

Kinetic analysis of solid-state reactions: errors involved in the determination of the kinetic parameters calculated by one type of integral methods

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The integral methods are extensively used for performing the kinetic analysis of solid-state reactions. As the Arrhenius integral function $p(u)$ does not have an exact analytical solution, many approximations have been proposed. One popular type of approximations is called the exponent approximation which can be put in the form $p(u) = e^{a+blnu+cu}$. In this study, a systematic analysis of the errors involved in the determination of the kinetic parameters calculated by the integral methods based on the exponent approximations for $p(u)$ has been carried out. The results have shown that the precision of the kinetic parameters computed from the integral methods analyzed in this paper depends on u and the errors of the kinetic parameters determined from Doyle approach are the largest.

KEY WORDS: nonisothermal kinetics, integral method, activation energy, frequency factor

1. Introduction

Generally the transformation rate during a reaction is assumed to be the product of two functions, one depending solely on the temperature, T , and the other depending solely on the fractional conversion of the reaction [1]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where α is the fractional conversion. For $k(T)$ usually an Arrhenius expression is assumed to valid, i.e. [2]:

$$k(T) = Ae^{-E/RT}, \quad (2)$$

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where A is the frequency factor, E is the activation energy, R is the gas constant.

The overwhelming majority of thermal analyses are conducted at constant heating rate [3]. Under nonisothermal conditions of a linear heating program, equation (1) becomes after taking into account equation (2):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha). \quad (3)$$

Furthermore

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT. \quad (4)$$

The integral $\int_0^T e^{-E/RT} dT$ of the right-hand side of equation (4) is named in the literature as the temperature integral [4, 5]. If E/RT is replaced by ' u ' and the integration limits are transformed, the above equation becomes:

$$g(\alpha) = \frac{AE}{\beta R} \int_u^\infty \frac{e^{-u}}{u^2} du = \frac{AE}{\beta R} p(u), \quad (5)$$

where $p(u)$ is the Arrhenius integral function. The $p(u)$ does not have an exact analytical solution, and a large number of approximations have been proposed in the literature for performing the kinetic analysis of solid-state reactions from integral experimental data [6]. Of these approximations, one type of approximations can be described by the following expression:

$$p(u) = e^{a+b \ln u + cu}, \quad (6)$$

where a , b , and c are constants. Those approximations proposed by Doyle [7], Starink [8, 9], Madhusudanan et al. [10, 11], and Wanjun et al. [12] can fall into the above type called the exponent approximations here. Values of the parameters of those exponent approximations are listed in table 1.

Based on the numerical values of $p(u)$, using a nonlinear regression method, a new exponent approximation for the $p(u)$ function can be easily obtained. The corresponding values of the parameters a , b , and c are also listed in table 1.

The main application of proposing the $p(u)$ approximations is the determination of the kinetic parameters, and not the computation of the $p(u)$ function. However, a systematic analysis of the errors involved in the determination of the kinetic parameters (including the activation energy and frequency factor) from those integral methods is still missing. The aim of this paper is to carry out a systematic analysis of the precision of the kinetic analysis from the integral methods based on the exponent approximations for $p(u)$. It is hoped that the results of this work aid process development of nonisothermal kinetics of solid-state reactions.

Table 1
Values of the parameters of the $p(u)$ approximations.

Approximation for $p(u)$	a	b	c
Doyle [7]	-5.3308	0	-1.0516
Starink I [8]	-0.235	-1.95	-1
Starink II [9]	-0.312	-1.92	-1.0008
Madhusudanan–Krishnan– Ninan I(MKN I) [10]	-0.297580	-1.921503	-1.000953
Madhusudanan–Krishnan– Ninan II (MKN II) [11]	-0.299963	-1.920620	-1.000974
Madhusudanan–Krishnan– Ninan III (MKN III) [11]	-0.389677	-1.884318	-1.001928
Wanjun–Yuwen–Hen–Cunxin (WYHC) [12]	-0.37773896	-1.89466100	-1.00145033
New approximation (Junmeng–Ronghou)	-0.460120828342246	-1.86847901883656	-1.00174866236974

