

NEW METHODS FOR WORKING NONISOTHERMAL KINETIC DATA

Ernest Urbanovici and Eugen Segal

Chair of Physical Chemistry and Electrochemical Technology,  
 Faculty of Chemical Engineering, Polytechnical Institute of  
 Bucharest, Bulevardul Republicii 13, Bucharest (Romania)

Starting from the general rate equation of the nonisothermal kinetics[1]:

$$-\frac{d\alpha}{dT} = \frac{A_r}{a} T^r f(\alpha) \exp(-E/RT) \quad (1)$$

Three methods for the evaluation of the kinetic parameters, for solid-gas decompositions have been worked up.

1) THE IMPROVED COATS-REDFERN METHOD

From equation 1 through integration one gets:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)T^{r+2}} = \frac{A_r}{a} \int_0^T \frac{\exp(-E/RT)}{T^2} dT \quad (2)$$

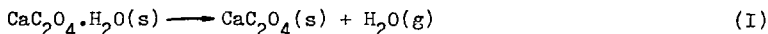
where in the left side integral  $T = T(\alpha)$ , and the right side integral can be solved exactly. Thus eqn.2 turns into:

$$\log \int_0^{\alpha} \frac{d\alpha}{f(\alpha)T^{r+2}} = \log \frac{A_r R}{aE} - \frac{E}{2,303R} \frac{1}{T} \quad (3)$$

For the proper form of  $f(\alpha)$  and the correct value of  $r$ , the plot

$$\left[ \log \int_0^{\alpha} \frac{d\alpha}{f(\alpha)T^{r+2}} , \frac{1}{T} \right] \text{ should be a straight line whose slope and}$$

intercept allow to calculate the values of  $E$  and  $A_r$ . The method was checked for the reaction:



taking  $f(\alpha) = (1 - \alpha)^n$ . The results are given in table 1.

Table 1

n	r	E (Kcal mol <sup>-1</sup> )	A <sub>r</sub> (s <sup>-1</sup> K <sup>-r</sup> )	r <sub>xy</sub>
1	0	23.86	1.2×10 <sup>8</sup>	0.9995
1	1	22.99	9.0×10 <sup>4</sup>	0.9993
1	2	22.45	7.7×10 <sup>1</sup>	0.9990

For r=0 the values of the kinetic parameters are in satisfactory agreement with those reported in literature [2,3].

2) METHOD OF NONISOTHERMAL KINETIC ANALYSIS USING THE INTEGRATION OVER SMALL TEMPERATURE INTERVALS (I)

For  $f(\alpha) = (1 - \alpha)^n$  and r = 0 performing in 1 the integration between T<sub>i</sub> and T<sub>j</sub>, T<sub>i</sub> and T<sub>j</sub> being two close temperatures one gets:

$$\int_{\alpha_i}^{\alpha_j} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{a} \int_{T_i}^{T_j} \exp(-E/RT) dT \quad (4)$$

Using the theorem of the average [4]

$$\int_a^b f(x)dx = (b-a)f(c) \quad c \in [a, b] \quad (5)$$

where if f(x) is a linear function with the general form f(x) = mx + n, then c = (a+b)/2. For T<sub>j</sub> - T<sub>i</sub> = ΔT ∈ [5K, 15K] the functions 1/(1-α)<sup>n</sup> and exp(-E/RT) can be considered as linear. After performing the calculations the following relationship has been obtained:

$$\log A + n \log \left( 1 - \frac{\alpha_i + \alpha_j}{2} \right) - \frac{2E}{2.303R(T_i + T_j)} = \log \frac{(\alpha_j - \alpha_i)}{(T_j - T_i)} a \quad (6)$$

Taking three pairs of T<sub>1</sub>, T<sub>2</sub> values, a system of three eqns. can be written whose solutions are the values of the kinetic parameters E, A and n. The method has been checked for reaction I. The following values of the kinetic parameters have been obtained.

$n = 0.98$  ;  $E = 22.7 \text{ Kcal mol}^{-1}$  ;  $A = 3.45 \times 10^7 \text{ s}^{-1}$   
 which are also in satisfactory agreement with the values reported in literature [2,3].

3) METHOD OF NONISOTHERMAL KINETIC ANALYSIS USING THE  
 INTEGRATION OVER SMALL TEMPERATURE INTERVALS (II)

Using the second average theorem [5],

$$\int_a^b f(x)g(x)dx = f(c) \int_a^b g(x)dx \quad c \in [a, b] \quad (7)$$

with  $c = (a+b)/2$ , from 1 after separation of the variables and integration one gets:

$$F(i, j) = \int_{\alpha_i}^{\alpha_j} \frac{d\alpha}{F(\alpha)} = \frac{A_0 R}{aE} T_{ij}^{r+2} \left[ \exp(-E/RT_j) - \exp(-E/RT_i) \right] \quad (8)$$

where  $T_{ij} = (T_i + T_j)/2$ .

A similar relationship can be obtained by considering one more temperature  $T_k$ , with the condition  $T_k - T_j = T_j - T_i = \Delta T \in [5K, 20K]$ . Introducing the notation:

$$G = \frac{F(j, k)}{F(i, j)} \left( \frac{T_{ij}}{T_{jk}} \right)^{r+2} \quad (9)$$

and taking the ratio of the two relationships of the general form 8, the following working formula was obtained:

$$E = \frac{2RT_i T_j T_k}{\Delta T} \frac{(T_k G - T_i)}{(T_k^2 G + T_i^2)} \quad (10)$$

For the dehydration of calcium oxalate the following values of the kinetic parameters have been obtained:

$n = 0.9$  ;  $E = 22.32 \text{ Kcal mol}^{-1}$  ;  $A_0 = 3.1 \times 10^7 \text{ s}^{-1}$   
 which are in fair good agreement with those reported in literature [2,3].

REFERENCES

- 1 E. Segal and D. Fătu, Introduction to Non-isothermal Kinetics, Publishing House of the Academy of Sciences of the Socialist Republic of Romania, Bucharest, 1983, p. 70,84 (in Romanian).
- 2 E.S. Freeman and B. Carroll, J. Phys. Chem., 82 (1958) 394.
- 3 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
- 4 W. Rudin, Principles of Mathematical Analysis, Mir, Moscow, 1976, pp. 117, 151 (in Russian).
- 5 Kleine Enzyklopädie der Mathematik, Technical Publishing House, Bucharest, 1980, p. 550 (in Romanian ).