Short Communications

CRITERION OF THE EXISTENCE OF COMPENSATION RELATIONSHIP FOR NON-ISOTHERMAL KINETICS

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If, for a series of similar-type chemical transformations in non-isothermal kinetics, identical or closely similar values of T_{cr} are observed in the equation $1/T_{cr} = 1/T_{si} + (R/E_i) \cdot \ln (E_i q/RT_{si}^2)$, the existence of the compensation relationship $\ln A_i = E_i/RT_{cr}$ may regularly be assumed.

In an earlier paper [1] we derived the analytical expression of the compensation relationship for non-isothermal kinetics in the form:

$$\ln A = \ln \frac{Eq}{RT_s^2} + \frac{E}{RT_s} \text{ or } \left(\frac{\mathrm{d} \ln A}{\mathrm{d}E}\right)_{T_s} = \frac{1}{RT_s} + \frac{1}{E} \quad (1)$$

This was obtained from the starting equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(1 - \alpha)^n \exp \frac{-E}{RT},$$

the usual symbols being applied, and the subscript s referring to the point where the rate of non-isothermal transformation is maximum. A rigorous inspection of Eq. (1) reveals, however, that the term $\ln \frac{Eq}{RT_s^2}$ is equivocal at variations of the temperature T_s, of the activation energy E and of the rate of linear temperature increase q (centigrade/second). Consequently, the observed compensation relationship $\ln A$ *vs.* E may become distorted, or its truth may become doubtful. This difficulty may be eliminated by introducing a criterion of the true existence of the compensation relationship for non-isothermal kinetics. In general case, the criterion of true compensation relationship will be the existence of a common isokinetic point in the graph $\ln K$ *vs.* $1/T$ for a series of similar-type transformations. If no such point exists, the observed linear relationship between $\ln A$ and E may be fictitious or a result of the ν-effect [3].

If the Arrhenius equation $K = A \exp \frac{-E}{RT}$ is utilized for describing the transformation process, this equation may be written in the following form:

$$K = \exp \frac{E}{RT_{cr}} \cdot \exp \frac{-E}{RT} \quad (2)$$

where T_{cr} is the critical temperature or reversal temperature [2] where $\ln K = 0$. Then the factor A in the Arrhenius equation can be expressed in the logarithmic form by

$$\ln A = \frac{E}{RT_{cr}}. \tag{3}$$

Hence, for a series of chemical reactions with similar values of T_{cr}, the compensation effect will automatically be satisfied, that is, the relationship between $\ln A$ and E will be linear.

Let us consider this criterion of the compensation relationship for non-isothermal kinetics, that is, the existence of a critical temperature at which $\ln K = 0$.

Table 1

Calculated critical temperatures for the dehydration of the chelate $Mg_2L \cdot 9H_2O$
$q = 0.1$ degree/sec

Parameters	Flow rate of the carrier gas N_2, $cm^3 \cdot min^{-1}$					
	6	10	15	20	25	40
T, K	448	423	409	420	418	398
E, kcal/mole	18.7	21.1	22.4	24.4	24.9	24.6
T_{cr}, K	603	532	500	506	501	472

According to our earlier work [4], the rate constant of the non-isothermal transformation is expressed by

$$K = \frac{(1-\alpha_s)^{1-n}}{n} \cdot \frac{Eq}{RT_s^2} \exp\frac{E}{RT_s} \cdot \exp\frac{-E}{RT}. \tag{4}$$

Taking into account that $(1 - \alpha_s)^{1-n}/n \approx 1$, Eq. (4), for the case $\ln K = 0$, may be written in the following form:

$$\frac{E}{RT_{cr}} = \frac{E}{RT_s} + \ln\frac{Eq}{RT_s^2} \tag{5}$$

which, after suitable transformations, will yield

$$\frac{1}{T_{cr}} = \frac{1}{T_s} + \frac{R}{E}\ln\frac{Eq}{RT_s^2}. \tag{6}$$

By experimentally determining the values of E, T_s and q, the absolute value of T_{cr} can be calculated. If, for a number of similar-type transformations, identical (or sufficiently close) values of T_{cr} will be observed, this is a basis for stating that compensation relationship exists. However, for a first assumption regarding the existence of compensation relationship, it continues to be useful to determine the temperature T_s where the rate of non-isothermal transformation $d\alpha/dt$ is maximum.

All that has been said can be demonstrated utilizing the experimental data reported in Ref. 1. The calculated values of T_{cr} are listed in Table 1. These values confirm the existence of the compensation relationship when the flow rate of the carrier gas is being varied from 10 to 40 cm^3/min. The value of A can be determined from Eq. (3).

References

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