n-1}}^{\alpha_n} \frac{d\alpha}{f(\alpha)h(\alpha, T_{n1})} = k(T_{n1}) \, \Delta t \tag{89}$$

where

$$T_{n1} = T_0 + \theta_1\left(\frac{2n-1}{2}\Delta t\right) + q_1\left(\frac{\alpha_n + \alpha_{n-1}}{2}\right) \tag{90}$$

Using the theorem from Appendix 2, from eqn. (89) one obtains

$$(N) \qquad \frac{\alpha_n - \alpha_{n-1}}{f\left(\dfrac{\alpha_n + \alpha_{n-1}}{2}\right)h\left(\dfrac{\alpha_n + \alpha_{n-1}}{2}, T_{n1}\right)} = k(T_{n1}) \, \Delta t \tag{91}$$

Relationship (91) for $n \to \infty$ and $\Delta t \to 0$ leads after rearrangement to eqn. (88).

MIIP ($\Delta\alpha$)

For the n-th infinitesimal interval

$$(N) \qquad \int_{(n-1)\Delta\alpha}^{n\Delta\alpha} \frac{d\alpha}{f(\alpha)h(\alpha, T_{n2})} = k(T_{n2})(t_n - t_{n-1}) \tag{92}$$

$$T_{n2} = T_0 + \theta_1\left(\frac{t_n + t_{n-1}}{2}\right) + q_1\left(\frac{2n-1}{2}\Delta\alpha\right) \tag{93}$$

From eqn. (92) one obtains (see Appendix 2)

$$\text{(N)} \quad \frac{\Delta\alpha}{f\left(\frac{2n-1}{2}\Delta\alpha\right)h\left(\frac{2n-1}{2}\Delta\alpha, T_{n2}\right)} = k(T_{n2})(t_n - t_{n-1}) \tag{94}$$

For $n \to \infty$ and $\Delta t \to 0$ eqn. (94) becomes eqn (88).

In these cases too, the use of MIIP leads to the same results as the use of CNC. Without going into details we mention that in these cases too the CNC of relationships (4) and (5) are not valid. Thus the equations

$$\text{(N)} \quad \alpha = u\left[t, T_0 + \theta_1(t) + q_1(\alpha)\right] \tag{95}$$

$$\text{(N)} \quad \frac{d\alpha}{dt} = v\left[t, T_0 + \theta_1(t) + q_1(\alpha)\right] \tag{96}$$

are incorrect.

The CNC of eqn. (6) leads to

$$\text{(N)} \quad \frac{d\alpha}{dt} = A f(\alpha)\, e^{-E/R[T_0 + \theta_1(t) + q_1(\alpha)]} \tag{97}$$

MIXED SYSTEMS WITH HEAT TRANSFER, ACCORDING TO THE NEWTON LAW, BETWEEN SUBSYSTEMS

In this case the temperature of the subsystem where the investigated non-isothermal process occurs is given by eqn. (85) to which a term T_{tr} due to the heat transfer between the heating and the process subsystems is added. This heat transfer will be considered as described by the Newton law [3–7]. Thus

$$T = T_0 + \theta_1(t) + q_1(\alpha) - T_{tr} \tag{98}$$

$$\frac{dT_{tr}}{dt} = \frac{K}{C_p}(-T_{tr} + q_1(\alpha)) \tag{99}$$

where K stands for the thermal transfer coefficient between the heat subsystem and the active subsystem, and C_p for the heat capacity of the active subsystem, considered as constant [5–7].

Applying the CNC from eqns. (1) and (98) one obtains

$$\text{(N)} \quad \frac{d\alpha}{dt} = f(\alpha)k(T_0 + \theta_1(t) + q_1(\alpha) - T_{tr})$$

$$\times h(\alpha, T_0 + \theta_1(t) + q_1(\alpha) - T_{tr}) \tag{100}$$

In this case the system is described by two differential equations (99) and (100).

By applying the MIIP one obtains successively

MIIP (Δt)

For the *n*-th interval,

$$\int_{\alpha_{n-1}}^{\alpha_n} \frac{d\alpha}{f(\alpha)h(\alpha, T_{n3})} = k(T_{n3}) \Delta t \tag{101}$$

$$T_{n3} = T_0 + \theta_1\left(\frac{2n-1}{2}\Delta t\right) + q_1\left(\frac{\alpha_n + \alpha_{n-1}}{2}\right) - \frac{T_{tr\,n} + T_{tr\,n-1}}{2} \tag{102}$$

From eqn. (101), taking into account the theorem given in Appendix 2, it turns out that

$$(N) \qquad \frac{\alpha_n - \alpha_{n-1}}{f\left(\frac{\alpha_n + \alpha_{n-1}}{2}\right)h\left(\frac{\alpha_n + \alpha_{n-1}}{2}, T_{n3}\right)} = k(T_{n3}) \Delta t \tag{103}$$

At the limit when $n \to \infty$, $\Delta t \to 0$

$$\lim_{n \to \infty} \frac{T_{tr\,n} + T_{tr\,n-1}}{2} = T_{tr}$$

and relationship (103) becomes eqn. (100).

