

# PRECISION OF INTEGRAL METHODS FOR THE DETERMINATION OF THE KINETIC PARAMETERS

## Use in the kinetic analysis of solid-state reactions

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In this paper, a systematic analysis of the errors involved in the determination of the kinetic parameters (including the activation energy and frequency factor) from five integral methods has been carried out. The integral methods analyzed here are Coats–Redfern, Gorbachev, Wanjun–Yuwen–Hen–Zhiyong–Cunxin, Junmeng–Fusheng–Weiming–Fang, Junmeng–Fang and Junmeng–Fang–Weiming–Fusheng method. The results have shown that the precision of the kinetic parameters calculated by the different integral methods is dependent on  $u$  ( $E/RT$ ), that is, on the activation energy and the average temperature of the process.

**Keywords:** integral method, kinetic parameter, non-isothermal kinetic analysis

### Introduction

In papers by Ortega *et al.* [1] and Pérez-Maqueda *et al.* [2, 3], the precision of the activation energy calculated by some integral methods has been estimated. However, the errors of the frequency factor from the integral methods are still missing.

Coats and Redfern [4], Gorbachev [5], Wanjun *et al.* [6] and Junmeng *et al.* [7–9] have proposed several integral methods based on the different approximations for the Arrhenius integral. Here we called these integral methods are Coats–Redfern, Gorbachev, Wanjun–Yuwen–Hen–Zhiyong–Cunxin, Junmeng–Fusheng–Weiming–Fang, Junmeng–Fang and Junmeng–Fang–Weiming–Fusheng method, respectively. These integral methods have been extensively used in the non-isothermal kinetic analysis of solid-state reactions, but their precision for the determination of the kinetic parameters can not be found in the published literatures.

To solve the above-mentioned problems, the aim of the present paper is to perform a systematic analysis of the error involved in the activation energy and frequency factor determined from the above-mentioned integral methods.

### Theoretical

Under non-isothermal conditions of a linear heating program which is the most common heating profile used for studying solid-state reactions, the reaction

rate of thermally stimulated solid-state reactions can be kinetically described [10–15]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (1)$$

where  $\alpha$  is the extent of reaction,  $T$  is the absolute temperature,  $A$  is the frequency factor,  $\beta$  is the heating rate,  $E$  is the activation energy,  $R$  is the ideal gas constant and  $f(\alpha)$  is the kinetic model function depending on the reaction mechanism.

The integration of Eq. (1), after rearranging leads to

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT = \frac{AE}{\beta R} \int_u^\infty \frac{e^{-u}}{u^2} du = \frac{AE}{\beta R} p(u) \quad (2)$$

where  $u=E/RT$ . The  $p(u)$  function does not have an exact analytical solution, and a lot of approximations for the  $p(u)$  function have been proposed for performing the kinetic analysis of solid-state reactions [16].

The approximations for the  $p(u)$  function can be written in the following form [17]:

$$p(u) = \frac{e^{-u}}{u^2} h(u) \quad (3)$$

From Eqs (2) and (3), it follows:

$$h(u) = u^2 e^u \int_u^\infty \frac{e^{-u}}{u^2} du \quad (4)$$

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The  $h(u)$  function does not have an exact analytical solution and can be numerically integrated. In this study, Simpson's 1/3 rule has been employed for numerical integration. For detailed information of Simpson's 1/3 rule, readers can refer to the literature [18]. The numerical values of the  $h(u)$  function as a function of the parameter  $u$  ( $E/RT$ ) are shown in Fig. 1.

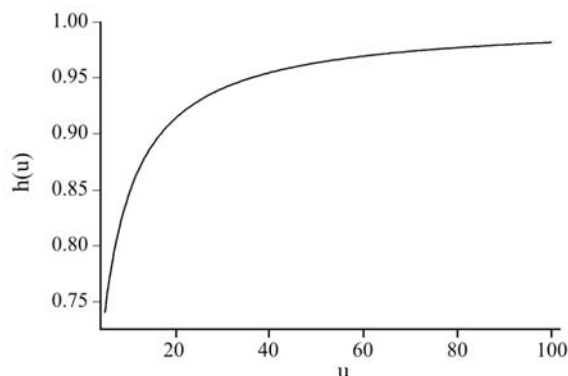


Fig. 1 Numerical values of  $h(u)$  at various  $u$

A number of rational fraction approximations for the  $h(u)$  function have been proposed. Table 1 lists the  $h(u)$  approximations proposed by Coats and Redfern [4], Gorbachev [5], Wanjun *et al.* [6] and Junmeng *et al.* [7–9].

If the integral methods were used for performing the kinetic analysis of solid-state reactions, the apparent activation energy,  $E_a$ , would satisfy the following equation:

$$g(\alpha) = \frac{A_a}{\beta} \frac{RT^2}{E_a} h_1(u_a) e^{-E_a/RT} \quad (11)$$

where the subscript  $a$  stands for the apparent values of kinetic parameters obtained from the integral methods,  $h_1(u)$  stands for the  $h(u)$  approximation and  $u_a = E_a/RT$ .

