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ON THE APPARENT COMPENSATION EFFECT OBSERVED FOR TWO CONSECUTIVE REACTIONS

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Abstract

A critical analysis is presented of the use of an overall single rate reaction equation instead of the true rate equation corresponding to a complex process consisting of two consecutive reactions. In accordance with this approximation, which is often used in the kinetic analysis of systems in which several reactions take place, the overall process is described by apparent activation parameters (the apparent activation energy E_{ap} and the apparent pre-exponential factor A_{ap}) and an apparent conversion function.

The theoretical isotherms ($\alpha=\alpha(t)$, where α is the conversion degree and t is time) were simulated for a system in which two consecutive reactions occur. In this case, the apparent activation parameters depend on (a) the considered range of temperature; and (b) the temperature for a given conversion degree. It is shown that the apparent activation parameters are correlated by the compensation effect relationship:

$$\ln A_{ap} = \alpha^* + \beta^* E_{ap}$$

where α^* and β^* are the linear regression parameters.

The possibility of using the apparent kinetic parameters to predict the isotherms $\alpha=\alpha(t)$ for temperatures lower than those for which these parameters were evaluated is discussed.

Keywords: apparent compensation effect, consecutive reactions, isothermal kinetics

Introduction

Kinetic investigations of solid–gas decompositions provide evidence of the following relation between the pre-exponential factor A and the activation energy E:

$$\ln A = \alpha^* + \beta^* E \tag{1}$$

where α^* and β^* are constant coefficients [1–19].

Relationship (1) reflects a compensation effect (CE) between the exponential and pre-exponential factors in the Arrhenius equation.

In recent paper [17, 18], Vyazovkin and Linert classify the CE into two main types: false and true. For the non-isothermal decomposition of solids, three kinds of false CE are considered [18]: due to a change in (1) reaction model, (2) conversion

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or (3) heating rate. Garn [1] and Vyazovkin and Linert [17] have shown that the true CE is associated with the modification of a reagent or an environment for a series of closely related reactions. From an analysis of the accelerated thermal degradation of polymeric materials, Audouin and Verdu [20] showed that the overall rate cannot be expressed by a single term, or, generally, near a transition between two temperature domains corresponding to different predominant mechanisms of thermal degradation, a pseudo-CE can be observed.

The present paper considers a theoretical kinetic model for an isothermal decomposition in a solid–gas system, which actually involves two consecutive reactions. A critical analysis of the use of an overall single rate reaction instead of the true rate equation will be presented. The apparent activation parameters will be evaluated. It will be shown that these parameters are correlated by relationship (1). The possibility of using the apparent kinetic parameters to predict the isotherms $\alpha=\alpha(t)$ for temperatures lower than those for which these parameters were evaluated (α is the conversion degree and t is time) will be discussed.

The kinetic model

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

$$\mathbf{A}_{(s)} \xrightarrow{k_1} \mathbf{B}_{(s)} + \nu_1 \mathbf{G}_{1_{(g)}} \qquad \text{(I)}$$

$$\mathbf{B}_{(s)} \xrightarrow{k_2} \mathbf{C}_{(s)} + \nu_2 \mathbf{G}_{2_{(g)}} \qquad \text{(II)}$$

where **B** and **C** are solid products 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:

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \qquad (2)$$

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

Both consecutive reactions are characterized by a reaction order equal to one. The following activation parameter values will be considered: E_1=58.5 kJ mol^{-1}; A_1=9·10^2 s^{-1}; E_2=125.4 kJ mol^{-1}; A_2=5·10^8 s^{-1}.

The system of kinetic differential equations is [21]

$$\frac{d\alpha_1}{dt} = k_1(1-\alpha_1) \qquad \frac{d\alpha_2}{dt} = k_2(\alpha_1-\alpha_2) \qquad (3)$$

where α_1 and α_2 are the degrees of conversion for reactions I and II, respectively.

The particular case to be considered is $\nu_1 M_1=\nu_2 M_2$, where M_i is the molecular mass of the gaseous product $\mathbf{G_i}$ and for which the total degree of conversion α is given by $\alpha=(\alpha_1+\alpha_2)/2$.