MIIP (Δα)

$$(N) \qquad \int_{(n-1)\Delta\alpha}^{n\Delta\alpha} \frac{d\alpha}{f(\alpha)h(\alpha, T_{n4})} = k(T_{n4})(t_n - t_{n-1}) \tag{104}$$

$$T_{n4} = T_0 + \theta_1\left(\frac{t_n + t_{n-1}}{2}\right) + q_1\left(\frac{2n-1}{2}\Delta\alpha\right) - \frac{T_{tr\,n} + T_{tr\,n-1}}{2} \tag{105}$$

From eqn. (104) (see Appendix 2) one obtains

$$(N) \qquad \frac{\Delta\alpha}{f\left(\frac{2n-1}{2}\Delta\alpha\right)h\left(\frac{2n-1}{2}\Delta\alpha, T_{n4}\right)} = k(T_{n4})(t_n - t_{n-1}) \tag{106}$$

which at the limit becomes eqn. (100); thus in this case the CNC is equivalent to MIIP too.

One has to notice that in this case too the CNC of relationships (4) and (5) taking into account eqn. (98) is not a correct procedure.

The problems concerning a more detailed analysis of the heat transfer will be considered in a following paper.

SOME GENERALISATIONS

A more general case than that described by eqn. (98) corresponds to a heat transfer between the active subsystem and *m* subsystems; thus

$$T = T_0 + \theta_1(t) + q_1(\alpha) - \sum_{i=1}^{m} (T_{tr})_i \equiv T_1^{\star} \tag{107}$$

where $T_1^\star$ means the temperature of the active subsystem. The CNC can be operated in eqn. (1) taking into account eqn. (107)

$$\text{(N)} \qquad \frac{d\alpha}{dt} = f(\alpha)k(T_1^\star)h(\alpha, T_1^\star) \qquad\qquad (108)$$

For a subsystem where r chemical and physical processes described by the following system of isothermal differential equations

$$\frac{d\alpha_j}{dt} = F_j(\alpha_1, \alpha_2, \ldots, \alpha_j, \ldots, \alpha_r, T) \qquad (j = 1, 2, \ldots, r) \qquad (109)$$

occur, the temperature is given by

$$T = T_0 + \theta_1(t) + \sum_{j=1}^{r} q_j(\alpha_j) + \sum T_{tr} = T_2^\star \qquad (110)$$

where $\sum_{j=1}^{r} q_j(\alpha_j)$ is the temperature variation due to the internal heat evolved and $\sum T_{tr}$ is the temperature variation due to heat transfers described by the Newton law.

Accepting the r isothermal differential kinetic equations as P-PIDKE one can apply the CNC to them, thus obtaining

$$\text{(N)} \qquad \frac{d\alpha_j}{dt} = F_j(\alpha_1, \alpha_2, \ldots, \alpha_j, \ldots, \alpha_r, T_2^\star) \qquad\qquad (111)$$

The system is described by j equations of the form (111) and the differential equations corresponding to the heat transfers [generalised form of equation (99)]. The detailed calculations will be given in a subsequent paper.

THE INVERSE PROBLEM OF NON-ISOTHERMAL KINETICS

As shown, the inverse problem of non-isothermal kinetics consists in the evaluation of the kinetic parameters from experimentally determined values of α, T and t.

For the temporal variation of the temperature one can always find an analytical dependence of the form

$$\text{(N)} \qquad T = \lambda(t) \qquad\qquad (112)$$

Relationship (112) does not take into account the factors which determine the non-isothermal character of the process. From the experimental data we find

$$\text{(N)} \qquad \alpha = e_1(t) \qquad\qquad (113)$$

or

$$\text{(N)} \qquad t = e_2(\alpha) \qquad\qquad (114)$$

From eqn. (113) taking the derivative one obtains

(N) $\dfrac{d\alpha}{dt} = e_1'(t) \equiv e_3(t)$ (115)

Concerning the applicability of MIIP for the IP, see ref. 2. In the following we will show that using relationships (112)–(115) we can obtain differential and integral equations which can be used in the evaluation of the kinetic parameters.

By working relationship (1) we get

(N) $\dfrac{d\alpha}{dt} \equiv e_3(t) = f(\alpha)k[\lambda(t)]h[\alpha, \lambda(t)]$ (116)

which can be used in the differential methods for the evaluation of the kinetic parameters.

