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ERRORS INVOLVED IN THE ACTIVATION ENERGY CALCULATED BY INTEGRAL METHODS WHEN THE FREQUENCY FACTOR DEPENDS ON THE TEMPERATURE ($A=A_0T^m$)

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The dependence of the frequency factor on the temperature ($A=A_0T^m$) has been examined and the errors involved in the activation energy calculated from some integral methods without considering such dependence have been estimated. Investigated integral methods are the Coats–Redfern method, the Gorbachev–Lee–Beck method, the Wanjun–Yuwen method and the Junmeng–Fusheng method. The results have shown that the error in the determination of the activation energy calculated ignoring the dependence of the frequency factor on the temperature can be rather large and it is dependent on $x=E/RT$ and the exponent m.

Keywords: *activation energy, frequency factor, integral method, non-isothermal kinetic analysis*

Introduction

Due to the fact that the temperature integral does not have an exact analytical solution, a number of temperature integral approximations for the kinetic analysis by assuming that the frequency factor is independent on the temperature have been proposed [1]. The application of those proposed approximations is the determination of the activation energy and not the accurate computation of the temperature integral. Pérez-Maqueda *et al*. [2] analyzed the errors in the activation energies obtained from several integral methods with the independence of the frequency factor on the temperature. Criado *et al*. [3] calculated the errors involved in the activation energy obtained from the modified Coats–Redfern method (this method is named sometimes in the literature as the Fischer method [4]) when the frequency factor depends on the temperature. The aim of this work is to carry out a systemic analysis of the errors involved in the activation energy obtained from four integral methods when the frequency factor is dependent on the temperature. Investigated integral methods are the Coats–Redfern method [5], the Gorbachev–Lee–Beck method [6, 7], the Wanjun–Yuwen method [8] and the Junmeng–Fusheng method [9].

Theory

Thermally stimulated solid-state reactions can be described by the following expression [10]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/RT} f(\alpha) \qquad (1)$$

where α is extent of reaction, t is the time, A is the frequency factor or preexponential factor, E is the activation energy, T is the absolute temperature, R is the gas constant, and $f(\alpha)$ is the differential conversion function depending on the reaction mechanism.

The most common heating profile used for studying the kinetics of the solid-state reactions is the linear heating program. Under the non-isothermal condition, Eq. (1) can be written

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\mathrm{e}^{-E/RT} f(\alpha) \qquad (2)$$

where β is the heating rate.

It is noted that all the integral methods for the kinetic analysis of solid-state reactions have been developed by assuming that the frequency factor is considered as a constant all over the temperature range investigated. However, some authors [11–14] after extending the theory of the activated complex to the thermal decomposition of single solid state reactions proposed that the frequency factor is connected with the temperature through the following relationship

$$A=A_0T^m \qquad (3)$$

where A_0 is a constant, and values of the exponent m from –1.5 to 2.5 [3].

Thus, from Eqs (2) and (3), it follows

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$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A_0}{\beta}\int_0^{T}T^{\mathrm{m}}\mathrm{e}^{-\mathrm{E/RT}}\mathrm{d}T \tag{4}$$

where $g(\alpha)$ is the integral conversion function.

After doing the variable change $x=E/RT$, Eq. (4) would be rearranged in the following way [1, 15]

$$g(\alpha)=\frac{A_0}{\beta}\frac{RT^{\mathrm{m}+2}}{E}h_{\mathrm{m}}(x)\mathrm{e}^{-\mathrm{E/RT}} \tag{5}$$

where

$$h_{\mathrm{m}}(x)=x^{\mathrm{m}+2}\mathrm{e}^{x}\int_{x}^{\infty}\frac{\mathrm{e}^{-x}}{x^{\mathrm{m}+2}}\mathrm{d}x \tag{6}$$

The $h_{\mathrm{m}}(x)$ function does not have an exact analytical solution [16], but can be numerically solved.

