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THE HEATING RATE AS A VARIABLE IN NON-ISOTHERMAL KINETICS: III. SOME THEORETICAL ASPECTS CONCERNING THIS PROBLEM AND THE INVERSE PROBLEM OF CLASSICAL NON-ISOTHERMAL KINETICS

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ABSTRACT

Following our earlier research concerning the heating rate as a variable in non-isothermal kinetics (E. Urbanovici and E. Segal, Thermochim. Acta, 95 (1985) 273; 107 (1986) 353), this paper aims to continue and develop our ideas concerning these topics from a theoretical standpoint based on two main assumptions: the validity of the classical hypothesis (constant kinetic parameters) and the invariability of the reaction mechanism with the heating rate.

INTRODUCTION

The well-known differential equation of classical non-isothermal kinetics [1–4]

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)\, e^{-(E/RT)} \tag{1}$$

with

$$T = T_0 + \beta t \tag{2}$$

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{3}$$

and the classical conditions

$$A = \text{const.} \tag{4}$$

$$E = \text{const.} \tag{5}$$

$$n = \text{const},\ m = \text{const},\ p = \text{const.} \tag{6}$$

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is derived from the isothermal kinetic equation

$$\frac{d\alpha}{dt} = Af(\alpha)\,e^{-(E/RT)}(T - \text{const}) \tag{7}$$

accepted as Postulated-Primary Isothermal Differential Kinetic Equation (P-PIDKE) [5], through the classical non-isothermal change (CNC) [5,6] taking into account the relationship

$$\frac{dT}{dt} = \beta \tag{8}$$

From eqn. (1), through integration between (0, α) and (α_i, α_k) one obtains

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0=0}^{T} e^{-(E/RT)}\,dT \tag{9}$$

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_i}^{T_k} e^{-(E/RT)}\,dT \tag{10}$$

where T_i and T_k are the temperatures corresponding to α_i and α_k.

DEVELOPMENT OF RELATIONSHIP (9)

Let us consider a given α_i which is reached using the heating rates β_1, $\beta_2,\ldots,\beta_k$, and introduce the notation

$$\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = Z_i \tag{11}$$

and consider the dependence $T_i(\beta)$ given by

$$T_i(\beta) = e_i(\beta) \tag{12}$$

where the function $e_i(\beta)$ can be obtained through interpolation from the pairs of experimental data: $T_i(\beta_1)$, β_1; $T_i(\beta_2)$, β_2; ... $T_i(\beta_k)$, β_k. We consider the minimum necessary number of heating rates to be three. In this case, $e_i(\beta)$ can be a second degree polynominal.

Considering in eqn. (9) the derivative with respect to β, we obtain [7]

$$Z_i = A\,e^{-(E/RT_i(\beta))}\frac{dT_i(\beta)}{d\beta} \tag{13}$$

A new derivation with respect to β in eqn. (13) leads to

$$e^{-(E/RT_i(\beta))}\frac{d^2T_i(\beta)}{d\beta^2} + e^{-(E/RT_i(\beta))}\left[\frac{E}{RT_i^2(\beta)}\left(\frac{dT_i(\beta)}{d\beta}\right)^2\right] = 0 \tag{14}$$

and

$$E = -RT_i^2(\beta)\frac{((d^2T_i(\beta)/d\beta^2))}{((dT_i(\beta)/d\beta))^2} = -R\,e_i^2(\beta)\frac{e_i''(\beta)}{e_i'^2(\beta)} \tag{15}$$

Relationship (15) allows the evaluation of the activation energy.

From eqn. (13), by taking natural logarithms, we obtain

$$\ln\left(\frac{dT_i(\beta)}{d\beta}\right) = \ln\frac{Z_i}{A} + \frac{E}{R}\frac{1}{T_i(\beta)} \tag{16}$$

a relationship which allows the evaluation of Z_i/A and E from a linear plot.