In order to integrate eqn. (116) one can distinguish two possibilities (1) the substitution of α given by eqn. (113) in $h[\alpha, \lambda(t)]$ which leads to

(N) $\displaystyle\int_0^\alpha \dfrac{d\alpha}{f(\alpha)} = \int_0^t k[\lambda(t)]h[e_1(t), \lambda(t)]\, dt$ (117)

(2) The substitution of t given by eqn. (114) in $h[\alpha, \lambda(t)]$ giving

(N) $\displaystyle\int_0^\alpha \dfrac{d\alpha}{f(\alpha)h(\alpha, \lambda[e_2(\alpha)])} = \int_0^t k[\lambda(t)]\, dt$ (118)

Equations (117) and (118) can be used in integral methods for the evaluation of the kinetic parameters.

CONCLUSIONS

1. The CNC in eqn. (1) (which is equivalent to the use of MIIP) is a correct procedure.
2. The CNC in eqns. (4) or (5) is not a correct procedure.
3. The shifts on surfaces obtained from isothermal curves $\alpha(t)$, $\dot{\alpha}(t)$ for various temperatures are not true shifts.
4. Non-isothermal kinetics with variable heating rates cannot be derived from non-isothermal kinetics with constant heating rates through a simple change $\beta \rightarrow \beta_1(t)$.
5. The CNC can even be applied to more complex systems than those described by eqn. (109) if the equations describing the system are accepted as P-PIDKE.

APPENDIX 1. RIEMANN INTEGRABLE FUNCTIONS [17,18]

Let us consider the positive continuous function $f(x)$ limited in the closed interval $[a, b]$. Let us equally consider a division (d) of the interval $[a, b]$

(d) $a = x_0 < x_1 < \ldots < x_i < x_{i+1} \ldots < x_n = b$ (A1)

The summations of the magnitudes

$$m_i = \inf f(x) \tag{A2}$$

$$x_i \leqslant x \leqslant x_{i+1} \qquad i = 0, 1, \ldots, n-1$$

$$M_i = \sup f(x) \tag{A3}$$

$$x_i \leqslant x \leqslant x_{i+1} \qquad i = 0, 1, \ldots, n-1$$

$$g_i = f\left(\frac{x_i + x_{i+1}}{2}\right) \qquad i = 0, 1, \ldots, n-1 \tag{A4}$$

leads to

$$s = \sum_{i=0}^{n-1} m_i(x_{i+1} - x_i) \tag{A5}$$

$$S = \sum_{i=0}^{n-1} M_i(x_{i+1} - x_i) \tag{A6}$$

$$\sigma = \sum_{i=0}^{n-1} g_i(x_{i+1} - x_i) \tag{A7}$$

where s and S are the Darboux sums. For $n \to \infty$ and $(x_{i+1} - x_i) \to 0$ we have

$$\lim_{n \to \infty} s = \lim_{n \to \infty} S = \lim_{n \to \infty} \sigma = I$$

where I is the integral of the function $f(x)$ in the closed interval $[a, b]$

$$I = \int_a^b f(x) \, dx \tag{A8}$$

The function $f(x)$ is called Riemann integrable.

APPENDIX 2. THE THEOREM OF THE AVERAGE VALUE FOR AN INFINITESIMAL INTERVAL OF INTEGRATION

The theorem of the average values from mathematical analysis can be formulated as follows: if a continuous function does not change its sign in the closed interval $[a, b]$, there is a point such that [18,19]

$$\int_a^b f(x) \, dx = (b - a)f(\xi) \tag{A9}$$

$$\xi \in (a, b) \tag{A10}$$

One can easily check that if $f(x)$ is a linear function

$$f(x) = mx + n \tag{A11}$$
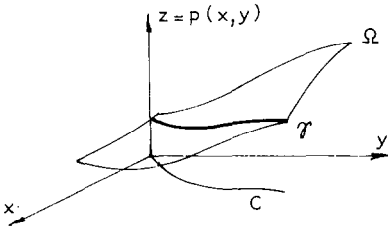
then

$$\xi = \frac{a + b}{2}. \tag{A12}$$

Fig. A1. The surface Ω in three-dimensional space.

If the difference between b and a is infinitesimal, i.e.

$$b = a + \Delta a \tag{A13}$$

then in the closed infinitesimal interval $[a, b]$, $f(x)$ can be considered as linear, thus

$$\int_a^b f(x)\, dx = (b-a)f\left(\frac{b+a}{2}\right) = \Delta a f\left(a + \frac{\Delta a}{2}\right) \tag{A14}$$

APPENDIX 3. SHIFTS ON THREE-DIMENSIONAL SURFACES

Let us consider the function z of two independent variables x and y

$$z = p(x, y) \tag{A15}$$

The three-dimensional diagram of the points (x, y, z) in a system of orthogonal axes leads to the surface Ω (Fig. A1) with two degrees of freedom corresponding to the two independent variables x and y. If $p(x, y)$ is a continuous function which fulfils the Schwartz theorem [17], we have

$$\frac{\partial^2 z}{\partial x\, \partial y} = \frac{\partial^2 z}{\partial y\, \partial x} \tag{A16}$$

In this case the differential of z

$$dz = \left(\frac{\partial p}{\partial x}\right)_y dx + \left(\frac{\partial p}{\partial y}\right)_x dy \tag{A17}$$

is a total exact differential.

