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Inequalities for the activation energy in non-isothermal kinetics

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Abstract

Two inequalities for the activation energy of a non-isothermal reaction have been obtained. Using them, the limits of the range within the real value of the activation energy lies may be estimated. The concepts are used to determine the limits of the activation energy values for calcium oxalate dehydration data.

THEORY

We assume, in the following, that the kinetic parameters do not change when either temperature or heating range is changed. The integral equation for non-isothermal kinetics is [1]

$$F(\alpha) = \frac{A}{\beta} I(T, E_r) \tag{1}$$

where the conversion integral is

$$F(\alpha) = \int_0^\alpha \frac{dx}{f(x)} \tag{2}$$

and the temperature integral is

$$I(T, E_r) = \int_{T_0}^{T} \exp(-E_r/Rz)\, dz \tag{3}$$

E_r is the real value of the activation energy and the other notations have their usual meanings. For a certain degree of conversion α_i, in the two measurements two different temperatures, T_{i1} and T_{i2}, are measured. As $\beta_1 < \beta_2$, it follows that $T_{i1} < T_{i2}$.

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From eqn. (1) we may write

$$\frac{I(T_{i1}, E_r)}{\beta_1} = \frac{I(T_{i2}, E_r)}{\beta_2} \tag{4}$$

Equation (4) must hold for any value of the degree of conversion α_i, and consequently for any pair of temperatures (T_{i1}, T_{i2}). Equation (4) may also be written as

$$\beta_2 \int_{T_0}^{T_{i1}} \exp(-E_r/Rz)\,\mathrm{d}z = \beta_1 \int_{T_0}^{T_{i2}} \exp(-E_r/Rz)\,\mathrm{d}z \tag{5}$$

where T_0 is the highest temperature for which during both experiments

$$\alpha(T_0) = 0 \tag{6}$$

Equation (5) may be used to obtain the limits of the real value of the activation energy E_r for a studied reaction.

Upper limit

As shown in ref. 2, one may consider a function of variable E

$$g_i(E) = \beta_1 \int_{T_0}^{T_{i2}} \exp(-E/Rz)\,\mathrm{d}z - \beta_2 \int_{T_0}^{T_{i1}} \exp(-E/Rz)\,\mathrm{d}z \tag{7}$$

where T_{i1} and T_{i2} are the values of the temperatures corresponding to the same α_i for the two experiments.

The real value of the activation energy E_r allows us to write

$$g_i(E_r) = 0 \tag{8}$$

for any i.

One may also observe that

$$g_i(0) = \beta_1 T_{i2} - \beta_2 T_{i1} + T_0(\beta_2 - \beta_1) \tag{9}$$

and

$$\lim_{E \to \infty} g_i(E) = 0 \tag{10}$$

In order to study the behaviour of function $g_i(E)$, its first derivative $g'_1(E)$ must be computed and compared to zero, i.e. the sign of the first derivative has to be determined.

The derivative of function $g_i(E)$ is

$$g'_i(E) = \frac{\beta_2}{R}\left(T_{i1}\mathrm{e}^{-\frac{E}{RT_{i1}}} - T_0\mathrm{e}^{-\frac{E}{RT_0}}\right)\left(\frac{\beta_1}{\beta_2}\,\frac{T_{i2}\mathrm{e}^{-\frac{E}{RT_{i2}}} - T_0\mathrm{e}^{-\frac{E}{RT_0}}}{T_{i1}\mathrm{e}^{-\frac{E}{RT_{i2}}} - T_0\mathrm{e}^{-\frac{E}{RT_0}}} - 1\right) \tag{11}$$

One may notice, first, that because of the monotony of the exponential function it follows that

$$\frac{\beta_2}{R}[T_{i1}\exp(-E/RT_{i1}) - T_0\exp(-E/RT_0)] > 0 \tag{12}$$

Also, because the conversion integral is zero for $\alpha = 0$, the exponential $\exp(-E/RT_0)$ has to tend to zero. Therefore this expression may be neglected in eqn. (11).

Taking into account these considerations, the sign of the first derivative will be given by the expression from the second parenthesis of eqn. (11), i.e.

$$\mathrm{sign}[g_i'(E)] = \mathrm{sign}\left(\frac{\beta_1 T_{i2}}{\beta_2 T_{i1}}\exp\frac{E}{R}\frac{T_{i2}-T_{i1}}{T_{i1}T_{i2}} - 1\right) \tag{13}$$

As the exponential is always higher than 1, the sign should be given by a comparison of the ratio $\beta_1 T_{i2}/\beta_2 T_{i1}$ with unity.

