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CRITICAL ANALYSIS OF THE ISOCONVERSIONAL METHODS FOR EVALUATING THE ACTIVATION ENERGY

II. The activation energy obtained from isothermal data corresponding to two successive reactions

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Abstract

An analysis is presented of the consequences of the use of a one term equation containing apparent activation parameters, instead of the true rate equation to describe two successive decomposition reactions undergone by a solid compound. It is demonstrated that the apparent activation energy, obtained by means of isoconversional differential and integral methods, varies with the conversion degree for a relatively narrow temperature range and with temperature at a given value of the conversion degree. The activation energy values obtained with the isoconversional differential method are higher than the corresponding values obtained with the isoconversional integral method.

Keywords: isoconversional methods, kinetics

Introduction

In the first part of these series [1], a critical analysis was presented of the isoconversional, differential and integral methods for the evaluation of the activation energy from isothermal data. It was established that, if the activation parameters depend on the conversion degree, the values of the activation energy obtained by means of differential and integral isoconversional methods are different. This statement will now be checked for simulated data corresponding to two successive decomposition reactions of a solid compound.

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The kinetic model

Let us consider that solid compound **A** undergoes two successive decompositions:

$$\mathbf{A}(s)\xrightarrow{k_1}\mathbf{B}(s)+\nu_1\mathbf{G}_1(g) \tag{I}$$

$$\mathbf{B}(s)\xrightarrow{k_2}\mathbf{C}(s)+\nu_2\mathbf{G}_2(g) \tag{II}$$

where **B** and **C** are solid compounds and $\mathbf{G}_1$ and $\mathbf{G}_2$ are gaseous products.

The rate constants k_1 and k_2, can be expressed by the Arrhenius equation:

$$k_\mathrm{i}=A_\mathrm{i}\exp\left(-\frac{E_\mathrm{i}}{RT}\right) \tag{1}$$

where i=1 for reaction I and i=2 for reaction II.

Each of the successive reactions is characterized by a reaction order which equals one. The following values of the activation parameters will be considered: E_1=58.5 kJ mol^{-1}; $A_1=9\cdot10^2$ s^{-1}; E_2=125.4 kJ mol^{-1}; and $A_1=5\cdot10^8$ s^{-1}.

The system of differential kinetic equations is as follows [2]:

$$\begin{aligned}\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}&=k_1(1-\alpha_1)\\ \frac{\mathrm{d}\alpha_2}{\mathrm{d}t}&=k_2(\alpha_1-\alpha_2)\end{aligned} \tag{2}$$

where α_1 and α_2 are the values of the degree of conversion for reactions I and II, respectively (α_i is the ratio between the mass of gaseous product at a given moment and the maximum mass of this product which can be evolved in the reaction).

We will consider the particular case $\nu_1M_1=\nu_2M_2$, where M_i is the molecular mass of the gaseous product $\mathbf{G}_1$. In this case the overall degree of conversion, α, is given by $\alpha=(\alpha_1+\alpha_2)/2$. Under such conditions, the integration of system (2) leads to:

$$\alpha=1-\left[\frac{1}{2}+\frac{k_2}{2(k_2-k_1)}\right]\mathrm{e}^{-k_1t}+\frac{k_1}{2(k_2-k_1)}\mathrm{e}^{-k_2t} \tag{3}$$

The isotherms $\alpha=\alpha(t)$ for temperatures in the range 200–350°C in steps of 10°C were plotted. Besides, the values of $\mathrm{d}\alpha/\mathrm{d}t$ for each temperature and the α values in the range 0.05–0.95 in steps of 0.05, were calculated.

The obtained isotherms, $\alpha=\alpha(t)$, apparently correspond to a single change whose rate is given by Eq. (1) [1]. In the following, the consequences of using this equation with overall activation parameters instead of the true kinetic Eq. (2) will be considered.

Evaluation of the activation energy

For each value of α, the isoconversional lines ln(dα/dt) *vs.* 1/T and ln$t$ *vs.* 1/T are seen to bend. This means that the apparent activation energy depends on temperature. The dependences E_{dif} *vs.* T and E_{int} *vs.* T were evaluated through numerical differentiation of the isoconversional curves ln(dα/dt) *vs.* 1/T and ln$t$ *vs.* 1/T. Figures 1 and 2 present such dependences for α=0.3 and α=0.5. Analysis of the E *vs.* T curves for various values of α reveals that the apparent activation energy depends on both α and tempera-

