Thermochimica Acta, 135 (1988) 193–198
Elsevier Science Publishers B.V., Amsterdam

NONISOTHERMAL KINETIC EQUATIONS WITH PARAMETERS DEPENDING ON THE DEGREE OF CONVERSION

E.URBANOVICI[1] **and E.SEGAL**[2]

1 Research Institute for Electrotechnics, Sfîntu Gheorghe Branch, Str. Josef Attila Nr.4, Sfîntu Gheorghe, Judeţul Covasna (R.S. România)
2 Department of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Bulevardul Republicii 13, Bucharest (R.S.România)

ABSTRACT

The authors present a discussion concerning variable nonisothermal kinetic parameters. The dependence of the nonisothermal kinetic parameters on the degree of conversion for some heterogeneous decompositions in solid-gas systems is considered.

INTRODUCTION

In order to describe kinetically heterogeneous decomposition reactions of the general form: A(s) ⟶ B(s) + C(g) (I), which occur in nonisothermal conditions, the following kinetic differential equation /1-4/ is used:

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

where all the notations have their usual meanings with

$$A = \text{const} \qquad (2)$$

$$E = \text{const} \qquad (3)$$

and for the most general case /3/

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \qquad (4)$$

with

$$n = \text{const},\ m = \text{const},\ p = \text{const}. \qquad (5)$$

Equation (1) is obtained by means of the classical nonisothermal change (CNC) /5,6/ of the isothermal kinetic equation:

$$\frac{d\alpha}{dt} = A\, f(\alpha)\, e^{-\frac{E}{RT}} \qquad (6)$$

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

accepted as Postulated-Primary Isothermal Differential Kinetic Equation (P-PIDKE) /5/.

A new formal theory describing better the complex phenomena which characterises reaction (I) could eventually be developed considering variable kinetic parameters with α, T ...,etc.

In this work the only considered variable is the degree of conversion, α. In our opinion this is the most important factor due to the fact that its change determines the most drastical change of the reaction matrix (as compared with the change determined by, e.g. the temperature variation).

As shown previously by us /5,6/, in the case of the direct problem of nonisothermal kinetics when the dependences of the kinetic parameters on α are known, then CNC can be applied to the isothermal kinetic equation. In such a way, the following equation is obtained:

$$\frac{d\alpha}{dT} = \frac{A(\alpha)}{\beta} f(\alpha, n(\alpha), m(\alpha), p(\alpha)) e^{-\frac{E}{RT}} \qquad (7)$$

THE INVERSE PROBLEM OF NONCLASSICAL NONISOTHERMAL KINETICS

The problem is to make evident the dependence of the nonisothermal kinetic parameters on α using the integration over small intervals of α and several heating rates. In order to accomplish this task, a method which uses two constant heating rates was previously worked out /7-11/. For a short description of the method we remember two fundamental assumptions used for its elaborations namely,

- the reaction does not change its mechanism with the change of the heating rate /12/
- the values of the nonisothermal kinetic parameters are not dependent on β.

From equation (7), through integration in the closed interval $\alpha \in [\alpha_i, \alpha_k]$ for a heating rate β_q, one obtains:

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f^*(\alpha)} = \frac{1}{\beta_{qik}} \int_{T_{qi}}^{T_{qk}} A(h_q(T))\, e^{-\frac{E(h_q(T))}{RT}}\, dT \qquad (8)$$

where

$$f^*(\alpha) = f(\alpha, n(\alpha), m(\alpha), p(\alpha)), \qquad (9)$$

T_{qi} and T_{qk} are the temperatures corresponding to α_i and α_k, and β_{qik} is the local heating rate /7-11/ defined by:

$$\beta_{qik} = \frac{T_{qk} - T_{qi}}{t_{qk} - t_{qi}} \tag{1o}$$

Relationship (8) contains $h_q(T)$ which means the change of α with T taken from the experimental curve

$$\alpha = h_q(T) \tag{11}$$

For $T_{qk} - T_{qi} \in [5\text{-}2oK]$, using the average theorem from mathematical analysis /7-11/ the integral from the right member of (8) takes the form:

$$\int_{T_{qi}}^{T_{qk}} A(h_q(T))\, e^{-\frac{E(h_q(T))}{RT}}\, dT \cong$$

$$= (T_{qk}-T_{qi})\, A(h_q(T_{qik}))\, e^{-\frac{E(h_q(T_{qik}))}{RT_{qik}}} \tag{12}$$

where

$$T_{qik} = (T_{qk} + T_{qi})/2 \tag{13}$$

Using the approximate relationship:

$$h(T_{qik}) = \frac{(h(T_{qi}) + h(T_{qk})}{2} = \frac{\alpha_i + \alpha_k}{2} = \alpha_{ik} \tag{14}$$

and taking into account relationship (1o),(12) and (14) it turns out that:

$$\int_{\alpha_i}^{\alpha_k} \frac{d\alpha}{f^*(\alpha)} = (t_{qk}-t_{qi})\, A(\alpha_{ik})\, e^{-\frac{E(\alpha_{ik})}{RT_{qik}}} \tag{15}$$

Considering in (15) two heating rates β_1 and β_2 and performing the calculations one obtains /7-11/:

$$E(\alpha_{ik}) = R\, \frac{T_{1ik}\, T_{2ik}}{T_{2ik}-T_{1ik}} \ln \frac{(t_{1k}-t_{1i})}{(t_{2k}-t_{2i})} \tag{16}$$

The use of pairs (α_i, α_k) which cover almost all the values of α allows to obtain the dependence of the activation energy on α.

