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CHANGE OF THE APPARENT REACTION ORDER WITH TEMPERATURE AS A CONSEQUENCE OF THE REACTION MECHANISM COMPLEXITY

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Abstract

The theoretical isotherms ($\alpha=\alpha(t)$, where α is the conversion degree and t is the time) and the theoretical thermogravimetric curves ($\alpha=\alpha(T)$, where T is the temperature) were simulated for a system in which two consecutive reactions occur. A critical analysis of the use of an overall single rate reaction equation instead of the use of the true rate equations is presented. Both for isothermal and non-isothermal data and $\alpha\leq 0.50$, the apparent reaction order depends on temperature. It is pointed out that the apparent reaction order for a given temperature can be evaluated if the parameters of the compensation effect are known.

Keywords: apparent kinetic parameters, compensation effect, isothermal, non-isothermal

Introduction

The kinetic investigation of heterogeneous reactions showed that in many cases the activation energy (E) and the pre-exponential factor (A) are mutually correlated by the kinetic compensation effect (KCE) relationship:

$$\ln A_{\mathrm{ap}}=\alpha^{*}+\beta^{*}E_{\mathrm{ap}} \tag{1}$$

where α^* and β^* are constants [1–16].

According to (1), any change in the activation energy is therefore ‘compensated’ by the change of A.

This paper considers a theoretical kinetic model for an isothermal and non-isothermal decomposition in solid-gas system, which involves two consecutive reactions. The theoretical isotherms ($\alpha=\alpha(t)$, where α is the conversion degree and t is the time) and the theoretical thermogravimetric curves ($\alpha=\alpha(T)$, where T is the temperature) will be derived. A critical analysis of the use of an overall single rate reaction equation instead of the true rate equations will be presented. We will focus on the de-

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pendence of the apparent reaction order on the temperature and on the possibility to evaluate this dependence on the compensation effect parameters corresponding to the apparent activation parameters.

The kinetic model

Following the previous work [16], we will consider that a solid compound A undergoes two consecutive steps of decomposition:

$$A(s)\xrightarrow{k_1}B(s)+\nu_1G_1(g) \tag{I}$$

$$B(s)\xrightarrow{k_2}C(s)+\nu_2G_2(g) \tag{II}$$

where B and C are solid products and G_1 and G_2 are gaseous products.

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

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

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

Both consecutive reactions are taken to have a value of the reaction order of unity. The following values of the activation parameters 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 then [16]:

$$\begin{aligned}\frac{d\alpha_1}{dt}&=k_1(1-\alpha_1)\\ \frac{d\alpha_2}{dt}&=k_2(\alpha_1-\alpha_2)\end{aligned} \tag{3}$$

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

The particular case to be considered is $\nu_1M_1=\nu_2M_2$, where M_i is the molecular mass of the gaseous product 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:

$$\alpha=1-\left[\frac{1}{2}+\frac{k_2}{2(k_2-k_1)}\right]e^{-k_1t}+\frac{k_1}{2(k_2-k_1)}e^{-k_2t} \tag{4}$$

Using this equation for the temperature range 200–300°C and a step of 10°C, the isotherms $\alpha=\alpha(t)$ and the values of $d\alpha/dt$ were calculated.

The thermogravimetric curves (TG), $\alpha=\alpha(T)$, were evaluated for 15 heating rates ($\beta=dT/dt=const.$) located in the range 0.25–20 K min^{-1}. In order to do that, we used the system of equations:

$$\beta\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}=k_1(1-\alpha_1)$$
$$\beta\frac{\mathrm{d}\alpha_2}{\mathrm{d}t}=k_2(\alpha_1-\alpha_2) \qquad (5)$$

The integration of the system (5) was performed numerically according to a method previously described [17]. In this case, too, the case with $\alpha=(\alpha_1+\alpha_2)/2$ was considered. The curves $\mathrm{d}\alpha/\mathrm{d}T$ *vs.* T were calculated through numerical differentiation.

This work is focussed on the consequences of using, instead of the true kinetic equations (Eq. (3) for isothermal case and Eq. (5) for non-isothermal one), of the equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_{\mathrm{ap}}f(\alpha) \qquad (6)$$

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

$$k_{\mathrm{ap}}=A_{\mathrm{ap}}\exp\left(-\frac{E_{\mathrm{ap}}}{RT}\right) \qquad (7)$$

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

Isothermal decomposition

For the evaluation of the apparent activation parameters, an isoconversional method based on the relation:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\ln A_{\mathrm{ap}}f(\alpha)\exp\left(-\frac{E_{\mathrm{ap}}}{RT}\right) \qquad (8)$$

which results directly from relationships (6) and (7), was applied.