Under such conditions, the integration of system (3) leads to

$$\alpha = 1 - \left[\frac{1}{2} + \frac{k_2}{2(k_2 - k_1)}\right] e^{-k_1 t} + \frac{k_1}{2(k_2 - k_1)} e^{-k_2 t} \tag{4}$$

An analysis will now be made of the consequences of using not the real kinetic Eqs (3), but of the following one:

$$\frac{d\alpha}{dt} = k_{ap} f(\alpha) \tag{5}$$

where $f(\alpha)$ is the apparent differential conversion function and k_{ap} is given by

$$k_{ap} = A_{ap} \exp\left(-\frac{E_{ap}}{RT}\right) \tag{6}$$

where A_{ap} and E_{ap} are the apparent activation parameters.

Table 1 The values of E_{ap} and $\ln A_{ap}f(\alpha)$ obtained from the straight lines $\ln(d\alpha/dt)$ *vs.* $1/T$, recorded for various temperature ranges

α	ΔT/°C	$\ln A_{ap}f(\alpha)$	E_{ap}/kJ mol^{-1}	r
0.20	200–240	6.2133	60.9	0.99997
	240–280	7.1802	65.0	0.99989
	280–320	8.4987	71.0	0.99993
	200–350	7.5933	66.6	0.99928
0.50	200–240	15.5748	106.3	0.99997
	240–280	14.2778	100.8	0.99994
	280–320	12.6036	93.1	0.99990
	200–350	13.6706	98.4	0.99930
0.75	200–240	18.6894	125.6	1.00000
	240–280	19.6421	129.7	0.99999
	280–320	15.9844	112.7	0.99926
	200–350	17.4922	120.4	0.99867

r is the correlation coefficient of the linear regression $\ln(d\alpha/dt)$ *vs.* $1/T$

Such an approximation to the true kinetic equation is often used when complex chemical reactions with unknown mechanisms (e.g. the thermal and/or thermooxidative degradation of polymers) are subjected to kinetic analysis.

Dependence of the apparent activation parameters on the degree of conversion and temperature

For the temperature range 200–350°C, step of 10°C and the previously mentioned activation parameter values, the isotherms $\alpha=\alpha(t)$ and the values of $d\alpha/dt$

were calculated. For evaluation of the apparent activation parameters, an isoconversional method was applied that was based on the relation

$$\ln\frac{d\alpha}{dt} = \ln A_{ap}f(\alpha) - \frac{E_{ap}}{RT} \tag{7}$$

which results directly from relationships (5) and (6).

For α=const, E_{ap} and $A_{ap}f(\alpha)$ can be obtained from the slope and intercept, respectively, of the straight lines $\ln(d\alpha/dt)$ *vs.* $1/T$. The values obtained for $A_{ap}f(\alpha)$ and E_{ap} depend on the degree of conversion and on the temperature range in which the straight lines $\ln(d\alpha/dt)$ *vs.* $1/T$ were recorded, as is shown in Table 1.

For a given values of the conversion degree, the dependence $E_{ap}=E_{ap}(T)$ was obtained from the derivative of the curve $\ln(d\alpha/dt)$ *vs.* $1/T$. Further, from the values of E_{ap} and $\ln(d\alpha/dt)$ for a given temperature, $a=\ln A_{ap}f(\alpha)$ was evaluated. For each value of the degree of conversion, a certain dependence of E_{ap} on T was obtained. It was observed that, for all values of the degree of conversion, a linear dependence of $a=\ln A_{ap}f(\alpha)$ on E_{ap} exists. In other words, the existence of the CE, as expressed by relation (1), is confirmed. Figure 1 shows how the CE is verified for α=0.50. Table 2 shows the values of the CE parameters for $0.10\leq\alpha\leq0.90$, corresponding to the changes in the apparent activation parameters with temperature.

