

Note

KINETIC ANALYSIS OF A SEQUENCE OF TWO CONSECUTIVE REACTIONS FROM THERMOGRAVIMETRIC DATA UNDER NON-ISOTHERMAL CONDITIONS. PART II. DEHYDRATION OF $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

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On the basis of the established model [1], the following system of differential equations is obtained for two consecutive reactions under isothermal conditions

$$\begin{aligned} \frac{d\alpha_1}{dt} &= k_1(1 - \alpha_1)^{n_1} \\ \frac{d\alpha_2}{dt} &= k_2(\alpha_1 - \alpha_2)^{n_2} \\ k_1 &= A_1 e^{-E_1/RT} \\ k_2 &= A_2 e^{-E_2/RT} \end{aligned} \quad (1)$$

where α_1 = conversion of the first reaction, α_2 = conversion of the second reaction, E_1 = activation energy of the first reaction, E_2 = activation energy of the second reaction, n_1 = reaction order of the first reaction, and n_2 = reaction order of the second reaction. For given values of the kinetic parameters A_1 , E_1 , n_1 , A_2 , E_2 , n_2 , system (1) can be solved by various methods (we used a modified Euler method, followed by a predictor—corrector method), which gives

$$\alpha = \alpha_1 + \alpha_2$$

and

$$\frac{d\alpha}{dT} = \frac{d\alpha_1}{dT} + \frac{d\alpha_2}{dT}$$

Assuming the influence of the experimental errors on the shape of the α vs. T and $d\alpha/dT$ vs. T curves to be insignificant when compared to the influence of large variations of the kinetic parameters, the condition for a minimum of the function

$$S = \sum_{i=1}^N (x_i^{\text{calc}} - x_i^{\text{exp}})^2 \quad (2)$$

where x_i is the value of α or $d\alpha/dT$ at point i , and N is the number of experimental points, is used to determine the kinetic parameters $A_1, E_1, n_1, A_2, E_2, n_2$.

The minimum of the function is sought on a set of points $Y \subset R^6$, described by the kinetic parameters $A_1, E_1, n_1, A_2, E_2, n_2$. The better the choice of method for optimization and accuracy of experimental data, the better the values of the kinetic parameters obtained.

METHOD OF MINIMIZATION OF THE S FUNCTION

In previous work [1], we have tried to determine the starting point Y_0 by means of the Coats—Redfern method applied twice. Experimental points were chosen such that, for the first set, the conversion was less than 0.4 (when the second reaction is supposed to be sufficiently slow) and, for the second set, the conversion was greater than 0.6 (when the first reaction is supposed to be complete). By means of this $Y_0 (A_1^{(0)}, E_1^{(0)}, n_1^{(0)}, A_2^{(0)}, E_2^{(0)}, n_2^{(0)})$ the system (1) was solved by subroutine CALC(Y). The value S_0 was computed from eqn. (2).

A direction of optimization is now sought on the set $Y \subset R^6$. Each parameter is modified by the value dY_i ($i = 1, 2, \dots, 6$) and the value $(S - S_0)/dY_i$ is computed.

If

$$\left| 1 - \frac{S}{S_0} \right| \geq 1$$

we choose the new step

$$dY_{i(\text{new})} = \frac{dY_i}{1 - \frac{S}{S_0}}$$

If

$$\left| 1 - \frac{S}{S_0} \right| < 1$$

we choose the new step

$$dY_{i(\text{new})} = \left(1 - \frac{S}{S_0} \right) dY_i$$

This choice is done for the sake of simplicity and to keep the step for each kinetic parameter under the initially chosen values of precision.

After the choice of the direction of motion, the length of the step is controlled by the introduction of a parameter λ , where $dY_{i(\text{new})} = \lambda dY_i$. If function S decreases, λ is doubled. If S increases, λ is decreased until a limit value λ_0 is reached. The criterion of convergence is the values under a chosen limit for either (1) the deviation S , or (2) the values of all $dY_{i(\text{new})}$. According to these principles a program has been established and run on a Felix computer.

EXPERIMENTAL

The dehydration reaction of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ powder (Merck) of medium particle size ($0.95 \mu\text{m}$) was studied in air, under non-isothermal conditions, with a heating rate β of 5°C min^{-1} . The weight of sample taken was 0.288 mg. The α vs. T curve shows a slight change in its slope at 110°C and $d\alpha/dT$ vs. T shows two maxima at 100°C and 120°C , with a minimum at 110°C , where the value $(d\alpha/dT)_{110^\circ\text{C}} > 0$.

Assuming the following system of reactions to be valid



the starting values

$$A_1 = 2.4 \times 10^{15} \text{ s}^{-1}; E_1 = 27.5 \text{ kcal mole}^{-1}, n_1 = 1$$

$$A_2 = 4.7 \times 10^{16} \text{ s}^{-1}; E_2 = 32.3 \text{ kcal mole}^{-1}, n_2 = 1$$

were determined.

The final values were

$$A_1 = 2.41 \times 10^{15} \text{ s}^{-1}; E_1 = 27.53 \text{ kcal mole}^{-1}, n_1 = 1.2$$

$$A_2 = 4.74 \times 10^{16} \text{ s}^{-1}, E_2 = 32.29 \text{ kcal mole}^{-1}, n_2 = 0.9$$

The medium deviation of the experimental and calculated α is 0.01. Both the α vs. T and the experimental curves have the same shape, with a minimum at 115°C between maxima at 100°C and 125°C . The number of iterations was 10. Values of pre-exponential factors have less influence on the shape of the α - T curve, which is why they are practically the same at the end of the process. In contrast, small changes of activation energy change the shape of the α - T curves greatly. The initial values seemed to be fairly accurately determined. The most important changes are those of the values of the reaction orders.

REFERENCE

- 1 V. Marcu and E. Segal, *Thermochim. Acta*, in press.