For $\alpha=$ *const.*, E_{ap} and $A_{\mathrm{ap}}f(\alpha)$ can be obtained from the slope and intercept, respectively, of the straight lines $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $(1/T)$. For $200°\mathrm{C}\leq T\leq 300°\mathrm{C}$ and $0.05\leq\alpha\leq 0.50$, these straight lines are characterized by values of the linear regression correlation coefficients, r , higher than 0.9992. The obtained results show that $A_{\mathrm{ap}}f(\alpha)$ and E_{ap} depend on α and, for $0.05\leq\alpha\leq 0.50$, The dependence of E_{ap} on α can be described by:

$$E_{\mathrm{ap}}=\varepsilon_0+\varepsilon_1\ln(1-\alpha) \qquad (9)$$

with $\varepsilon_0=51.487$ (± 2.806) kJ mol^{-1} and $\varepsilon_1=-61.050$ (± 7.050) kJ mol^{-1}.

In a previous work [16] we showed that for the analysis of this system of consecutive reactions, the most suitable form of $f(\alpha)$ correspond to the ‘reaction order’ model:

$$f(\alpha)=(1-\alpha)^{\mathrm{m}} \qquad (10)$$

Following Tanaka and Koga [5], we assume that the most probable differential conversion function (value of the reaction order) that describes the overall process is corresponding to the best correlation coefficient of the straight line $\ln A_{ap}=\alpha^*+\beta^* E_{ap}$ (KCE relationship). From Table 1 one can see that, for $1\leq m\leq 1.7$, these straight lines have $r\geq 0.99992$ and $r=1$ for $m=1.5$ and $m=1.6$.

Table 1 The values of the compensation parameters α^* and β^* and the values of r for the straight lines $\ln A_{ap}$ *vs.* E_{ap}, plotted for $1\leq m\leq 1.7$

m	α^*/A_{ap} in s^{-1}	β^*/mol kJ^{-1}	r
1.0	–6.241 (±0.068)	0.210 (±9.23E–4)	0.99992
1.1	–6.314 (±0.055)	0.211 (±7.53E–4)	0.99995
1.2	–6.386 (±0.043)	0.213 (±5.84E–4)	0.99997
1.3	–6.459 (±0.031)	0.214 (±4.15E–4)	0.99998
1.4	–6.532 (±0.018)	0.216 (±2.50E–4)	0.99999
1.5	–6.605 (±0.008)	0.217 (±1.05E–4)	1
1.6	–6.678 (±0.010)	0.219 (±1.34E–4)	1
1.7	–6.751 (±0.021)	0.220 (±2.89E–4)	0.99999

From relations (6), (7), (9) and (10) one obtains:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A_0\,(1-\alpha)^{(n+m)} \tag{11}$$

where:

$$n=\beta^*\varepsilon_1-\frac{\varepsilon_1}{RT} \tag{12}$$

$$A_0=\exp\left(\alpha^*+\beta^*\varepsilon_0-\frac{\varepsilon_0}{RT}\right) \tag{13}$$

It shows that the overall process is apparently described by the reaction order model (the reaction order is $(n+m)$). However, according to Eq. (12), n depends on temperature, thus violating the hypothesis on which the reaction order model is based. The variation in the reaction order for complex kinetics has recently been reported by Vyazovkin and Sbirrazzuoli [18] who observed it when fitting isothermal and non-isothermal experimental data to $(1-\alpha)^{\mathrm{n}}$ and $\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}}$ reaction models.

Table 2 lists the values of $\ln A_0$ and $(n+m)$ calculated by Eqs (12) and (13), for temperatures located between 200 and 300°C and for $m=1$ and $m=1.5$. One can observe that the dependence of the compensation parameters on m (Table 1) determines a slight change of the values of $\ln A_0$ and $(n+m)$ when m changes from 1 to 1.5.

Table 2 Values of $\ln A_0$ and $(n+m)$ calculated by Eqs (12) and (13)

T/°C	m=1		m=1.5	
	$\ln A_0$	$n+m$	$\ln A_0$	$n+m$
200	–8.523	3.706	–8.527	3.779
220	–7.992	3.077	–7.996	3.149
240	–7.503	2.496	–7.506	2.569
260	–7.050	1.959	–7.053	2.032
280	–6.630	1.461	–6.633	1.533
300	–6.239	0.997	–6.242	1.070

On the other hand, the logarithmic form of Eq. (11):

$$\ln\frac{d\alpha}{dt}=\ln A_0+(n+m)\ln(1-\alpha) \tag{14}$$

suggests that $\ln A_0$ and $(n+m)$, for a given temperature, can be evaluated from the parameters of the straight line $\ln(d\alpha/dt)$ *vs.* $\ln(1-\alpha)$. The results in Tables 2 and 3 show a good agreement between the values $\ln A_0$ and $(n+m)$ calculated by means of the two mentioned methods.