Considering the ratio of two relationships, eqn. (13) can be written, for the two heating rates β_1 and β_2 [7]

$$E = R\frac{T_i(\beta_1)T_i(\beta_2)}{T_i(\beta_2) - T_i(\beta_1)} \ln\left[\frac{(dT_i(\beta)/d\beta)_{\beta_1}}{(dT_i(\beta)/d\beta)_{\beta_2}}\right] \tag{17}$$

From eqns. (9), (11) and (13) it is easy to obtain

$$\frac{1}{\beta}\int_0^{T_i(\beta)} e^{-(E/RT)}\, dT = e^{-(E/RT_i(\beta))}\frac{dT_i(\beta)}{d\beta} \tag{18}$$

Taking into account the approximate relationship [4]

$$\int_0^T e^{-(E/RT)}\, dT = \frac{RT^2}{E} e^{-(E/RT)} Q(T, E) \tag{19}$$

where $Q(T, E)$ is a function with slow variation which in a first approximation equals unity. From eqns. (18) and (19)

$$E = \frac{RT_i^2(\beta)}{\beta}\left(\frac{dT_i(\beta)}{d\beta}\right)^{-1} Q(T_i(\beta), E) \tag{20}$$

To evaluate E, one can solve eqn. (20), or alternatively an iterative procedure can be applied.

$$E^{(0)} = \frac{RT_i^2(\beta)}{\beta}\left(\frac{dT_i(\beta)}{d\,\beta}\right)^{-1} \tag{21}$$

$$E^{(1)} = E^{(0)} Q\big(T_i(\beta), E^{(0)}\big) \tag{22}$$

$$E^{(j)} = E^{(0)}\big(T_i(\beta), E^{(j-1)}\big) \tag{23}$$

The relationships (15), (16), (17) and (20) allow the evaluation of the activation energy E for a given value of the degree of conversion.

From eqns. (15) and (20) one obtains

$$\frac{dT_i(\beta)}{d\beta} = -\frac{\beta}{Q(T_i(\beta), E)}\frac{d^2T_i(\beta)}{d\beta^2} \tag{24}$$

In a first approximation, $Q(T, E) \approx 1$, and eqn. (24) becomes

$$\frac{dT_i(\beta)}{d\beta} = -\beta\frac{d^2T_i(\beta)}{d\beta^2} \tag{25}$$

whose solution is

$$T_i(\beta) = A_i + B_i \ln \beta \tag{26}$$

where A_i and B_i are constants.

Comparing relationship (20) and Kissinger's relationship [8]

$$\frac{\mathrm{d}\ln\left(\beta/T_{\max}^2\right)}{\mathrm{d}(1/T_{\max})} = -\frac{E}{R} \tag{27}$$

or after performing the calculations

$$\frac{\left(T_{\max}^2/\beta\right)\left[\left(1/T_{\max}^2\right) - \left(2\beta/T_{\max}^3\right)\left(\mathrm{d}T_{\max}/\mathrm{d}\beta\right)\right]\,\mathrm{d}\beta}{-\left(1/T_{\max}^2\right)\left(\mathrm{d}T_{\max}/\mathrm{d}\beta\right)\,\mathrm{d}\beta} = -\frac{E}{R} \tag{28}$$

From eqn. (28)

$$E = \frac{RT_{\max}^2}{\beta}\left(1 - \frac{2\beta}{T_{\max}}\frac{\mathrm{d}T_{\max}}{\mathrm{d}\beta}\right)\left(\frac{\mathrm{d}T_{\max}}{\mathrm{d}\beta}\right)^{-1} \tag{29}$$

where

$$1 - \frac{2\beta}{T_{\max}}\frac{\mathrm{d}T_{\max}}{\mathrm{d}\beta} \simeq 1 \tag{30}$$

Thus there is a perfect analogy between relationships (29) and (20). This analogy can be explained by taking into account the fact that in Kissinger's model $\alpha_{\max}$ does not change with β; thus relationship (20) can be considered valid for $\alpha_{\max}$ too.

In order to obtain $f(\alpha)$, we shall use the arguments in ref. 7. Introducing into eqn. (13) an average value of the activation energy

$$\bar{E} = \frac{E_1 + E_2 + \ldots E_N}{N} \tag{31}$$

where N values of α_i have been used, one obtains

$$Z_i = A\,\mathrm{e}^{-(\bar{E}/RT_i(\beta))}\frac{\mathrm{d}T_i(\beta)}{\mathrm{d}\beta} \quad (i = 1, 2, \ldots N) \tag{32}$$

By introducing the notation

$$\mathrm{e}^{-(\bar{E}/RT_i(\beta))}\frac{\mathrm{d}T_i(\beta)}{\mathrm{d}\beta} = a_i \tag{33}$$

we obtain from (32)

$$\frac{\sum Z_j}{\sum Z_k} = \frac{\sum a_j}{\sum a_k},\ j \neq k \tag{34}$$

a relationship which allows us to determine $f(\alpha)$. The particular form of eqn. (34) which we recommend is

$$\frac{Z_1 + Z_3 + \ldots}{Z_2 + Z_4 + \ldots} = \frac{a_1 + a_3 + \ldots}{a_2 + a_4 + \ldots} \tag{35}$$

