

## **CHARACTERISTIC PARAMETER METHOD FOR STUDYING CHEMICAL KINETICS IN CALORIMETER**

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### **Abstract**

A novel thermokinetic research method for determination of rate constants of simple-order reaction in batch conduction calorimeter under isothermal condition, the characteristic parameter method, is proposed in this paper. Only needing the characteristic time parameter  $t_m$  obtained from the measured thermoanalytical curve, the kinetic parameters of reactions studied can be calculated conveniently with this method. The saponifications of ethyl propionate and ethyl acetate in aqueous ethanol solvent, the polymerization of acrylamide in aqueous solution, the ring opening reaction of epichlorohydrin with hydrobromic acid have been studied. The experimental results indicate that the characteristic parameter method for simple-order reaction is correct.

**Keywords:** calorimetry, characteristic parameter method, simple-order reaction, thermokinetics

### **Introduction**

The calorimeter is an important tool for the thermokinetic investigation and has been applied widely to study reaction involving thermal change processes in many fields [1–8]. When a chemical reaction was taking place in a batch conduction calorimeter, the thermoanalytical curve measured with a calorimeter implies kinetic and thermodynamic information that the reaction has. It is an important aim of the thermokinetics to establish a research method for obtaining such valuable information. So far, several thermokinetic research method for simple-order reaction have been proposed to determine the rate constants of reactions studied in a batch conduction calorimeter under isothermal condition, including the dimensionless parameter method [2, 9], the reduced-extent method [10], the analog thermoanalytical curve method [11] and the time parameter method [12, 13]. However, these methods all need a completed thermoanalytical curve for the acquisition of data for analysis, and their mathematical models were much more complex and there existed a lower de-

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gree of precision in evaluating the kinetic parameters. In order to enrich and perfect the thermokinetic research method, the integral and differential thermokinetic equations of simple-order reaction have been derived, and the mathematical models of the characteristic parameter method have been established in this paper. The method does not require the thermokinetic reaction to be completed. Only needing the characteristic time parameter  $t_m$  obtained from the measured curve, the kinetic parameters of reactions studied can be calculated conveniently. Four reaction systems, including the first-order reaction, the second-order reaction, the third-order reaction and the fractional-order reaction, have been studied with this method. The validation of the theory and method of the characteristic parameter method for simple-order reactions is verified by the experimental results.

## Theory and method

### *Thermokinetic equation of simple-order reactions*

When a chemical reaction is taking place in a batch conduction calorimeter, the dynamic properties of calorimetric system are described by Tian's equation [14], and then we have

$$\Phi = K\Delta + \Lambda \frac{d\Delta}{dt} \quad (1)$$

where  $\Phi$  is the rate of heat generation,  $\Delta$  is the peak height of thermoanalytical curve at time  $t$ ,  $K$  and  $\Lambda$  are apparatus constants of the calorimeter.

On integrating Eq. (1) with respect to time  $t$ , we get

$$Q = Ka + \Lambda\Delta \quad (2)$$

$$Q_\infty = KA \quad (3)$$

Rearrangement of Eqs (1)–(3) leads to

$$\frac{Q_\infty - Q}{Q_\infty} = \frac{a^*}{A} - \frac{\Delta}{kA} \quad (4)$$

$$\frac{\Phi}{Q_\infty} = \frac{\Delta}{A} + \frac{(d\Delta/dt)}{kA} \quad (5)$$

where  $Q$  and  $Q_\infty$  are the heat evolved before time  $t$  and the total heat evolved by the reaction studied respectively,  $a$  and  $a^*$  are the peak areas before and after time  $t$ , respectively, and  $A = a + a^*$ , which is the total area under the curve,  $k (= K/\Lambda)$  is called the cooling constant of thermokinetic system.

According to the principle of chemical kinetics, it can be proved that the kinetic equations of simple-order reactions can be expressed as [15]

$$\frac{\chi_{\infty} - \chi}{\chi_{\infty}} = F(t) \quad (6)$$

$$\frac{d\chi/dt}{\chi_{\infty}} = G(t) \quad (7)$$

where  $\chi$  and  $\chi_{\infty}$  are the reaction extents at time  $t$  and  $t_{\infty}$ , respectively.  $F(t)$  and  $G(t)$  are functions with respect to time  $t$ . For different reaction orders,  $F(t)$  and  $G(t)$  have different expression (as shown in Table 1).

