

Note

Distortion of the Arrhenius parameters by the inappropriate kinetic model function

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In general, the following equation can be assumed for the kinetics of solid state reactions

$$\frac{d\alpha}{dt} = f(\alpha)A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where α is the fractional conversion at time t , $f(\alpha)$ the kinetic model function, A the pre-exponential factor, E the activation energy, R the gas constant and T the temperature. Table 1 lists typical $f(\alpha)$ proposed for solid state reactions [1]. Various methods of kinetic analysis for a single non-isothermal thermoanalytical (TA) curves have been derived on the basis of eqn. (1); the $f(\alpha)$, A and E values are obtained as the kinetic parameters. It is well known that the Arrhenius parameters, A and E , are distorted by the “mis-estimation” of $f(\alpha)$. Although this problem has been discussed from the empirical [2–7] and mathematical [8–11] points of view, the mathematical relationship between inappropriate functions, $f(\alpha)$, and the distorted values of A and E has not yet been established.

If a false kinetic model function, $h(\alpha)$, was used instead of the appropriate one, $f(\alpha)$, eqn. (1) can be rewritten as

$$\frac{d\alpha}{dt} = h(\alpha)A_{\text{app}} \exp\left(-\frac{E_{\text{app}}}{RT}\right) \quad (2)$$

where A_{app} and E_{app} are the apparent Arrhenius parameters distorted by the inappropriate kinetic model function. At the peak temperature, T_p , the following equation can be obtained from eqns. (1) and (2)

$$\frac{h(\alpha_p)}{f(\alpha_p)} = \frac{A}{A_{\text{app}}} \exp\left(\frac{E_{\text{app}} - E}{RT_p}\right) \quad (3)$$

where α_p is the fractional conversion at T_p .

TABLE 1

Typical kinetic model functions, $f(\alpha)$, and their differential forms, $f'(\alpha)$

Model	$f(\alpha)$	$f'(\alpha)$
A_m	$m(1-\alpha)[- \ln(1-\alpha)]^{1-1/m}$	$(m-1)[- \ln(1-\alpha)]^{-1/m} - m[- \ln(1-\alpha)]^{1-1/m}$
$R_{(1/(1-n))}$	$(1-\alpha)^n$	$-n(1-\alpha)^{n-1}$
D_1	$\frac{1}{2}\alpha$	$-\frac{1}{2}\alpha^2$
D_2	$\frac{1}{-\ln(1-\alpha)}$	$\frac{-1}{[\ln(1-\alpha)]^2(1-\alpha)}$
D_3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$\frac{1/2-(1-\alpha)^{-1/3}}{[1-(1-\alpha)^{1/3}]^2}$
D_4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$\frac{-(1-\alpha)^{-4/3}}{2[(1-\alpha)^{-1/3}-1]^2}$

However, the mathematical condition for the peak is expressed as [11,12]

$$\frac{\phi E}{RT_p^2} \frac{1}{f'(\alpha_p)} = A \exp\left(-\frac{E}{RT_p}\right) \quad (4)$$

with

$$f'(\alpha) = \frac{df(\alpha)}{d\alpha} \quad (5)$$

where ϕ is the constant heating rate. The functions $f'(\alpha)$ are also listed in Table 1 [13]. Using a false model function, $h'(\alpha)$

$$\frac{\phi E_{app}}{RT_p^2} \frac{1}{h'(\alpha_p)} = A_{app} \exp\left(-\frac{E_{app}}{RT_p}\right) \quad (6)$$

Equations (4) and (6) give

$$\frac{E}{E_{app}} \frac{f'(\alpha_p)}{h'(\alpha_p)} = \frac{A}{A_{app}} \exp\left(\frac{E_{app}-E}{RT_p}\right) \quad (7)$$

From eqns. (3) and (7), the distortion in the values of E can be expressed by

$$\frac{E_{app}}{E} = \frac{f(\alpha_p) h'(\alpha_p)}{h(\alpha_p) f'(\alpha_p)} \quad (8)$$

In addition, eqns. (3) and (8) give the following equation concerning the distortion in the value of $\ln A$

$$\ln \frac{A_{app}}{A} = \frac{E}{RT_p} \left[\frac{f(\alpha_p) h'(\alpha_p) - h(\alpha_p) f'(\alpha_p)}{h(\alpha_p) f'(\alpha_p)} \right] + \ln \frac{f(\alpha_p)}{h(\alpha_p)} \quad (9)$$

TABLE 2

Comparison of the distortion in the Arrhenius parameters arising from inappropriate kinetic model functions, with the values calculated according to eqns. (8) and (9)

Theoretical TA curve ^a			Freeman and Carroll method					Calculated value ^b	
$f(\alpha)$	α_p	T_p (K)	E_{app} (kJ mol ⁻¹)	n	$\ln A_{app}$ (s ⁻¹)	$\frac{E_{app}}{E}$	$\ln \frac{A_{app}}{A}$	$\frac{E_{app}}{E}$	$\ln \frac{A_{app}}{A}$
D_2	0.804	474.05	46.1	0.303	6.31	0.46	-13.7	0.49	-12.8
D_3	0.661	446.77	46.8	0.673	7.28	0.47	-12.7	0.47	-12.7
D_4	0.742	448.10	46.6	0.434	7.20	0.47	-12.8	0.47	-12.6
A_2	0.619	485.63	207.6	1	47.26	2.08	27.3	2.08	27.3
A_3	0.623	486.64	315.3	1	74.27	3.15	54.3	3.19	55.3
A_4	0.626	486.82	423.0	1	101.17	4.23	81.2	4.21	80.7

^a $E = 100$ kJ mol⁻¹, $\ln A = 20$ s⁻¹ and $\phi = 10$ K min⁻¹.

^b According to eqns. (8) and (9).

The validity of eqns. (8) and (9) was investigated by the kinetic analysis of the theoretical TA curves [5,12] obtained by assuming $E = 100$ kJ mol⁻¹, $\ln A = 20$ s⁻¹, $\phi = 10$ K min⁻¹ and various forms of $f(\alpha)$. The theoretical TA curves were analysed by the Freeman and Carroll (FC) method [14], which was derived for the n th order reaction. Table 2 shows the kinetic results obtained by the FC method and the values of E_{app}/E and $\ln(A_{app}/A)$ calculated according to eqns. (8) and (9). As can be seen from Table 2, the distortion of the Arrhenius parameters by the inappropriate kinetic model function can be expressed by eqns. (8) and (9).

The slight differences in the calculated values of E_{app}/E and $\ln(A_{app}/A)$ from those obtained by the FC method for the theoretical TA curves of D_2 , A_3 and A_4 , can be explained as follows. Equations (8) and (9) were derived on the basis of the empirical fact that the isokinetic temperature, T_{iso} , in the kinetic compensation effect arose from a single TA curve by the use of various inappropriate $f(\alpha)$, corresponding to T_p [6]. The T_{iso} is close to T_p only when $D = |\ln[f(\alpha_p)/h(\alpha_p)]|$ in eqn. (9) is zero [15]. The larger difference between the empirical and theoretical values is observed for larger values of D .

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