As far as the pre-exponential factor is concerned, it can be obtained from the following relationships

$$A_i = Z_i \ e^{-(\bar{E}/RT_i(\beta))}\left(\frac{dT_i(\beta)}{d\beta}\right)^{-1} \tag{36}$$

where

$$\bar{A} = (A_1 A_2 \dots A_N)^{1/N} \tag{37}$$

Another way of finding $f(\alpha)$ can also be considered. From relationships (1) and (13)

$$Z_i f(\alpha_i) = \beta\left(\frac{dT_i(\beta)}{d\beta}\right)\left(\frac{d\alpha}{dT}\right)_{\alpha_i}(\beta) \tag{38}$$

where the values of the derivative $(d\alpha/dT)$, at various points and various heating rates are presumably known. By introducing the notations

$$\left(\frac{dT_i(\beta)}{d\beta}\right)\left(\frac{d\alpha}{dT}\right)_{\alpha_i}(\beta) = b_i \tag{39}$$

we obtain from (38) by summation

$$\frac{Z_1 f(\alpha_1) + Z_3 f(\alpha_3) + \dots}{Z_2 f(\alpha_2) + Z_4 f(\alpha_4) + \dots} = \frac{b_1 + b_3 + \dots}{b_2 + b_4 + \dots} \tag{40}$$

a relationship which can be used to find $f(\alpha)$.

The pre-exponential factor can be obtained from eqns. (36) and (37), or from eqn. (1) written in the form

$$A_i = \frac{\beta \ e^{-(E/RT_i(\beta))}}{f(\alpha_i)}\left(\frac{d\alpha}{dT}\right)_{\alpha_i}(\beta) \tag{41}$$

and from eqn. (37).

DERIVATIONS FROM RELATIONSHIP (10)

We introduce the notation

$$Z_{ik} = \int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f(\alpha)} \tag{42}$$

Let us suppose that α_i and α_k are constants. Taking the derivative of eqn. (10) with respect to β

$$Z_{ik} = A\left[e^{-(E/RT_k(\beta))}\frac{dT_k(\beta)}{d\beta} - e^{-(E/RT_i(\beta))}\frac{dT_i(\beta)}{d\beta}\right] \tag{43}$$

From eqn. (43), taking the derivative with respect to β one obtains

$$e^{-(E/RT_k(\beta))}\left[\frac{d^2T_k(\beta)}{d\beta^2}+\frac{E}{RT_k^2(\beta)}\left(\frac{dT_k(\beta)}{d\beta}\right)^2\right]$$
$$=e^{-(E/RT_i(\beta))}\left[\frac{d^2T_i(\beta)}{d\beta^2}+\frac{E}{RT_i^2(\beta)}\left(\frac{dT_i(\beta)}{d\beta}\right)^2\right] \quad (44)$$

From two relationships of the form of eqn. (43) for two heating rates β_1 and β_2 one obtains [9]

$$\frac{e^{-(E/RT_k(\beta_2))}(dT_k(\beta)/d\beta)_{\beta_2}-e^{-(E/RT_i(\beta_2))}((dT_i(\beta)/d\beta))_{\beta_2}}{e^{-E/RT_k(\beta_1)}((dT_i(\beta)/d\beta))_{\beta_1}-e^{-(E/RT_i(\beta_1))}((dT_i(\beta)/d\beta))_{\beta_1}}=1 \quad (45)$$

From eqns. (10) and (43)

$$\frac{1}{\beta}\int_{T_i(\beta)}^{T_k(\beta)}e^{-(E/RT)}\,dT=e^{-(E/RT_k(\beta))}\frac{dT_k(\beta)}{d\beta}-e^{-(E/RT_i(\beta))}\frac{dT_i(\beta)}{d\beta} \quad (46)$$

Taking into account eqn. (19), eqn. (46) becomes

$$\frac{1}{\beta}\left(\frac{RT_k^2(\beta)}{E}\,e^{-(E/RT_k(\beta))}Q(T_k(\beta),\,E)\right.$$
$$\left.-\frac{RT_i^2(\beta)}{E}\,e^{-(E/RT_i(\beta))}Q(T_i(\beta),\,E)\right)$$
$$=e^{-(E/RT_k(\beta))}\frac{dT_k(\beta)}{d\beta}-e^{-(E/RT_i(\beta))}\frac{dT_i(\beta)}{d\beta} \quad (47)$$

From eqns. (44), (45) and (47) the activation energy can be evaluated.