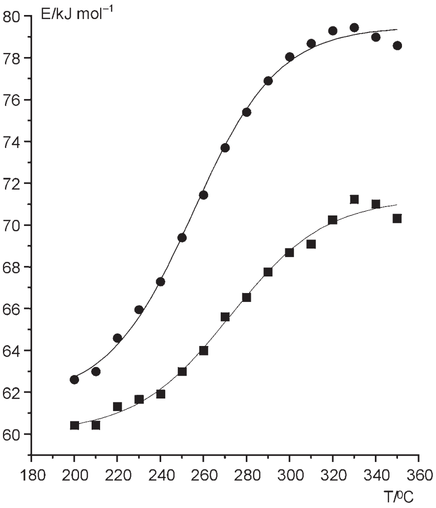

Fig. 1 The dependences E *vs.* T for α=0.30. • – E_{dif}; ▪ – E_{int}

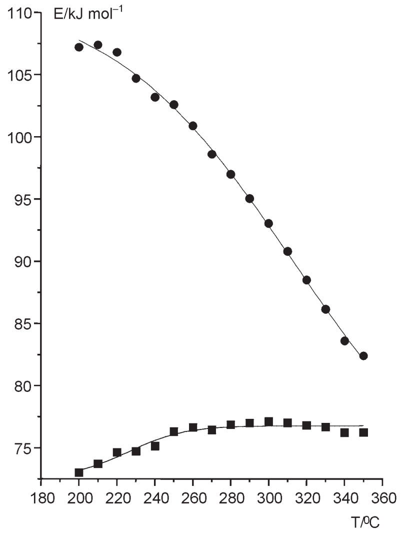

Fig. 2 The dependences E *vs.* T for α=0.50. • – E_{dif}; ▪ – E_{int}

ture. It turns out that the relative contributions of the two elementary reactions to the overall rate vary with temperature and degree of conversion. Figures 1 and 2 show that, for a given (α, *T*) pair, $E_{\mathrm{dif}}^{\alpha,\mathrm{T}} \neq E_{\mathrm{int}}^{\alpha,\mathrm{T}}$.

In relatively narrow temperature ranges (40–50°C) practically linear isoconversional plots ln(dα/d*t*) *vs.* 1/*T* and ln*t* *vs.* 1/*T* ($r>0.9997$) were obtained. From the slopes of the corresponding straight lines, E_{dif} and E_{int} values for the corresponding temperature range were calculated. Figure 3 depicts the plots of E_{dif} *vs.* α and E_{int} *vs.* α for the temperature range 280–320°C. The values of E_{dif} and E_{int} increase with α; further for a given value of α, $E_{\mathrm{dif}}>E_{\mathrm{int}}$. The dependence of the relative deviation of E_{int}

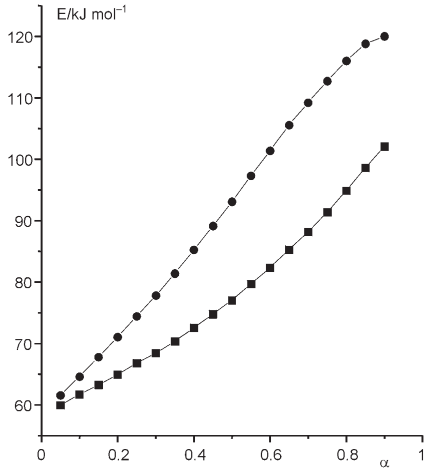

Fig. 3 The dependences *E* *vs.* α, calculated for the interval 280≤*T*≤320°C. ● – E_{dif}; ■ – E_{int}

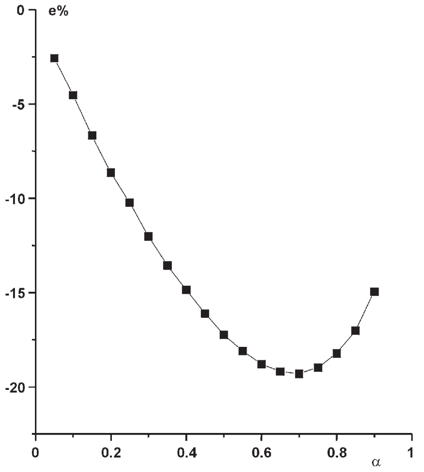

Fig. 4 The dependence $e\%=[(E_{\mathrm{int}}-E_{\mathrm{dif}})/E_{\mathrm{dif}}]\times100$ *vs.* α. E_{dif} and E_{int} evaluated for the interval 280≤*T*≤320°C

with respect to E_{dif} is shown in Fig. 4. It may be observed that e% has the maximum absolute value (≈20%) at $\alpha=0.75$.

Conclusions

1. The isotherms $\alpha=\alpha(t)$, were simulated for a solid compound that undergoes two successive decomposition reactions with the generation of a gaseous and a solid compound in each of them.
2. It was shown that the apparent activation energy values obtained for a single term rate equation depend on temperature for a given conversion degree, and on the conversion degree in a relatively narrow temperature range.
3. It has been shown that there is a difference between the activation energy values obtained by means of the isoconversional differential and integral methods. The absolute value of the relative deviation of E_{int} with respect to E_{dif} is ≈20%.

References

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