To find $f^*(\alpha)$, for $\alpha_j \in (\alpha_i, \alpha_k)$, two relationships of the form (15) should be written with E (α_{ik}) instead of E(α_{ij}) and E (α_{jk}) and A(α_{ik}) instead of A(α_{ij}) and A(α_{jk}). This rough approximation should be carefully considered. Thus from two relationships of the form (15) with α_j, it turns out that /7/:

$$\frac{\int_{\alpha_i}^{\alpha_j}\frac{d\alpha}{f^*(\alpha)}}{\int_{\alpha_j}^{\alpha_k}\frac{d\alpha}{f^*(\alpha)}} = \frac{R_1+R_2}{2} \qquad (17)$$

where

$$R_q = \frac{(t_{qj}-t_{qi})}{(t_{qk}-t_{qi})}\;\frac{e^{-\frac{E(\alpha_{ik})}{RT_{qij}}}}{e^{-\frac{E(\alpha_{ik})}{RT_{qik}}}} \qquad (q=1,2) \qquad (18)$$

To find $f^*(\alpha)$ using the same compromise instead of $n(\alpha_{ij})$, $n(\alpha_{jk})$, $m(\alpha_{ij})$, $m(\alpha_{jk})$; $p(\alpha_{ij})$, $p(\alpha_{jk})$; we shall determine $n(\alpha_{ik})$, $m(\alpha_{ik})$, $p(\alpha_{ik})$.

The preexponential factor can be obtained using equation (15). It appears that:

$$A_q(\alpha_{ik}) = \frac{\int_{\alpha_i}^{\alpha_k}\frac{d\alpha}{f^*(\alpha)}}{(t_{qk}-t_{qi})}\, e^{\frac{E(\alpha_{ik})}{RT_{qik}}} \qquad q=(1,2) \qquad (19)$$

and correspondingly

$$\log A(\alpha_{ik}) = \frac{\log A_1(\alpha_{ik})+\log A_2(\alpha_{ik})}{2} \qquad (2o)$$

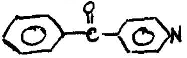
Such a procedure was applied for the dehydration of $CaC_2O_4 \cdot H_2O$ at $\beta_1 = 1$ K min^{-1} and $\beta_2 = 5$ K min^{-1}. The results are given in Table I from reference /7/.

Another possibility to find $f^*(\alpha)$ consists in averaging it for all the values of α, i.e., to obtain a $f^*(\alpha)$ /9,1o/. In this case E (α_{ik}) is evaluated by help of relationship (16) but for $f^*(\alpha)$ an average value of the activation energy

$$\bar{E} = \frac{E_1+E_2+\ \ldots\ E_m}{m} \quad (m = \text{nr. of pairs } \alpha_i, \alpha_k) \qquad (21)$$

should be used /9,1o/. Obviously in such conditions an average value of A should be considered too.

This procedure was applied to investigate the kinetic parameters for the decompositions of some coordination compounds of the form $Me^{II}L_pX_2(Me^{II} = Co^{II}$ or Ni^{II}

L =  p= 2 or 4, X= NCS or Cl) /9/

$CaC_2O_4 \cdot H_2O$ and $KMnO_4$ /8,1o/. A linear dependence of the activation energy on the degree of conversion,

$$E = E_0 + E_1\alpha \qquad (E_0 = ct, \quad E_1 = ct) \qquad (22)$$

has been made evident.

As far as the preexponential factor is concerned the following relationships:

$$\ln A = a + bE \qquad (a = const, \ b = const) \qquad (23)$$

and

$$A = A_0 e^{A_1\alpha} \qquad (A_0 = const, \ A_1 = const) \qquad (24)$$

have been obtained.

Taking into account relationships (22) and (24), equation (7) turns into:

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} \overleftarrow{f^*(\alpha)} e^{A_1\alpha} e^{-\frac{E_0}{RT}} e^{-\frac{E_1\alpha}{ER}} \qquad (25)$$

which can be considered as a first equation of the nonclassical nonisothermal kinetics.

CONCLUSIONS

1 Some relationships showing the dependence of the nonisothermal kinetic parameters on the degree of conversion have been derived.

2 A new equation for nonclassical nonisothermal kinetics has been derived .

REFERENCES

1 E.Segal and D.Fătu "Introduction to Nonisothermal Kinetics" Publishing House of the Academy of the Socialist Republic of Roumania, Bucharest, 1983, p.7o (in Rumanian)

2 J.Šesták,"Thermophysical Properties of Solids," Academia Prague, 1984, p.218.

3 J.Šesták and G.Berggren, Thermochim.Acta. 3 (1971) 1

4 J.Šesták, V.Šatava and W.W.Wendlandt, ibidem, 7(1973) 447

5 E.Urbanovici and E.Segal, ibidem, 118 (1987) 65

6 E.Urbanovici and E.Segal, ibidem, 125 (1988) 261

7 E.Urbanovici and E.Segal, ibidem, 91 (1985) 373

8 E.Urbanovici and E.Segal, ibidem, 94 (1985) 399

9 M.Andruh , E.Urbanovici, M.Brezeanu and E.Segal, ibidem 95 (1985) 257

lo E.Urbanovici and E.Segal, ibidem, 98 (1986) 385

11 E.Urbanovici and E.Segal, ibidem, lo7 (1986) 339

12 E.Urbanovici and E.Segal, ibidem, 118 (1987) 3o9