Table 2 The CE parameters corresponding to changes in the activation parameters with temperature

α	α^*–ln$f(\alpha)$	β^*/mol kJ^{-1}	r
0.10	–6.522	0.213	0.99966
0.20	–7.282	0.222	0.99926
0.30	7.825	0.226	0.99978
0.40	–8.912	0.236	0.99939
0.50	–7.461	0.216	0.99948
0.60	–7.767	0.217	0.99968
0.70	–7.284	0.209	0.99977
0.80	–7.341	0.206	0.99994
0.90	–7.826	0.204	0.99996

r is the correlation coefficient of the linear regression $\ln A_{ap}f(\alpha)$ *vs.* E_{ap}

In order to evidence the dependence of the activation parameters on the degree of conversion, the temperature range 280–320°C was considered and the straight lines $\ln(d\alpha/dt)$ *vs.* $1/T$ were recorded. It was shown that, during the change of α from 0.05 to 0.95, E_{ap} increases from 61.5 to 122 kJ mol^{-1}, and for $0.05\leq\alpha\leq0.50$, E_{ap} exhibits the following dependence on α:

$$E_{ap} = E_o + E_1\ln(1-\alpha) \tag{8}$$

with E_o=57.762 kJ mol^{-1}, E_1=–49.312 kJ mol^{-1} and r=0.99894 (Fig. 2).

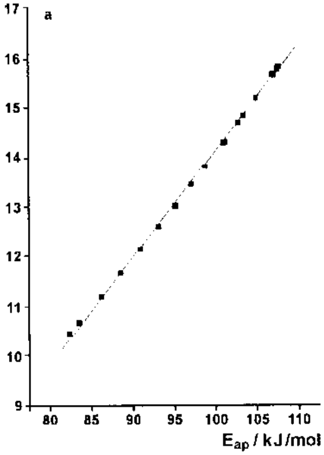

Fig. 1 Checking the existence of the CE for the dependence of the apparent activation parameters on the temperature: α=0.50; a=ln$A_{ap}f(\alpha)$

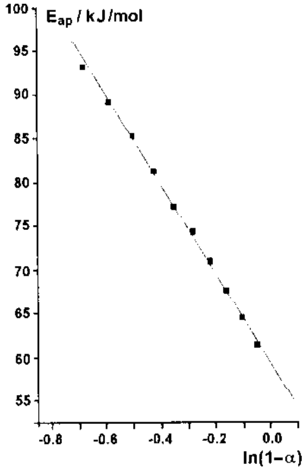

Fig. 2 The linear dependence E_{ap} *vs.* ln(1–α)

As relation (8) concerns a kinetic model to be discussed below, in the following we shall concentrate on the range 0.05≤α≤0.50. In order to evaluate the pre-exponential factor, the expressions for the differential conversion function given in Table 3 will be considered. We will suppose that the most probable differential conversion function that describes the overall process is that corresponding to the closest to unity correlation coefficient of the straight line $\ln A_{ap}=\alpha^*+\beta^* E_{ap}$ (CE relationship).

Table 3 The considered kinetic models

Model	Code	$f(\alpha)$
Reaction order	R0.5	$(1-\alpha)^{0.5}$
	R1.0	$(1-\alpha)$
	R1.5	$(1-\alpha)^{1.5}$
	R2.0	$(1-\alpha)^{2.0}$
	R2.2	$(1-\alpha)^{2.2}$
	R2.3	$(1-\alpha)^{2.3}$
	R2.5	$(1-\alpha)^{2.5}$
Diffusion mechanism, one-dimensional	D1	α^{-1}
Diffusion mechanism, two-dimensional	D2	$[-\ln(1-\alpha)]^{-1}$
Sigmoidal α–time curves Prout Tompkins	B1	$\alpha(1-\alpha)$