Let us consider, first, that

$$\frac{\beta_1 T_{i2}}{\beta_2 T_{i1}} > 1 \tag{14}$$

which is equivalent to

$$\beta_1 T_{i2} - \beta_2 T_{i1} > 0 \tag{15}$$

From this condition it follows that the investigated sign should be positive, i.e.

$$g_i(E) > 0 \tag{16}$$

for any value of E. This means that $g_i(E)$ is a monotonous increasing function.

However, because

$$T_0(\beta_2 - \beta_1) > 0 \tag{17}$$

and taking into account relationship (15), from eqn. (7) one obtains

$$g_i(0) > 0 \tag{18}$$

By comparing relationships (18) and (10), it follows that

$$g_i(0) > g_i(\infty) \tag{19}$$

Because a function cannot increase from a larger value to a smaller one, it may be concluded that relationships (19) and (16) are contradictory. This suggests that assumption (14), or its equivalent, (15), is not correct.

It follows that one has to consider only

$$\frac{\beta_1 T_{i2}}{\beta_2 T_{i1}} < 1 \tag{20}$$

or

$$\beta_1 T_{i2} - \beta_2 T_{i1} < 0 \tag{21}$$

The nature of the extremes should now be considered. The condition for having extremes is

$$g_i(M) = 0 \tag{22}$$

where M is the value of E for which the extreme of the $g_i(E)$ function is reached. This value may easily be computed by taking into account eqns. (11) and (22) and it is given by

$$M_i = R\frac{T_{i1}T_{i2}}{T_{i2}-T_{i1}}\ln\frac{\beta_2 T_{i1}}{\beta_1 T_{i2}} \tag{23}$$

Using relationship (20) in eqn. (23), we obtain

$$\begin{aligned} &g_i(E < M_i) > 0 \\ &g_i(E > M_i) < 0 \end{aligned} \tag{24}$$

which leads to the conclusion that the extreme is a maximum.

Obviously

$$g_i(M_i) > 0 \tag{25}$$

The condition

$$g_i(0) < 0 \tag{26}$$

should also be fulfilled, otherwise eqn. (5) has no real solutions.

Taking into account relationship (9), relationship (26) may also be written as

$$\beta_2 T_{i1} - \beta_1 T_{i2} > T_0(\beta_2 - \beta_1) \tag{27}$$

It follows from the above considerations that the value of the activation energy E_r which satisfies eqn. (8) should lie between 0 and M_i for any value of i

$$0 \leqslant E_r \leqslant M_i = R\frac{T_{i1}T_{i2}}{T_{i2}-T_{i1}}\ln\frac{\beta_2 T_{i1}}{\beta_1 T_{i2}} \tag{28}$$

Based on these results, plots of the $g_i(E)$ functions are easily obtained, as shown in Fig. 1.

Figure 1 shows that for different pairs (T_{i1}, T_{i2}) measured at different degrees of conversion α_i, different values of M_i are obtained. The smallest value of M_i is still higher than E_r and, in consequence, an upper boundary $E_{\max}$ of the value of the activation energy E_r may be defined

$$E_r \leqslant E_{\max}(M_i) \tag{29}$$

Lower limit

As $T_{i1} < T_{i2}$, eqn. (5) becomes

$$(\beta_1 - \beta_2)\int_{T_0}^{T_{i1}} \exp(-E_r/Rz)\,\mathrm{d}z = \beta_1 \int_{T_{i1}}^{T_{i2}} \exp(-E_r/Rz)\,\mathrm{d}z \tag{30}$$

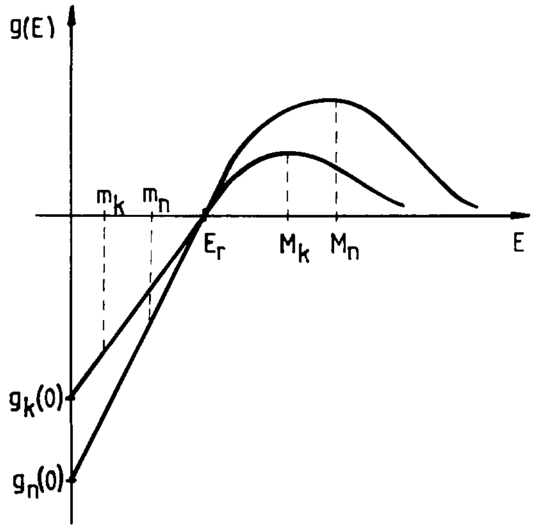

Fig. 1. The plot of functions $g_k(E)$ and $g_n(E)$ obtained at two different conversion degrees α_k and α_n, respectively.