2. Errors in the activation energy

Equation (5) can be written in the logarithmic form as

$$\ln(g(\alpha)) = \ln \frac{AE}{\beta R} + \ln(p(u)). \quad (7)$$

By introducing equation (6) into equation (7), it follows:

$$\ln(g(\alpha)) = \ln \frac{A_a E_a}{\beta R} + a + b \ln u_a + c u_a. \quad (8)$$

The subscript a stands for the apparent values of the kinetic parameters obtained from the above approaches and $u_a = E_a/RT$.

By differentiating equation (8)

$$\frac{\partial \ln(g(\alpha))}{\partial(1/T)} = \frac{E_a}{R} \left(c + \frac{b}{u_a} \right). \quad (9)$$

The real value of the left-hand side of equation (9) as a function of the true activation energy can be easily determined by differentiating equation (7):

$$\frac{\partial \ln(g(\alpha))}{\partial(1/T)} = \frac{\partial \ln(p(u))}{\partial(1/T)} = \frac{E}{R} \frac{d \ln(p(u))}{du}. \quad (10)$$

The relative error in the activation energy can be defined by the following expression:

$$\varepsilon_E = \frac{E_a - E}{E} \cdot 100\% \quad (11)$$

From equation (11), one can obtain

$$E_a = (\varepsilon_E + 1)E, \quad (12)$$

$$u_a = (\varepsilon_E + 1)u. \quad (13)$$

The relative error in the activation energy would be estimated from equations (9), (10), (12), and (13):

$$\varepsilon_E = \frac{1}{c} \left(\frac{d \ln(p(u))}{du} - \frac{b}{u} \right) - 1. \quad (14)$$

3. Errors in the frequency factor

From equations (7) and (8), it follows:

$$\frac{AE}{\beta R} p(u) = \frac{A_a E_a}{\beta R} e^{a+b \ln u_a + c u_a}. \quad (15)$$

We define the relative error of the frequency factor $\varepsilon_A = \frac{A_a - A}{A} \cdot 100\%$, and ε_A can be easily derived from equation (15):

$$\varepsilon_A = \frac{p(u)}{(\varepsilon_E + 1) e^{a+b \ln[(\varepsilon_E + 1)u] + c[(\varepsilon_E + 1)u]}} - 1. \quad (16)$$

4. Results and discussion

From equation (14), it is obtained that the relative error is a function of $u = E/RT$. The relative error percentages in the activation energy computed from the integral methods are listed in table 2.

From equation (16), we can obtain that ε_A is a function of u after taking into account ε_E depending on u . Table 3 includes the numerical values of ε_A for various u .

The obtained results included in tables 2 and 3 point out that the relative error percentages in the calculation of the kinetic parameters are rather large for small values of u and on the other hand for high values of u yields relatively small errors. Moreover, of the integral methods analyzed in this paper, Doyle approach is the most imprecision.

All the above calculations have been performed by the Mathematica software system, which is powerful for the numerical calculation [13].

Table 2
Relative error percentages in the activation energy determined from the integral methods.