Table 3 Values of $\ln A_0$ and $(n+m)$ calculated from the parameters of the straight line $\ln(d\alpha/dt)$ *vs.* $\ln(1-\alpha)$. Isothermal data: $0.05\leq\alpha\leq0.50$

T/°C	$\ln A_0$	$n+m$	r
200	–8.472	3.759	0.97308
220	–7.976	3.144	0.98768
240	–7.508	2.547	0.99596
260	–7.058	1.990	0.99939
280	–6.615	1.499	0.99999
300	–6.176	1.092	0.99997

As expected, according to relations (12) and (13), one obtains that $\ln A_0$ and $(n+m)$ change linearly with $(1/T)$. The regressions $\ln A_0$ *vs.* $(1/T)$ and $(n+m)$ *vs.* $(1/T)$ are:

$$\ln A_0=4.590(\pm0.130)-6.196(\pm0.067)\frac{1000}{T}\quad(r=-0.99947) \tag{15}$$

$$n+m=-11.773(\pm0.101)+7.350(\pm0.052)\frac{1000}{T}\quad(r=0.99977) \tag{16}$$

From the parameters of these straight lines we obtained ε_0= 51.490 kJ mol^{-1}, ε_1=–61.075 kJ mol^{-1}, as well as the values of the KCE parameters listed in Table 4. It is easy to notice the good agreement of the values of these parameters and those obtained using the previous method.

Table 4 The values of α^* and β^* obtained by using the dependencies (15) and (16)

	m=1	m=1.1	m=1.2	m=1.3	m=1.4	m=1.5	m=1.6	m=1.7
α^*	–6.179	–6.263	–6.347	–6.432	–6.516	–6.600	–6.684	–6.769
β^*/mol kJ^{-1}	0.209	0.211	0.212	0.214	0.216	0.217	0.219	0.221

Non-isothermal decomposition

The high number of heating rates used to simulate the TG curves allowed for plotting the straight lines $\ln(d\alpha/dt)$ *vs.* $\ln(1-\alpha)$ for T=*const.*, in the temperature range 200–300°C and for $0.05\leq\alpha\leq0.50$. The values of the intercept ($\ln A_0$) as well as of the slope ($n+m$) of these straight lines are listed in Table 5. From this Table, as well as from Tables 2 and 3, a good agreement between the $\ln A_0$ and ($n+m$) values obtained from isothermal and non-isothermal data can be noticed.

Table 5 Values of $\ln A_0$ and ($n+m$) calculated from the parameters of the straight line $\ln(d\alpha/dt)$ *vs.* $\ln(1-\alpha)$. Non-isothermal data: $0.05\leq\alpha\leq0.50$

T/°C	$\ln A_0$	$n+m$	r
200	–8.640	3.519	0.95613
220	–7.995	3.205	0.98436
240	–7.485	2.738	0.99540
260	–7.024	2.154	0.99814
280	–6.623	1.556	0.99875
300	–6.180	1.099	0.99970

Also in this case $\ln A_0$ and ($n+m$) change linearly with ($1/T$). The regressions $\ln A_0$ *vs.* ($1/T$) and ($n+m$) *vs.* ($1/T$) are:

$$\ln A_0 = 5.211(\pm0.148)-6.527(\pm0.077)\frac{1000}{T} \quad (r=-0.99938) \tag{17}$$

$$n+m=-10.544(\pm0.705)+6.742(\pm0.367)\frac{1000}{T} \quad (r=0.98695) \tag{18}$$

From the parameters of these straight lines ε_0=54.237 kJ mol^{-1}, ε_1= –56.026 kJ mol^{-1}, as well as the values of the KCE parameters listed in Table 6 were obtained. A satisfactory agreement between the values of these parameters and those obtained using the previous method should be noticed.

Table 6 The values of α^* and β^* obtained by using the dependencies (17) and (18)

	m=1	m=1.1	m=1.2	m=1.3	m=1.4	m=1.5	m=1.6	m=1.7
α^*	–5.974	–6.071	–6.168	–6.264	–6.361	–6.458	–6.555	–6.652
β^*/mol kJ^{-1}	0.206	0.208	0.210	0.212	0.213	0.215	0.217	0.219

Conclusions

For a sequence of two successive first-order reactions, the isotherms $\alpha=\alpha(t)$ and the TG curves were simulated. For both isothermal and non-isothermal data, the use of an overall single rate equation instead of the true rate equations was critically analyzed.

It was shown that for the analyzed system, the overall process is apparently described by the 'reaction order' model with a reaction order, which depends on temperature. It was pointed out that the dependence of the reaction order on temperature is due to the dependence of the apparent activation parameters on the conversion degree and to their correlation through the compensation effect relationship.

It was found that for the analyzed system the apparent reaction orders values obtained from isothermal data are in good agreement with those obtained from non-isothermal data.

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