From Eq. (11), it follows:

$$\frac{d \ln[g(\alpha)/T^2]}{d(1/T)} = -\frac{E_a}{R} \left[ 1 - \frac{d \ln h_1(u_a)}{du_a} \right] \quad (12)$$

The real value of the left hand side of Eq. (12) as a function of the true activation energy,  $E$ , can be determined from Eqs (2)–(4).

$$\frac{d \ln[g(\alpha)/T^2]}{d(1/T)} = -\frac{E}{R} \left[ 1 - \frac{d \ln h(u)}{du} \right] \quad (13)$$

The relative error,  $\varepsilon_E$ , of the apparent activation energy ( $E_a$ ) can be defined by the following equation:

$$\varepsilon = \frac{E_a - E}{E} \quad (14)$$

From the above equation, we get the following expressions:

$$E_a = (\varepsilon_E + 1)E \quad (15)$$

$$u_a = (\varepsilon_E + 1)u \quad (16)$$

Thus, from Eqs (12), (13), (15) and (16), we can obtain:

$$(\varepsilon_E + 1) \left\{ 1 - \frac{d \ln h_1[(\varepsilon_E + 1)u]}{d[(\varepsilon_E + 1)u]} \right\} = 1 - \frac{d \ln h(u)}{du} \quad (17)$$

The above equation for the relative error of the apparent activation energy cannot be analytically solved. But for certain  $u$  values, the equation can be solved by numerical techniques. For this purpose, either general purposed mathematical software or a computer program developed in any programming language is used. In this study, the Mathematica software system has been used for the numerical solution of Eq. (17). A detailed description of the Mathematica software system can be found in the literature [19].

From Eqs (2)–(4) and (11), it follows

$$\frac{A_a}{\beta} \frac{RT^2}{E_a} h_1(u_a) e^{-E_a/RT} = \frac{A}{\beta} \frac{RT^2}{E} h(u) e^{-E/RT} \quad (18)$$

Table 1 The expressions of the  $h(u)$  approximations

Author	Approximation for $h(u)$	Equation
Coats–Redfern [4]	$\frac{u-2}{u}$	(5)
Gorbachev–Lee–Beck [5]	$\frac{u}{u+2}$	(6)
Wanjun–Yuwen–Hen–Zhiyong–Cunxin [6]	$\frac{u}{1.00198882u+1.87391198}$	(7)
Junmeng–Fusheng–Weiming–Fang [7]	$\frac{u+0.66539}{u+2.64774}$	(8)
Junmeng–Fang [8]	$\frac{0.99962u+0.60462}{u+2.56879}$	(9)
Junmeng–Fang–Weiming–Fusheng [9]	$\frac{u+0.25403 \ln u + 0.36665}{u+0.24598 \ln u + 2.41457}$	(10)

**Table 2** The relative error percentages of the activation energy obtained from the integral methods

$u$	Coats–Redfern	Gorbachev	Wanjun–Yuwen– Hen–Zhiyong– Cunxin	Junmeng–Fusheng– Weiming–Fang	Junmeng–Fang	Junmeng–Fang– Weiming–Fusheng
5	7.1501E+00	9.1369E-01	6.5499E-01	−1.8376E-01	−1.3066E-01	−2.4747E-03
10	9.9939E-01	1.9421E-01	1.0439E-01	−1.9290E-04	3.6268E-03	2.1153E-04
15	3.0924E-01	7.1066E-02	2.6124E-02	4.2700E-03	3.5754E-03	2.5795E-05
20	1.3395E-01	3.3624E-02	6.7579E-03	2.7648E-03	1.5409E-03	−3.7481E-05
30	4.0938E-02	1.1258E-02	−1.4452E-03	9.5144E-04	−2.1183E-05	−2.6978E-05
50	9.1035E-03	2.6992E-03	−2.1099E-03	9.5223E-05	−3.9582E-04	6.5755E-06
100	1.1667E-03	3.6652E-04	−8.8251E-04	−5.6730E-05	−2.0879E-04	1.0808E-05

**Table 3** The relative error percentages of the frequency factor obtained from the integral methods

$u$	Coats–Redfern	Gorbachev	Wanjun–Yuwen– Hen–Zhiyong– Cunxin	Junmeng–Fusheng– Weiming–Fang	Junmeng–Fang	Junmeng–Fang– Weiming–Fusheng
5	8.0762E+01	9.0686E+00	5.6954E+00	−1.2349E+00	−8.5743E-01	−1.5741E-02
10	1.7417E+01	3.3924E+00	1.4861E+00	4.5591E-02	6.8136E-02	2.5393E-03
15	7.5995E+00	1.7751E+00	4.7930E-01	9.7874E-02	6.3652E-02	7.8412E-05
20	4.2751E+00	1.0922E+00	1.3159E-01	7.0071E-02	2.6633E-02	−1.0423E-03
30	1.9146E+00	5.3464E-01	−6.7574E-02	2.4595E-02	−1.1994E-02	−7.2173E-04
50	6.9785E-01	2.0917E-01	−8.7357E-02	−7.7977E-03	−2.5323E-02	5.8248E-04
100	1.7684E-01	5.5893E-02	1.0897E-03	−1.7016E-02	−1.1150E-02	7.5847E-04

