

THERMOKINETIC RESEARCH METHOD FOR FASTER FIRST-ORDER REACTION Double-parameter method

S.-Q. Cheng, Z. Huang, X.-G. Meng and X.-C. Zeng^{*}

Faculty of Chemistry, Sichuan University, Chengdu 610064, P. R. China

(Received January 2, 2000; in revised form July 5, 2000)

Abstract

This paper presents a novel data processing method for thermokinetics of faster first-order reaction on the basis of the double-parameter theoretical model of a conduction calorimeter, in which the rate constant of a first-order reaction can be calculated from only four peak height data from the same thermoanalytical curve without using any peak-area. The saponifications of ethyl acetate and methyl acetate in aqueous solution and ethyl benzoate in aqueous alcohol have been studied to test the validity of this method. The rate constants calculated with this method are in fair agreement with those in literature; hence the validity of this method is demonstrated.

Keywords: double-parameter method, faster first-order reaction, thermokinetic research method, thermokinetics

Introduction

The conduction calorimeter is an important tool for thermokinetic investigations [1]. The thermal inertial of the calorimeter will cause the distortion of the measured thermoanalytical curve. In order to analyze the kinetic characteristics of the investigated process correctly, a double-parameter theoretical model of the conduction calorimeter, in which the delay of sensing was considered, was suggested [2] and used to study faster chemical and biochemical reactions with thermoanalytical curve reconstruction and reduced extent method together [2, 3]. But in this method the thermoanalytical curve data $\int_0^t \Delta dt$ and $d\Delta/dt$ must be used during the thermoanalytical curve reconstruction, which will cause the complexity and the less accuracy of data processing. On the other hand, the data processing method for the thermoanalytical curve of a first-order reaction measured with a conduction calorimeter has been an attractive subject for a long time, because most chemical and biochemical reactions can be treated as pseudo-

^{*} Author to whom all correspondence should be addressed.

first-order reactions under certain conditions [4–8]. Specially, it is still few for the thermokinetic research method of faster first-order reaction up to now [9].

In this paper, based on the double-parameter theoretical model of conduction calorimeter and thermokinetic equation, the double-parameter thermoanalytical curve equation for a first-order reaction and the corresponding mathematical model have been derived, by which the rate constant of a first-order reaction can be calculated from only four peak-height data from the same thermoanalytical curve without using any peak-area. Its validity is tested by comparison with experimental results.

Theory and method

Double-parameter thermoanalytical curve equation for a first-order reaction

As pointed in literature [2], the double-parameter theoretical model for the conduction calorimeter, in which the delay of sensing was considered,

$$\frac{\Omega}{K} = \Delta + \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) \frac{d\Delta}{dt} + \frac{1}{\alpha\beta} \frac{d^2\Delta}{dt^2} \quad (1)$$

where Ω is the heat-evolving rate of a thermal change process in the calorimetric system at time t , K is the apparatus constant of the calorimeter, Δ is the peak-height of thermoanalytical curve at time t , α and β are the cooling constants of the calorimetric system and the sensor, respectively.

According to the rate equation of a first-order reaction and the relationship between the energy change and the concentration change of a reacting system, it can be proved that [10]

$$\frac{\Omega}{Q_\infty} = k_1 e^{-k_1 t} \quad (2)$$

where $Q_\infty (=KA)$ is the total heat effect, A is the total area under the thermoanalytical curve, and k_1 is the rate constant of a first-order reaction.

According to Eqs (1) and (2), we obtain

$$Ak_1 e^{-k_1 t} = \Delta + \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) \frac{d\Delta}{dt} + \frac{1}{\alpha\beta} \frac{d^2\Delta}{dt^2} \quad (3)$$

This is called the double-parameter differential equation of the thermoanalytical curve for a first-order reaction.

Applying the Laplace transformation to Eq. (3) under zero initial conditions, we obtain

$$\frac{Ak_1}{k_1 + s} = f(s) + \left(\frac{s}{\alpha} + \frac{s}{\beta} \right) f(s) + \frac{s^2}{\alpha\beta} f(s) \quad (4)$$

where s is a Laplace operator, and $f(s)$ is Laplace transform of peak-height. Equation (4) can be written in the form

$$f(s) = \frac{Ak_1\alpha\beta}{(k_1+s)(\alpha+s)(\beta+s)} \quad (5)$$

The inverse Laplace transform Δ

$$\Delta = L^{-1}\{f(s)\} = Ak_1\alpha\beta \left[\frac{e^{-k_1t}}{(k_1-\alpha)(k_1-\beta)} + \frac{e^{-\alpha t}}{(k_1-\alpha)(\beta-\alpha)} - \frac{e^{-\beta t}}{(k_1-\beta)(\beta-\alpha)} \right] \quad (6)$$

This is called the double-parameter equation of the thermoanalytical curve for a first-order reaction.