Let us suppose that x and y are connected through a relationship of the form

$$r(x, y) = 0 \tag{A18}$$

In this case x and y become dependent variables, and from eqn. (A18) one can derive the explicit forms for y and x

$$y = r_1(x) \tag{A19}$$

$$x = r_2(y) \tag{A20}$$

In the plane XOY curve C corresponds to the equivalent relationships (A18), (A19) or (A20). The points with coordinates x, y, z

$$\gamma: \begin{cases} x = x \\ y = r_1(x) \\ z = p[x, r_1(x)] \end{cases} \tag{A21}$$

$$\gamma: \begin{cases} x = r_2(y) \\ y = y \\ z = p[r_2(y), y] \end{cases} \tag{A22}$$

describe the three-dimensional curve γ on the surface Ω. Thus curve γ is defined by relationships (A21) or (A22).

Curves γ and C have only one degree of freedom. The two-dimensional equivalent of γ (in the planes XOZ or YOZ) can be obtained considering x or y as variable

$$C_1: \begin{cases} x = x \\ z = p[x, r_1(x)] \end{cases} \tag{A23}$$

$$C_2: \begin{cases} y = y \\ z = p[r_2(y), y] \end{cases} \tag{A24}$$

The curves C_1 and C_2 given by the parametric equations (A23) and (A24) are equivalent from the standpoint of the information contained in them and represent the two-dimensional equivalents of γ.

Let us analyse the differential and derivatives of z (with respect to x or y) when x and y are connected through eqn. (A18).

An erroneous procedure consists in dividing relationship (A17) by dx or dy, forgetting that x and y are independent variables. The division of (A17) by dx or dy leads to quantities dy/dx or dx/dy which cannot be interpreted. Thus from eqn. (A17) the following incorrect relationships can be derived

$$\frac{dz}{dx} = \left(\frac{\partial p}{\partial x}\right)_y + \left(\frac{\partial p}{\partial y}\right)_x \frac{dy}{dx} \tag{A25}$$

$$\frac{dz}{dy} = \left(\frac{\partial p}{\partial x}\right)_y \frac{dx}{dy} + \left(\frac{\partial p}{\partial y}\right)_x \tag{A26}$$

In these relationships, as far as x and y are connected through eqn. (A18) it means that x cannot be changed for $\cdot y = $ constant and vice versa.

Actually if a relationship of the form (A18) is valid, one has to start from (A15). In this case z depends on one independent variable, either x or y.

$$z(x) = p[x, r_1(x)] \tag{A27}$$

$$z(y) = p[r_2(y), y] \tag{A28}$$

In such conditions

$$dz(x) = \frac{\partial p}{\partial x} dx + \frac{\partial p}{\partial r_1} \frac{dr_1(x)}{dx} dx \tag{A29}$$

$$dz(y) = \frac{\partial p}{\partial y} dy + \frac{\partial p}{\partial r_2} \frac{dr_2(y)}{dy} dy \tag{A30}$$

$$\frac{dz(x)}{dx} = \frac{\partial p}{\partial x} + \frac{\partial p}{\partial r_1} \frac{dr_1(x)}{dx} \tag{A31}$$

$$\frac{dz(y)}{dy} = \frac{\partial p}{\partial y} + \frac{\partial p}{\partial r_2} \frac{dr_2(y)}{dy} \tag{A32}$$

Although formally relationships (A25) and (A31) or (A26) and (A32) are equivalent from the standpoint of the results obtained, there is a difference between them from the standpoint of the physical meaning. In eqns. (A25) and (A26) one can change x at $y =$ constant or y at $x =$ constant whereas in (A31) for example the partial derivative $\partial p / \partial x$ does not mean $r_1(x) =$ constant, representing in fact a formal mathematical procedure.

Relationships (A25) and (A26) can be correctly written in the following forms

$$\frac{dz}{dx} = \frac{\partial p}{\partial x} + \frac{\partial p}{\partial y} \frac{dy}{dx} \tag{A33}$$

$$\frac{dz}{dy} = \frac{\partial p}{\partial x} \frac{dx}{dy} + \frac{\partial p}{\partial y} \tag{A34}$$

the connection between x and y being given by eqn. (A18).

Relationships (A33) and (A34) are equivalent to (A31) and (A32) taking into account (A19) and (A20).

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