If the frequency factor were considered as constant and the integral methods were used for performing the kinetic analysis, the apparent activation energy, E_{a}, would satisfy the following equation

$$g(\alpha)=\frac{A_{\mathrm{a}}}{\beta}\frac{RT^{2}}{E}h(x_{\mathrm{a}})\mathrm{e}^{-\mathrm{E_a/RT}} \tag{7}$$

where the subscript *a* refers to the apparent values of kinetic parameters obtained from the integral methods, $x_{\mathrm{a}}=E_{\mathrm{a}}/RT$.

Table 1 Expressions of the $h(x_{\mathrm{a}})$ functions

Method	$h(x_{\mathrm{a}})$	Eq.
Coats–Redfern	$1-\frac{2}{x_{\mathrm{a}}}$	(8)
Gorbachev–Lee–Beck	$\frac{x_{\mathrm{a}}}{x_{\mathrm{a}}+2}$	(9)
Wanjun–Yuwen	$\frac{x_{\mathrm{a}}}{1.00198882x_{\mathrm{a}}+1.87391198}$	(10)
Junmeng–Fusheng	$\frac{x+0.66691}{x+2.64943}$	(11)

Here, the following integral methods for kinetic analysis are investigated: Coats–Redfern method, the Gorbachev–Lee–Beck method, the Wanjun–Yuwen method and the Junmeng–Fusheng method. The expressions of the $h(x_{\mathrm{a}})$ functions for the four integral methods are shown in Table 1.

From Eq. (7), it follows

$$\frac{\mathrm{dln}[g(\alpha)/T^2]}{\mathrm{d}(1/T)}=-\frac{E_{\mathrm{a}}}{R}\left[1-\frac{\mathrm{dln}h(x_{\mathrm{a}})}{\mathrm{d}x_{\mathrm{a}}}\right] \tag{12}$$

The real value of the left hand side of Eq. (12) as a function of the true activation energy can be determined from Eq. (5)

$$\frac{\mathrm{dln}[g(\alpha)/T^2]}{\mathrm{d}(1/T)}=-\frac{E}{R}\left[1-\frac{\mathrm{dln}h_{\mathrm{m}}(x)}{\mathrm{d}x}+\frac{m}{x}\right] \tag{13}$$

The relative error of the apparent activation energy can be defined by the following equation

$$\varepsilon=\frac{E_{\mathrm{a}}-E}{E}=\left(\frac{E_{\mathrm{a}}/R}{E/R}-1\right)=\frac{x_{\mathrm{a}}}{x}-1 \tag{14}$$

From Eqs (12)–(14), the following equation of the relative error can be obtained

$$(\varepsilon+1)\left\{1-\frac{\mathrm{dln}h[(\varepsilon+1)x]}{\mathrm{d}[(\varepsilon+1)x]}\right\}=1-\frac{\mathrm{dln}h_{\mathrm{m}}(x)}{\mathrm{d}x}+\frac{m}{x} \tag{15}$$

For given values of *m* and *x*, the above equation can be numerically solved using some numerical techniques. For this purpose, either general purposed mathematical software or a computer program developed in any programming language is used. In this study, we have solved the above equation by means of the Mathematica software system. Detailed information of the Mathematica software system can be found in the literature [17].

Table 2 Relative error percentages for the activation energies determined from the Coats–Redfern method when the frequency factor depends on the temperature ($A=A_0T^{\mathrm{m}}$)