Mathematical model of double-parameter method for a first-order reaction

If four data ($\Delta_1, \Delta_2, \Delta_3, \Delta_4$) are taken from the same thermoanalytical curve of a first-order reaction at fixed time intervals, i.e., $t_4-t_3=t_3-t_2=t_2-t_1=\Delta t$, according to Eq. (6), we obtain a group of equations

$$\Delta_i = Ak_1\alpha\beta \left[\frac{e^{-k_1t_i}}{(k_1-\alpha)(k_1-\beta)} + \frac{e^{-\alpha t_i}}{(k_1-\alpha)(\beta-\alpha)} - \frac{e^{-\beta t_i}}{(k_1-\beta)(\beta-\alpha)} \right] \quad (i=1, 2, 3, 4) \quad (7)$$

Applying self-function regression method [11] to the above equation group, we obtain

$$e^{k_1\Delta t} = \frac{\Delta_1 - \Delta_2 (e^{\alpha\Delta t} + e^{\beta\Delta t}) + \Delta_3 e^{(\beta+\alpha)\Delta t}}{\Delta_2 - \Delta_3 (e^{\alpha\Delta t} + e^{\beta\Delta t}) + \Delta_4 e^{(\beta+\alpha)\Delta t}} \quad (8)$$

and

$$k_1 = \frac{1}{\Delta t} \ln \left(\frac{\Delta_1 - \Delta_2 (e^{\alpha\Delta t} + e^{\beta\Delta t}) + \Delta_3 e^{(\beta+\alpha)\Delta t}}{\Delta_2 - \Delta_3 (e^{\alpha\Delta t} + e^{\beta\Delta t}) + \Delta_4 e^{(\beta+\alpha)\Delta t}} \right) \quad (9)$$

From Eq. (9), it can be seen that the rate constant for a first-order reaction k_1 can be calculated from only four peak height data if the cooling constants α and β are determined by using electric calibration in advance.

Thermokinetic research method for faster first-order reaction: Double-parameter method

Differentiating both sides of Eq. (6), we obtain

$$\frac{d\Delta}{dt} = Ak_1\alpha\beta \left[\frac{-k_1 e^{-k_1t}}{(k_1-\alpha)(k_1-\beta)} - \frac{\alpha e^{-\alpha t}}{(k_1-\alpha)(\beta-\alpha)} + \frac{\beta e^{-\beta t}}{(k_1-\beta)(\beta-\alpha)} \right] \quad (10)$$

According to Eqs (6) and (10), it can be proved that

$$\Delta + \frac{1}{\beta} \frac{d\Delta}{dt} = \frac{Ak_1\alpha}{\alpha - k_1} (e^{-k_1t} - e^{-\alpha t}) \quad (11)$$

In the previous article [11], on the basis of Tian's equation, we proved that

$$\Delta = \frac{Akk_1}{k - k_1} (e^{-k_1t} - e^{-kt}) \quad (12)$$

where k is the cooling constant of the calorimetric system.

Comparing Eq. (11) with Eq. (12), it can be seen that the double-parameter method corrects the influence of the delay of sensing ($1/\beta \cdot d\Delta/dt$). When the thermal change process is slower, the influence of the delay of sensing ($1/\beta \cdot d\Delta/dt$) can be neglected, i.e. $1/\beta \cdot d\Delta/dt \ll \Delta$. So Eq. (11) is equivalent to Eq. (12), that is to say, the double-parameter theoretical model can be returned to the single-parameter theoretical model based on Tian's equation.

From Eq. (12), using self-function regression method, we also have obtained the single-parameter mathematical model for calculating the rate constant of a first-order [11], i.e.

$$k_1 = \frac{1}{\Delta t} \ln \frac{b + \sqrt{b^2 - 4a}}{2} \quad (13)$$

$$k = \frac{1}{\Delta t} \ln \frac{b - \sqrt{b^2 - 4a}}{2} \quad (14)$$

where

$$a = \frac{\Delta_2^2 - \Delta_1\Delta_3}{\Delta_3 - \Delta_2\Delta_4}, \quad b = \frac{\Delta_2\Delta_3 - \Delta_1\Delta_4}{\Delta_3 - \Delta_2\Delta_4} \quad (15)$$

Experimental

Reactions and reactants

The saponifications of ethyl acetate and methyl acetate in aqueous solution were studied to test the validity of the double-parameter method applicable to those faster first-order reactions. Chemically pure ethyl acetate and methyl acetate were further purified by distillation three times under reduced pressure. The potassium hydroxide used was of guaranteed grade and its concentration in solution was standardized with potassium hydrogen phthalate. Meanwhile, in order to test the validity of the double-parameter method applicable to those slow chemical reactions, some thermo-analytical curve data for the saponification of ethyl benzoate in aqueous alcohol were taken from literature [12].