Taking into account that the exponential function is monotonous and using the first mean value theorem for the definite integral, eqn. (30) may be written as

$$(\beta_2-\beta_1)(T_{i1}-T_0)\exp(-E_r/RT_0)\leqslant\beta_1(T_{i2}-T_{i1})\exp(-E_r/RT_{i2}) \qquad (31)$$

Equation (31) allows us to write

$$E_r\geqslant R\frac{T_0T_{i2}}{T_{i2}-T_0}\ln\frac{(\beta_2-\beta_1)(T_{i1}-T_0)}{\beta_1(T_{i2}-T_{i1})} \qquad (32)$$

For different pairs (T_{i1}, T_{i2}) measured for different values of α_i, the right side of the inequality (32) leads to different values, m_i, as shown on Fig. 1. Obviously if the real value of the activation energy E_r is higher than the highest value of m_i, it should be higher than any other m_i. We may, thus, define the highest value of m_i as the lower boundary $E_{\min}$ for the values of the activation energy

$$E_r\geqslant E_{\min}=\max(m_i) \qquad (33)$$

From relationships (28) and (32), one may write

$$R\frac{T_0T_{i2}}{T_{i2}-T_0}\ln\frac{\beta_2-\beta_1}{\beta_1}\frac{T_{i1}-T_0}{T_{i2}-T_{i1}}=E_{\min}\leqslant E_r\leqslant E_{\max}=R\frac{T_{j1}T_{j2}}{T_{j2}-T_{j1}}\ln\frac{\beta_2T_{j1}}{\beta_1T_{j2}} \qquad (34)$$

The indices i and j suggest that the lower and upper limits of the real value of the activation energy E_r, as defined by the relationships (29) and (33), are

TABLE 1

The values of m_i and M_i at various conversion degrees

α_i	$\beta_1 = 2.3$ K min^{-1}	$\beta_2 = 14.8$ K min^{-1}	m_i/(kJ mol^{-1})	M_i/(kJ mol^{-1})
0.1	426	450.5	44.8	113.8
0.2	440	467	40.6	110.5
0.3	449	478	38.1	107.1
0.4	455	486	36.0	103.4
0.5	460.5	493	34.3	100.9
0.6	465.5	499.5	33.1	98.8
0.7	471	505	33.1	100.9
0.8	475	509.5	32.2	101.3
0.9	479.5	514.5	31.8	101.7

calculated at different values of the conversion degree, α_i and α_j respectively, to which different pairs of temperatures (T_{i1}, T_{i2}) and (T_{j1}, T_{j2}), respectively correspond.

The theoretical considerations presented above have been tested using data obtained for the dehydration of $CaC_2O_4 \cdot H_2O$ at two different heating rates, $\beta_1 = 2.3$ K min^{-1} and $\beta_2 = 14.8$ K min^{-1}, as given in ref. 3. The calculated values of m_i and M_j according to eqns. (23) and (32), for $T_0 = 397$ K, are listed in Table 1.

According to relationships (29) and (33), Table 1 gives the results

$$E_{\min} = \max(m_i) = 44.8 \text{ kJ mol}^{-1}$$

$$E_{\max} = \min(M_j) = 98.8 \text{ kJ mol}^{-1}$$

i.e. the real value of the activation energy for the calcium oxalate dehydration reaction studied in ref. 3 should fall within the range 44.8–98.8 kJ mol^{-1}. In fact, the value cited is $E_r = 97.3$ kJ mol^{-1} [3], which falls within the calculated range.

CONCLUSIONS

In summary for a reaction studied at two different heating rates one may determine the limits of the range within which the real value of the activation energy should lie, as given by relationship (34).

It must be stressed that the basic assumption used to calculate the limits is that the kinetic parameters of the reaction do not change during the non-isothermal experiments. The only mathematical condition imposed on eqn. (5) for having a solution is relationship (27). In other words, if relationship (27) is not fulfilled, the kinetic parameters of the reaction may be considered as being variable with the experimental conditions. Relationship (27) may therefore be used as a criterion for the invariance of the reaction mechanism when the heating rate, or another experimental condition, is changed.

REFERENCES

1 C. Popescu and E. Segal, Rev. Roum. Chim., 34 (1989) 567.
2 C. Popescu, M. Tucsnak, Z. Tucsnak and E. Segal, Thermochim. Acta, 164 (1990) 411.
3 J. Leyko, M. Maciejewski and R. Szuniewicz, J. Therm. Anal., 17 (1979) 263.