x	*m*								
	–1.5	–1.0	–0.5	0.0	0.5	1.0	1.5	2.0	2.5
10	–1.245E+01	–8.008E+00	–3.524E+00	9.994E-01	5.559E+00	1.015E+01	1.477E+01	1.942E+01	2.409E+01
20	–7.009E+00	–4.633E+00	–2.252E+00	1.340E-01	2.525E+00	4.919E+00	7.318E+00	9.721E+00	1.213E+01
30	–4.800E+00	–3.188E+00	–1.574E+00	4.094E-02	1.658E+00	3.276E+00	4.895E+00	6.516E+00	8.138E+00
40	–3.643E+00	–2.423E+00	–1.203E+00	1.758E-02	1.239E+00	2.461E+00	3.684E+00	4.907E+00	6.130E+00
50	–2.933E+00	–1.953E+00	–9.720E-01	9.100E-03	9.905E-01	1.972E+00	2.954E+00	3.937E+00	4.919E+00
60	–2.454E+00	–1.635E+00	–8.148E-01	5.310E-03	8.256E-01	1.646E+00	2.467E+00	3.288E+00	4.109E+00
70	–2.110E+00	–1.406E+00	–7.011E-01	3.360E-03	7.080E-01	1.413E+00	2.118E+00	2.823E+00	3.528E+00
80	–1.850E+00	–1.233E+00	–6.152E-01	2.260E-03	6.198E-01	1.237E+00	1.855E+00	2.473E+00	3.091E+00
90	–1.647E+00	–1.098E+00	–5.480E-01	1.600E-03	5.513E-01	1.101E+00	1.651E+00	2.201E+00	2.750E+00
100	–1.484E+00	–9.891E-01	–4.940E-01	1.170E-03	4.964E-01	9.916E-01	1.487E+00	1.982E+00	2.478E+00

Table 3 Relative error percentages for the activation energies determined from the Gorbachev–Lee–Beck method when the frequency factor depends on the temperature ($A=A_0T^m$)

x	m								
	–1.5	–1.0	–0.5	0.0	0.5	1.0	1.5	2.0	2.5
10	–1.353E+01	–8.984E+00	–4.409E+00	1.942E-01	4.824E+00	9.476E+00	1.415E+01	1.885E+01	2.356E+01
20	–7.126E+00	–4.744E+00	–2.357E+00	3.362E-02	2.429E+00	4.828E+00	7.231E+00	9.638E+00	1.205E+01
30	–4.833E+00	–3.220E+00	–1.605E+00	1.126E-02	1.629E+00	3.248E+00	4.868E+00	6.490E+00	8.113E+00
40	–3.656E+00	–2.436E+00	–1.216E+00	5.066E-03	1.227E+00	2.449E+00	3.672E+00	4.895E+00	6.119E+00
50	–2.940E+00	–1.959E+00	–9.785E-01	2.699E-03	9.843E-01	1.966E+00	2.948E+00	3.931E+00	4.914E+00
60	–2.458E+00	–1.639E+00	–8.186E-01	1.605E-03	8.220E-01	1.643E+00	2.463E+00	3.284E+00	4.105E+00
70	–2.112E+00	–1.408E+00	–7.035E-01	1.031E-03	7.057E-01	1.410E+00	2.115E+00	2.820E+00	3.526E+00
80	–1.852E+00	–1.234E+00	–6.168E-01	7.009E-04	6.183E-01	1.236E+00	1.854E+00	2.472E+00	3.089E+00
90	–1.648E+00	–1.099E+00	–5.491E-01	4.981E-04	5.502E-01	1.100E+00	1.650E+00	2.200E+00	2.749E+00
100	–1.485E+00	–9.899E-01	–4.948E-01	3.665E-04	4.956E-01	9.908E-01	1.486E+00	1.981E+00	2.477E+00

Table 4 Relative error percentages for the activation energies determined from the Wanjun–Yuwen method when the frequency factor depends on the temperature ($A=A_0T^m$)