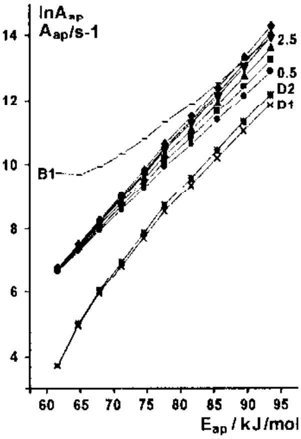

Fig. 3 The curves $\ln A_{ap}$ *vs.* E_{ap} for various forms of $f(\alpha)$

This method of finding the conversion function was suggested by Tanaka and Koga [22]. As shown in Fig. 3, the models D_1, D_2 and B_1 do not verify the CE relation. This relation is verified by the reaction order models with a maximum correlation coefficient for the model R1.0. Thus, for $f(\alpha)=1-\alpha$, the values of the CE parameters are $\alpha^*=-6.039$ and $\beta^*=0.208$ mol kJ^{-1}. It is worth mentioning that, for the temperature range 200–240°C, the differential conversion function $f(\alpha)$ found by the same procedure corresponds to the model R2.2.

Prediction of the isotherms $\alpha(t)$ by using the CE parameters and the dependence $E=E(\alpha)$

We suppose that the kinetic parameters were determined by using the previously discussed method, the isotherms $\alpha=\alpha(t)$ recorded in the temperature range 280–320°C being known. The problem now is to predict the isotherms $\alpha=\alpha(t)$ at temperatures lower than 280°C, the parameters α^*, β^*, E_0 and E_1 being known. In order to accomplish this task, we suggest a simple kinetic model based on relations (1), (5), (6) and (8), which lead to

$$\frac{d\alpha}{dt}=A_0(1-\alpha)^n f(\alpha) \tag{9}$$

where

$$n=\beta^* E_1-\frac{E_1}{RT} \tag{10}$$

and

$$A_0=\exp\left(\alpha^*+\beta^* E_0-\frac{E_0}{RT}\right) \tag{11}$$

For the particular case $f(\alpha)=1-\alpha$, relation (9) takes the form

$$\frac{d\alpha}{dt}=A_0(1-\alpha)^{n+1} \tag{12}$$

This equation shows that the overall process is apparently described by the reaction order model (the reaction order is $(n+1)$). However, according to Eq. (10), n depends on temperature, thus violating the hypothesis on which the reaction order model is based.

Through integration of Eq. (12) for $n\neq0$, one obtains

$$t=\frac{(1-\alpha)^{-n}-1}{nA_0} \tag{13}$$

By use of the values of the CE parameters α^* and β^*, and the values E_0 and E_1 obtained from the true isotherms recorded for the interval $280°\text{C}\leq T\leq 320°\text{C}$, the values of n and A_0 for 230, 240, 250, 260 and 270°C were calculated. These were introduced into relation (12), and the values of t for $0.05\leq\alpha\leq0.50$ and each previously mentioned temperature were calculated. As shown in Table 4, the deviation of the calculated values of t with respect to the exact ones (which check Eq. (4)) increases with decrease of temperature. It turns out that, for the considered case, the approximation of the true kinetic equation with an overall kinetic equation can be used for prediction of the isotherms for temperatures lower by at most 50°C with respect to the minimum temperature of the range in which the kinetic parameters were evaluated.

Table 4 Relative errors of *t* calculated by means of Eq. (13)

α	*e*/% for 230°C	*e*/% for 240°C	*e*/% for 250°C	*e*/% for 260°C	*e*/% for 270°C
0.10	6.80	5.18	3.75	2.50	1.45
0.20	10.18	7.39	5.06	3.17	1.66
0.30	12.68	8.87	5.78	3.40	1.64
0.40	12.81	8.52	5.26	2.92	1.30
0.50	6.18	4.00	2.43	1.36	0.58

Conclusions

For a sequence of two successive first-order reactions, the isotherms $\alpha=\alpha(t)$ were simulated. The use of an overall single rate equation instead of the true rate equation was critically analyzed.

It was shown that the apparent activation parameters depend on the degree of conversion, the temperature range in which they were evaluated, and the temperature for a given degree of conversion.

It was equally shown that the apparent activation parameters are correlated through the CE relation.

A model was suggested for prediction of the isotherms $\alpha=\alpha(t)$ by using the apparent kinetic parameters.

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