We define the relative error of the frequency factor  $\varepsilon_A = (A_a - A)/A$  and  $\varepsilon_A$  can be easily derived from Eq. (18):

$$\varepsilon_A = (\varepsilon_E + 1)e^{\varepsilon_E u} \frac{h(u)}{h_1[(\varepsilon_E + 1)u]} - 1 \quad (19)$$

## Results and discussion

Equations (17) and (19) indicates that the values of  $\varepsilon_E$  and  $\varepsilon_A$  depend on  $u$  ( $E/RT$ ), and therefore, on the value of the activation energy and on the average temperature of the process. Additionally, this average temperature of the process depends on the value of  $E$ ,  $A$  and the kinetic model function followed by the reaction mechanism. Thus, the errors of the activation energy and frequency factor calculated by the integral methods are influenced by the kinetic parameters of the process.

The relative error percentages of the activation energy and frequency factor obtained from the integral methods are shown in Tables 2 and 3, respectively. The resulting  $\varepsilon_E$  and  $\varepsilon_A$  values included in Tables 2 and 3 illustrate that there is a significant influence of  $u$  in the precision of the calculated activation energy and frequency factor values. Furthermore, of the integral methods analyzed here, Junmeng–Fang–Weiming–Fusheng method has the highest accuracy in the determination of the kinetic parameters.

## Conclusions

In this paper, a systematic analysis of the precision of the integral methods for the determination of the kinetic parameters (including the activation energy and frequency factor) has been carried out. Our results have shown that for all the integral methods analyzed here, the relative errors of the activation energy and frequency factor very much depend on  $u$  ( $E/RT$ ). Of the integral methods analyzed here, Junmeng–Fang–Weiming–Fusheng method has the highest accuracy in the determination of the kinetic parameters.

## Acknowledgements

This work was performed under the auspices of National Natural Science Foundation of China under Contract 50276039.

## References

- 1 A. Ortega, L. A. Pérez-Maqueda and J. M. Criado, *Thermochim. Acta*, 282, 283 (1996) 29.
- 2 L. A. Pérez-Maqueda, P. E. Sánchez-Jiménez and J. M. Criado, *Polymer*, 46 (2005) 2950.
- 3 L. A. Pérez-Maqueda, P. E. Sánchez-Jiménez and J. M. Criado, *Int. J. Chem. Kinet.*, 37 (2005) 658.
- 4 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 5 V. M. Gorbachev, *J. Thermal Anal.*, 8 (1975) 349.

- 6 T. Wanjun, L. Yuwen, Z. Hen, W. Zhiyong and W. J. Cunxin, *J. Therm. Anal. Cal.*, 74 (2003) 309.
- 7 C. Junmeng, Y. Fusheng, Y. Weiming and H. Fang, *AIChE J.*, 52 (2006) 1554.
- 8 C. Junmeng and H. Fang, *AIChE J.*, 52 (2006) 2656.
- 9 C. Junmeng, H. Fang, Y. Weiming and Y. Fusheng, *Chem. Eng. J.*, 124 (2006) 15.
- 10 J. M. Criado, L. A. Pérez-Maqueda and P. E. Sánchez-Jiménez, *J. Therm. Anal. Cal.*, 82 (2005) 671.
- 11 B. V. L'vov, *J. Therm. Anal. Cal.*, 79 (2005) 151.
- 12 N. Liu, H. Chen, L. Shu and M. Statheropoulos, *J. Therm. Anal. Cal.*, 81 (2005) 99.
- 13 T. Wanjun, L. Yuwen, Y. Xil, W. Zhiyong and W. Cunxin, *J. Therm. Anal. Cal.*, 81 (2005) 347.
- 14 A. K. Galwey, *J. Therm. Anal. Cal.*, 86 (2006) 267.
- 15 S. Vyazovkin, *Anal. Chem.*, 78 (2006) 3875.
- 16 S. Vyazovkin and S. A. Wight, *Int. Rev. Phys. Chem.*, 17 (1998) 407.
- 17 J. H. Flynn, *Thermochim. Acta*, 300 (1997) 83.
- 18 E. Süli and D. Mayers, *An introduction to Numerical Analysis*, Cambridge University Press, 2003.
- 19 S. Wolfram, *The Mathematica Book* (5<sup>th</sup> Ed.). Wolfram Media, Inc., 2003.

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Received: January 5, 2007

Accepted: January 31, 2007

OnlineFirst: October 25, 2007

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DOI: 10.1007/s10973-007-8328-9