x	m								
	–1.5	–1.0	–0.5	0.0	0.5	1.0	1.5	2.0	2.5
10	–1.363E+01	–9.080E+00	–4.502E+00	1.044E-01	4.736E+00	9.392E+00	1.407E+01	1.877E+01	2.348E+01
20	–7.154E+00	–4.772E+00	–2.385E+00	6.758E-03	2.403E+00	4.802E+00	7.206E+00	9.613E+00	1.202E+01
30	–4.846E+00	–3.233E+00	–1.618E+00	–1.445E-03	1.616E+00	3.236E+00	4.856E+00	6.478E+00	8.101E+00
40	–3.664E+00	–2.444E+00	–1.223E+00	–2.308E-03	1.219E+00	2.442E+00	3.665E+00	4.888E+00	6.112E+00
50	–2.945E+00	–1.964E+00	–9.834E-01	–2.110E-03	9.795E-01	1.961E+00	2.944E+00	3.926E+00	4.909E+00
60	–2.462E+00	–1.642E+00	–8.220E-01	–1.777E-03	8.186E-01	1.639E+00	2.460E+00	3.281E+00	4.102E+00
70	–2.115E+00	–1.410E+00	–7.060E-01	–1.477E-03	7.032E-01	1.408E+00	2.113E+00	2.818E+00	3.523E+00
80	–1.854E+00	–1.236E+00	–6.187E-01	–1.232E-03	6.164E-01	1.234E+00	1.852E+00	2.470E+00	3.088E+00
90	–1.650E+00	–1.100E+00	–5.507E-01	–1.037E-03	5.486E-01	1.098E+00	1.648E+00	2.198E+00	2.748E+00
100	–1.486E+00	–9.912E-01	–4.961E-01	–8.825E-04	4.943E-01	9.896E-01	1.485E+00	1.980E+00	2.476E+00

Table 5 Relative error percentages for the activation energies determined from the Junmeng–Fusheng method when the frequency factor depends on the temperature ($A=A_0T^m$)

x	m								
	–1.5	–1.0	–0.5	0.0	0.5	1.0	1.5	2.0	2.5
10	–1.377E+01	–9.211E+00	–4.619E+00	–4.697E-04	4.642E+00	9.308E+00	1.399E+01	1.870E+01	2.342E+01
20	–7.161E+00	–4.777E+00	–2.390E+00	2.739E-03	2.399E+00	4.800E+00	7.204E+00	9.611E+00	1.202E+01
30	–4.844E+00	–3.231E+00	–1.616E+00	9.484E-04	1.619E+00	3.238E+00	4.859E+00	6.481E+00	8.104E+00
40	–3.661E+00	–2.441E+00	–1.221E+00	3.280E-04	1.222E+00	2.444E+00	3.667E+00	4.891E+00	6.115E+00
50	–2.943E+00	–1.962E+00	–9.812E-01	9.697E-05	9.817E-01	1.964E+00	2.946E+00	3.928E+00	4.911E+00
60	–2.460E+00	–1.640E+00	–8.202E-01	3.691E-06	8.204E-01	1.641E+00	2.462E+00	3.283E+00	4.104E+00
70	–2.113E+00	–1.409E+00	–7.046E-01	–3.518E-05	7.046E-01	1.409E+00	2.114E+00	2.819E+00	3.525E+00
80	–1.852E+00	–1.235E+00	–6.176E-01	–5.069E-05	6.175E-01	1.235E+00	1.853E+00	2.471E+00	3.089E+00
90	–1.649E+00	–1.099E+00	–5.497E-01	–5.564E-05	5.496E-01	1.099E+00	1.649E+00	2.199E+00	2.749E+00
100	–1.485E+00	–9.903E-01	–4.952E-01	–5.570E-05	4.952E-01	9.904E-01	1.486E+00	1.981E+00	2.476E+00

Results and discussion

The relative error percentages involved in the activation energy obtained from the four integral methods, after numerically solving Eq. (15), are shown in Tables 2–5, respectively.

The results obtained have shown that in the case that the frequency factor were independent of the temperature (i.e. $m=0$), the errors for the activation energies are very low, in particular for the Junmeng–Fusheng method. Tables 2–5 show that the relative errors involved in the activation energy are considerably large if it is determined by assuming that A is independent of T when it is really dependent on T, according to Eq. (3).

Conclusions

A number of the integral methods for the kinetic analysis have been proposed since the temperature integral does not have an exact analytical solution. These integral methods were obtained from the assumption that the frequency factor is independent on the temperature. However, the frequency factor of some solid-state reactions is really dependent on the temperature. The main application of the integral methods is the determination of the kinetic parameters, in particular the activation energy. In this study, a systemic analysis of the errors involved in the determination of the activation energy from four integral methods when the frequency factor depends on the temperature ($A=A_0T^m$) has been performed. The results have shown that the precision of the activation energy determined from these integral methods is dependent on $x=E/RT$ and m.

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