Table 1 Saponifications of ethyl acetate and methyl acetate in aqueous solution at 25°C ^{a)}

	No.	$C_0(\text{ester})/\text{mol dm}^{-3}$	$C_0(\text{KOH})/\text{mol dm}^{-3}$	$\Delta t/\text{s}$	Δ_1/mm	Δ_2/mm	Δ_3/mm	Δ_4/mm	$10^2 \cdot k_1^*/\text{s}^{-1}$	$k_2/\text{dm mol}^{-1}$	
Ethyl acetate	1	0.03280	0.8185	30.0	69.4	68.3	43.7	40.5	9.00 ^b	9.04 ^c	0.110 ^b
	2	0.05143	0.8185	30.0	75.9	67.5	62.5	58.1	9.05	8.07	0.111
	3	0.03280	0.8028	30.0	68.2	59.3	54.9	51.1	8.97	8.57	0.112
	4	0.05413	0.8028	30.0	70.5	61.3	57.5	54.1	8.97	11.2	0.112
	5	0.03468	0.8329	30.0	62.1	55.1	51.3	47.9	9.41	9.71	0.113
										average:	
									[14]		0.111
Methyl acetate	1	0.05123	0.4803	30.0	78.0	63.1	57.2	52.4	7.50 ^b	8.48 ^c	0.156 ^b
	2	0.05312	0.4803	30.0	80.7	66.5	61.1	56.6	7.18	9.11	0.149
	3	0.05312	0.4721	30.0	74.1	62.3	57.0	52.5	7.10	8.91	0.150
	4	0.05123	0.4721	30.0	67.7	58.8	53.3	48.5	7.17	8.44	0.152
	5	0.05212	0.4701	30.0	69.7	60.4	54.9	50.1	7.09	8.68	0.151
										average:	
									[15]		0.152

^{a)} Ethyl acetate: $\alpha=2.41 \cdot 10^{-3} \text{ s}^{-1}$; $\beta=1.15 \cdot 10^{-2} \text{ s}^{-1}$; methyl acetate: $\alpha=2.48 \cdot 10^{-3} \text{ s}^{-1}$; $\beta=1.14 \cdot 10^{-2} \text{ s}^{-1}$

^{b)} with the double-parameter method

^{c)} with the single-parameter method

Apparatus

The experiments were carried out in a twin conduction calorimeter, which has been described in detail in previous paper [13]. The heat effects of mixing, dilution, stirring in the reacting cell can be compensated for by the same effects produced in the reference cell. The calculation and electric calibration of the cooling constants α and β are the same as those in the previous work [2].

Results and discussion

If the initial concentrations of reactants are unequal and $C_0(\text{KOH}) > C_0(\text{ester})$, the saponifications may be treated as a pseudo-first-order reaction and $k_1^* = k_2 C_0(\text{KOH})$. The thermoanalytical curve data, the rate constant k_1^* (and k_2) calculated with the double-parameter method and the single-parameter method are summarized in Table 1.

From Table 1, it can be seen that the cooling constants α and β are determined in the investigated systems by using electric calibration, which avoids the system errors due to the difference of α and β at different dynamic systems because the cooling constants α and β play an important role in describing the dynamic calorimetric systems. Meanwhile, it is found that the calculated values of rate constants on the basis of the double-parameter are reproducible and are in fair agreement with the literature value with tolerable errors. What is more, the values of k_2 are less dispersive. On the contrary, the value of k_2 calculated on the basis of the single-parameter model are considerably dispersive and in poor agreement with the literature value. These results show that the double-parameter method is better at describing the dynamic properties of the calorimetric system involving a faster first-order reaction, and is applicable to thermokinetic studies of faster first-order reactions.

As stated above, our novel method has a simple principle and a concise mathematical model to calculate the kinetic parameter. It is not necessary to reconstruct the distorted conduction thermoanalytic curve into the ideal real conduction one or the ideal adiabatic one and the kinetic parameter can be calculated from only four peak height data on the same thermoanalytical curve without using any peak area; and hence avoid the error due to the reconstruction of the distorted thermoanalytical curve or drifting of the thermoanalytical curve at the latter stage of the reaction. Therefore, the double parameter method suggested in this paper is more convenient for dealing with the thermoanalytical curve involving a faster thermal change process and also introduces fewer errors compared with the former methods for the faster thermal change process [2, 9].