u	Doyle	Starink I	Starink II	MKN I	MKN II	MKN III	WYHC	Junneng-Ronghou
5	2.86007E+01	-3.76355E+00	-3.24095E+00	-3.28577E+00	-3.27016E+00	-2.63762E+00	-2.79774E+00	-2.30396E+00
10	1.27142E+01	-9.69766E-01	-7.49167E-01	-7.79354E-01	-7.72614E-01	-5.04773E-01	-5.60596E-01	-3.28848E-01
15	7.09450E+00	-3.79423E-01	-2.59216E-01	-2.84472E-01	-2.80683E-01	-1.34084E-01	-1.55304E-01	-1.07970E-02
20	4.20238E+00	-1.70782E-01	-1.00702E-01	-1.23480E-01	-1.21164E-01	-3.51045E-02	-3.90635E-02	6.18483E-02
25	2.43654E+00	-7.77381E-02	-3.77080E-02	-5.89939E-02	-5.75621E-02	-7.79509E-03	-1.41307E-03	7.33513E-02
30	1.24535E+00	-3.03864E-02	-1.03781E-02	-3.06672E-02	-2.98240E-02	-4.23821E-03	9.03086E-03	6.63679E-02
35	3.87229E-01	-4.21871E-03	1.49438E-03	-1.80815E-02	-1.76586E-02	-9.33785E-03	8.84689E-03	5.37382E-02
40	-2.60533E-01	1.10239E-02	6.01909E-03	-1.30212E-02	-1.29135E-02	-1.75373E-02	4.33212E-03	3.98904E-02
45	-7.66905E-01	2.01889E-02	6.85007E-03	-1.17732E-02	-1.19106E-02	-2.65998E-02	-1.86586E-03	2.64342E-02
50	-1.17366E+00	2.57781E-02	5.77349E-03	-1.25160E-02	-1.28494E-02	-3.55893E-02	-8.56447E-03	1.39295E-02
55	-1.50758E+00	2.91726E-02	3.71504E-03	-1.43011E-02	-1.47948E-02	-4.41206E-02	-1.52220E-02	2.52188E-03
60	-1.78663E+00	3.11757E-02	1.17477E-03	-1.66135E-02	-1.72408E-02	-5.20539E-02	-2.15943E-02	-7.80857E-03
65	-2.02332E+00	3.22752E-02	-1.56972E-03	-1.91650E-02	-1.99054E-02	-5.93611E-02	-2.75809E-02	-1.71442E-02
70	-2.22662E+00	3.27772E-02	-4.36215E-03	-2.17920E-02	-2.26293E-02	-6.60640E-02	-3.31520E-02	-2.55857E-02
75	-2.40312E+00	3.28797E-02	-7.11465E-03	-2.44011E-02	-2.53223E-02	-7.22051E-02	-3.83124E-02	-3.32338E-02
80	-2.55780E+00	3.27133E-02	-9.77886E-03	-2.69398E-02	-2.79345E-02	-7.78341E-02	-4.30834E-02	-4.01814E-02
85	-2.69448E+00	3.23664E-02	-1.23297E-02	-2.93798E-02	-3.04393E-02	-8.30007E-02	-4.74931E-02	-4.65115E-02
90	-2.81612E+00	3.18991E-02	-1.47557E-02	-3.17073E-02	-3.28244E-02	-8.77517E-02	-5.15713E-02	-5.22968E-02
95	-2.92508E+00	3.13535E-02	-1.70539E-02	-3.39173E-02	-3.50860E-02	-9.21299E-02	-5.53476E-02	-5.76004E-02
100	-3.02324E+00	3.07587E-02	-1.92259E-02	-3.60099E-02	-3.72250E-02	-9.61738E-02	-5.88499E-02	-6.24773E-02

Table 3
Relative error percentages in the frequency factor determined from the integral methods.

