Short Communication

THE COMPENSATION EFFECT IN THE KINETICS OF THE THERMAL DECOMPOSITION OF CALCIUM CARBONATE

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The kinetic parameters of the Arrhenius equation for the thermal decomposition of $CaCO_3$ depending on the values of the sample weight and of the linear heating rate are interrelated by the compensation relationship $\lg A = a + b\Delta H^*$.

Gallagher and Johnson [1] reported on experiments uniquely effectuated, concerning the kinetics of the thermal decomposition of calcium carbonate under isothermal and non-isothermal conditions, in dependence of the sample weight and of the linear heating rate.

Results and discussion

Sample weights for the decomposition of $CaCO_3$ under isothermal conditions were 1, 2, 4, 8, 16 and 32 mg, resp. The kinetic curves were best described by the equation of a sphere being compressed:

$$1 - (1 - \alpha)^{1/2} = Kt, \tag{1}$$

or in the differential form

$$\frac{d\alpha}{dt} = K'(1 - \alpha)^{1/2} \tag{2}$$

and also by the Erofeev equation with the kinetic exponent 2:

$$[-\ln(1 - \alpha)]^{1/2} = K''t \tag{3}$$

The analysis of experimental weight loss data at the isothermal decomposition of $CaCO_3$ indicated a relationship between the logarithm of the rate constant and the logarithm of the sample weight W expressed by a straight line. From the Arrhenius relationship $\lg K$ *vs.* $1/T$, activation enthalpies ΔH^* were calculated. These were found to depend on sample weight W conforming to the following equation:

$$\Delta H^* = -2.9134 \lg W + 49.675 \text{ kcal mole}^{-1}. \tag{4}$$

Correspondingly

$$\lg A_1 = -1.3152 \lg W + 8.4026 \tag{5}$$

$$\lg A_2 = -1.3425 \lg W + 8.6597. \tag{6}$$

In the following, let us consider only the value A_1 for the equation of the sphere being compressed (1). Uniting Eqs (4) and (5) to obtain the Arrhenius equation, we arrive to

$$\lg K = (636.7\, T^{-1} - 1.3152) \lg W + 8.4026 - 10855\, T^{-1} \tag{7}$$

Eq. (7) describes the experimentally observed rate constant as a function of sample weight and temperature. Consequently, it appears possible that a compensation relationship [2] exists between the kinetic parameters A and ΔH^* according to the equation

$$\lg A = a + b\Delta H^* \quad \text{or} \quad \lg A = a + bE \tag{8}$$

where E is the activation energy, a and b are constants.

Let us assume that – for a series of chemical transformations belonging to the same type – we have a series of Arrhenius straight lines (e.g. Fig. 12 in [1]), viz.

$$\ln K = \ln A_1 - \frac{E_1}{RT}; \quad \ln K = \ln A_2 - \frac{E_2}{RT}; \quad \ln \quad K = \ln A_i - \frac{E_i}{RT}$$

that meet in a common isokinetic point $\left(\ln K_x \text{ and } \frac{1}{T_x}\right)$. At this point, we have a new functional relationship with the new variables $\ln A_i$ and E_i, namely

$$\ln A_i = \frac{E_i}{RT_x} + \ln K_x . \tag{9}$$

If the straight lines $\ln K$ *vs.* $\frac{1}{T}$ meet on the abscissa at point $\frac{1}{T_0}$, then $\ln K_x = 0$. In this case, the compensation relationship will assume a classical form, namely $\ln A_i = \frac{E_i}{RT_0}$.

The experimentally found Eq. (7) for the isothermal decomposition of $CaCO_3$ also allows the existence of a common isokinetic point $\left(\ln K_x \text{ and } \frac{1}{T_x}\right)$. In fact, at a certain temperature T_x Eq. (7) can be written in the following form:

$$\lg K_x = 8.4026 - 10855\, T_x^{-1} = \lg A_i - \frac{\Delta H_i^*}{RT_x} \tag{10}$$

For this case, the equation of the compensation relationship will be

$$\lg A_i = \frac{\Delta H_i^*}{RT_x} + (8.4026 - 10855\, T_x^{-1}) \tag{11}$$

The temperature T_x of the isokinetic point can readily be calculated from the condition $636.7\,T_x^{-1} - 1.3152 = 0$, and is equal to $T_x = 484$ K.

An analogous linear relationship $\lg A_i = f(\Delta H_i^*)$ is obtained from the experimental decomposition data of $CaCO_3$ at varying sample weights and linear heating rates. All required data are listed in Table 2 of [1], in Table 4 (Fig. 3) of [3] and [4].

Thus, notwithstanding the apparent ambiguity – as shown by the experiment – of the kinetic values $\lg A$ and E at various conditions of the decomposition process, their logical interrelationship may be expressed in the form of the compensation relationship $\lg A = f(E)$.

References

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