In order to be sure that the double-parameter method is applicable to general slow chemical reaction, we took some thermoanalytical curve data from literature [12] and calculated the rate constants. The calculated results listed in Table 2. From Table 2, it can be seen that the calculated rate constant on the basis of the double-parameter method is in agreement with the literature value.

Table 2 Saponification of ethyl benzoate (solvent: 85%(mass/mass) EtOH–H₂O)^a

<i>i</i>	Δ_i/V		Group of data	k_i^*/s^{-1}	
	25°C	35°C		25°C(10 ⁻⁴)	35°C(10 ⁻³)
1	0.8605	1.0980	($\Delta_1\Delta_2\Delta_3\Delta_4$)	6.36	1.69
2	0.7159	1.5290	($\Delta_2\Delta_3\Delta_4\Delta_5$)	6.06	1.19
3	0.5225	1.2140	($\Delta_3\Delta_4\Delta_5\Delta_6$)	7.47	1.71
4	0.3605	0.7908	($\Delta_4\Delta_5\Delta_6\Delta_7$)	6.80	1.21
5	0.2542	0.5050			
6	0.1676	0.2972			
7	0.1110	0.1773			
			average:	6.67	1.45
			$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	6.88	1.76
			[13]	6.21	1.68

^a 25°C: $C_0(\text{ester})=0.05126 \text{ mol dm}^{-3}$; $C_0(\text{KOH})=0.9699 \text{ mol dm}^{-3}$; $\Delta t=600 \text{ s}$;
 35°C: $C_0(\text{ester})=0.04760 \text{ mol dm}^{-3}$; $C_0(\text{KOH})=0.8233 \text{ mol dm}^{-3}$; $\Delta t=400 \text{ s}$; $\alpha=2.325 \cdot 10^{-3} \text{ s}^{-1}$;
 $\beta=1.140 \cdot 10^{-2} \text{ s}^{-1}$

In conclusion, the double-parameter method for a first-order reaction suggested in this paper is applicable to both faster and slow reactions and its validity is verified by the experimental results in this paper. Therefore, it can be extensively applied to thermokinetic studies of chemical and biochemical reactions.

* * *

This work is supported by the National Natural Science Foundation of China (grant. 29873031).

References

- 1 W. Zielenkiewicz, J. Thermal Anal., 29 (1984) 179.
- 2 J. S. Liu, X. C. Zeng, A. M. Tian and Y. Deng, Science in China (Ser. B), 25 (1995) 264.
- 3 Y. Liang, C. Wang, S. Qu, Y. Wu, D. Li and G. Zou, Thermochim. Acta, 322 (1998) 1.
- 4 R. P. Bell and J. C. Clunie, Proc. R. Soc. London, Ser. A, 212 (1952) 16.
- 5 E. Calvet and H. Prat, Recent Progress in Microcalorimetry, Pergamon Press, Oxford 1963.
- 6 K. A. Engdahl and P. Ahlberg, Chem. Scrip., 18 (1988) 176.
- 7 Y. Deng, Z. M. Qin and X. P. Wu, Thermochim. Acta, 123 (1988) 213.
- 8 J. S. Liu, X. C. Zeng, A. M. Tian and Y. Deng, Thermochim. Acta, 231 (1994) 39.
- 9 X. C. Zeng, Y. Chen, X. N. Chen, J. Q. Xie and F. B. Jiang, Thermochim. Acta, 332 (1999) 97.
- 10 Y. Deng, Chem. J. Chinese Univ., 6 (1985) 621.
- 11 X. C. Zeng, X. G. Meng, Y. Q. Zhang, M. Z. Chen and Z. M. Qin, Chem. J. Chinese Univ., 18 (1997) 581.
- 12 J. S. Liu, X. C. Zeng, Y. Deng and A. M. Tian, Acta Chim. Sinica, 52 (1994) 767.
- 13 A. M. Tian, Z. M. Qin, X. C. Zeng, S. G. Zhan and Y. Deng, Chem. J. Chinese Univ., 2 (1981) 2.
- 14 A. M. White and G. A. Olah, J. Am. Chem. Soc., 521 (1956) 78.
- 15 H. M. Humphreys and L. P. Hammett, J. Am. Chem. Soc., 521 (1956) 78.