In the following, the notation λ will be used for the pairs $(i,\ k)$. In such terms the average values of the activation energy is

$$\bar{E}=\frac{\sum_{\lambda=1}^{N}E_\lambda}{N} \quad (48)$$

Equation (43) can be written in the short form

$$Z_{ik}=AC_\lambda \quad (49)$$

where

$$C_\lambda=e^{-(\bar{E}/RT_k(\beta))}\frac{dT_k(\beta)}{d\beta}-e^{-(\bar{E}/RT_i(\beta))}\frac{dT_i(\beta)}{d\beta} \quad (50)$$

In order to find f(α), a relationship of the form of eqn. (34) can be used, for instance

$$\frac{Z_1^\star+Z_3^\star+\ldots}{Z_2^\star+Z_4^\star+}=\frac{C_1+C_3+\ldots}{C_2+C_4+\ldots} \quad (51)$$

where

$$Z_\lambda^\star = Z_{ik},\ (i,\ k) = \lambda \tag{52}$$

Writing relationship (43) in the form

$$A = \frac{Z^\star}{C_\lambda} (\lambda = 1, 2, \ldots, N) \tag{53}$$

and using eqn. (37), the value of the pre-exponential factor can be calculated.

From eqns. (7) and (43)

$$Z_{ik} = \beta\left(\frac{\mathrm{d}T_k(\beta)}{\mathrm{d}\beta}\right)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha_k}(\beta)\frac{1}{\mathrm{f}(\alpha_k)} - \beta\left(\frac{\mathrm{d}T_i(\beta)}{\mathrm{d}\beta}\right)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha_i}(\beta)\frac{1}{\mathrm{f}(\alpha_i)} \tag{54}$$

From eqn. (54), the function $\mathrm{f}_\lambda(\alpha)$ for pairs $(i,\ k)$ can be obtained. Averaging such functions for all the values of λ allows the determination of $\mathrm{f}(\alpha)$.

DERIVATIONS FROM RELATIONSHIP (7)

In this case, an interpolation function

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha_i}(\beta) = g_i(\beta) \tag{55}$$

is assumed to be known from the experimental data.

From the derivative of eqn. (7) with respect to β

$$\frac{\mathrm{d}g_i(\beta)}{\mathrm{d}\beta} = -\frac{A}{\beta^2}\mathrm{f}(\alpha_i)\mathrm{e}^{-(E/RT_i(\beta))} + \frac{A}{\beta}\mathrm{f}(\alpha_i)\mathrm{e}^{-(E/RT_i(\beta))}\frac{E}{RT_i^2(\beta)}\frac{\mathrm{d}T_i(\beta)}{\mathrm{d}\beta} \tag{56}$$

and eqn. (7) one obtains

$$\frac{\mathrm{d}g_i(\beta)}{\mathrm{d}\beta} = -\frac{g_i(\beta)}{\beta} + g_i(\beta)\frac{E}{RT_i^2(\beta)}\frac{\mathrm{d}T_i(\beta)}{\mathrm{d}\beta} \tag{57}$$

and

$$E = RT_i^2(\beta)\frac{g_i(\beta) + \beta((\mathrm{d}g_i(\beta)/\mathrm{d}\beta))}{\beta g_i(\beta)((\mathrm{d}T_i(\beta)/\mathrm{d}\beta))} \tag{58}$$

In this case, also from the ratio of two relationships of the form of eqn. (56) for two heating rates β_1 and β_2, an equation to calculate the activation energy can be obtained.

In order to find $f(\alpha)$, we shall use eqn. (7) with the notation

$$f(\alpha_i) = \frac{\beta}{A} g_i(\beta)\ e^{(E/RT_i(\beta))} = \frac{1}{A}\ d_i \tag{59}$$

with these conditions

$$f(\alpha_i) = \frac{1}{A}\ d_i \tag{60}$$

$$\frac{f(\alpha_1) + f(\alpha_3) + \dots}{f(\alpha_2) + f(\alpha_4) + \dots} = \frac{d_1 + d_3 + \dots}{d_2 + d_4 + \dots} \tag{61}$$

As far as the pre-exponential factor is concerned, it can be obtained from

$$A_i = \frac{\beta}{f(\alpha_i)} g_i(\beta)\ e^{(E/RT_i(\beta))} \tag{62}$$

and eqn. (37).

The applications of the presented results will be given in a following paper.

CONCLUSIONS

Some alternative solutions of the inverse problem of non-isothermal kinetics were discussed using the constant heating rate as a variable. All the theoretical considerations are based on the assumption of the validity of classical non-isothermal kinetics.

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