u	Doyle	Starink I	Starink II	MKN I	MKN II	MKN III	WYHC	Junmeng-Ronghou
5	2.66700E+03	-3.10610E+01	-2.64421E+01	-2.74633E+01	-2.73164E+01	-2.16899E+01	-2.22660E+01	-1.64987E+01
10	8.86477E+02	-1.44750E+01	-1.09613E+01	-1.20897E+01	-1.19752E+01	-7.91501E+00	-7.82471E+00	-3.05551E+00
15	4.05506E+02	-7.66820E+00	-5.14299E+00	-6.28291E+00	-6.19738E+00	-3.42670E+00	-2.89172E+00	9.66130E-01
20	2.07264E+02	-4.11728E+00	-2.39286E+00	-3.52165E+00	-3.45958E+00	-1.69918E+00	-8.43723E-01	2.27992E+00
25	1.06505E+02	-2.02944E+00	-9.63098E-01	-2.07414E+00	-2.03129E+00	-1.08374E+00	1.71562E-02	2.54262E+00
30	4.83232E+01	-7.12841E-01	-1.99464E-01	-1.29107E+00	-1.26434E+00	-9.89190E-01	3.07940E-01	2.33523E+00
35	1.16931E+01	1.53953E-01	1.93360E-01	-8.78911E-01	-8.65957E-01	-1.15997E+00	2.99059E-01	1.90302E+00
40	-1.28592E+01	7.39342E-01	3.65716E-01	-6.87972E-01	-6.86996E-01	-1.47182E+00	1.24008E-01	1.36205E+00
45	-3.011175E+01	1.13939E+00	4.00883E-01	-6.35203E-01	-6.44785E-01	-1.85928E+00	-1.45689E-01	7.71578E-01
50	-4.27108E+01	1.41248E+00	3.47958E-01	-6.71549E-01	-6.90547E-01	-2.28588E+00	-4.69394E-01	1.63327E-01
55	-5.21813E+01	1.59592E+00	2.37304E-01	-7.66618E-01	-7.94092E-01	-2.73051E+00	-8.22995E-01	-4.45203E-01
60	-5.94827E+01	1.71447E+00	8.84117E-02	-9.00857E-01	-9.36024E-01	-3.18061E+00	-1.19174E+00	-1.04428E+00
65	-6.52304E+01	1.78514E+00	-8.58292E-02	-1.06130E+00	-1.10350E+00	-3.62861E+00	-1.56639E+00	-1.62858E+00
70	-6.98361E+01	1.81992E+00	-2.76690E-01	-1.23915E+00	-1.28782E+00	-4.06994E+00	-1.94110E+00	-2.19531E+00
75	-7.35835E+01	1.82745E+00	-4.78146E-01	-1.42832E+00	-1.48297E+00	-4.50190E+00	-2.31217E+00	-2.74323E+00
80	-7.66734E+01	1.81407E+00	-6.85978E-01	-1.62451E+00	-1.68473E+00	-4.92294E+00	-2.67773E+00	-3.27197E+00
85	-7.92511E+01	1.78453E+00	-8.97198E-01	-1.82470E+00	-1.89010E+00	-5.33227E+00	-3.03484E+00	-3.78174E+00
90	-8.14239E+01	1.74243E+00	-1.10967E+00	-2.02668E+00	-2.09694E+00	-5.72956E+00	-3.38414E+00	-4.27303E+00
95	-8.32723E+01	1.69054E+00	-1.32188E+00	-2.22890E+00	-2.30371E+00	-6.11481E+00	-3.72466E+00	-4.74653E+00
100	-8.48580E+01	1.63100E+00	-1.53271E+00	-2.43020E+00	-2.50932E+00	-6.48819E+00	-4.05623E+00	-5.20302E+00

5. Conclusions

Due to the fact that the Arrhenius integral function $p(u)$ does not have an exact analytical solution, many approximating formulas have been proposed with the objective of increasing the precision in the determination of the Arrhenius integral. However, the main application of these proposed approximations is the determination of the kinetic parameters and not the computation of the Arrhenius integral function $p(u)$. In this paper, we calculated the errors in the kinetic parameters (including the activation energy and frequency factor) obtained from the integral methods based on the exponent approximations for the Arrhenius integral function. Our results have shown that for all approaches analyzed in this paper, the relative errors of the kinetic parameters very much depend on $u = E/RT$. In general, small values of u yield relatively high errors, and the integral methods are not appropriate. On the other hand, for high values of u , the errors are quite small. Furthermore, of the integral methods analyzed here, Doyle approach is the most imprecise.

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