**Table 1** Expressions of  $F(t)$  and  $G(t)$  for reactions with different orders

Reaction type	$F(t)$	$G(t)$
First-order reaction	$e^{-k_1 t}$	$k_1 e^{-k_1 t}$
Second-order reaction	$\frac{1}{1+K_2 t}$	$\frac{K_2}{(1+K_2 t)^2}$
$N^{\text{th}}$ -order reaction	$\frac{1}{[1+(n-1)K_n t]^{1/n-1}}$	$\frac{K_n}{[1+(n-1)K_n t]^{n/n-1}}$

$K_2 = k_2 C_0$ ,  $K_n = k_n C_0^{n-1}$  ( $n \neq 1$ ),  $C_0$  is the initial concentration of reactants.

In the previous article [13], we have proved that the thermokinetic transformation equations for chemical reaction can be described as

$$\frac{Q_{\infty} - Q}{Q_{\infty}} = \frac{\chi_E - \chi}{\chi_E} \quad (8)$$

$$\frac{\Phi}{Q_{\infty}} = \frac{d\chi/dt}{\chi_E} \quad (9)$$

So, from Eqs (4)–(9), it turns to

$$\frac{a^*}{A} - \frac{\Delta}{kA} = F(t) \quad (10)$$

$$\frac{\Delta}{A} + \frac{(d\Delta/dt)}{kA} = G(t) \quad (11)$$

Equations (10) and (11) are the integral and differential thermokinetic equations of simple-order reactions, respectively.

#### *Mathematical model of characteristic parameter method for opposing reactions*

According to the expression for  $F(t)$  and  $G(t)$  listed in Table 1, it can be proved that for a first-order reaction

$$G(t) = k_1 F(t) \quad (12)$$

and for a  $n^{\text{th}}$ -order reaction

$$G(t)=K_n[F(t)]^n \quad (n \neq 1) \quad (13)$$

where  $k_1$  is the first-order constant,  $K_n=k_n C_0^{n-1}$ ,  $C_0$  is the initial concentration of reactants, and  $k_n$  is the rate constant of  $n^{\text{th}}$ -order reaction.

Defining

$$R=\frac{Q_\infty-Q}{Q_\infty}, \quad r=\frac{\Phi}{Q_\infty} \quad (14)$$

where  $R$  is the ratio of the heat evolved after time  $t$  to the total heat evolved by the reaction studied;  $r$  is the ratio of the rate of heat production to the total heat.

$t_m$  is the time corresponding to the maximum peak height  $\Delta_m$  of the curve, which is called the characteristic time parameter. When  $t=t_m$ , we can get  $R_m$  and  $r_m$  using the corresponding thermoanalytical data. Therefore, from Eqs (4), (5) and (10)–(14), we have

$$k=\frac{r_m}{R_m} \quad (15)$$

$$K_n=\frac{r_m}{R_m^n} \quad (n \neq 1) \quad (16)$$

Equations (15) and (16) are the mathematical models of the characteristic parameter method for determination of the kinetic parameter of simple-order reactions.

In the previous article [16], we have established the characteristic equation for the thermoanalytical curve of chemical reaction

$$\Delta=\Delta_m \frac{t}{t_m} e^{(1-t/t_m)} \quad (17)$$

Integrating Eq. (17) with respect to time  $t$ , we get

$$a_m^*=\int_m^\infty \Delta dt=2\Delta_m t_m \quad (18)$$

$$A=\int_0^\infty \Delta dt=e\Delta_m t_m \quad (19)$$

where  $e$  is the base of natural logarithm. From Eqs (14), (18) and (19), it can be proved that

$$R_m=\frac{2kt_m-1}{ekt_m} \quad (20)$$

$$r_m=\frac{1}{et_m} \quad (21)$$

Equations (22) and (23) are the formulae to determine values of  $R_m$  and  $r_m$  using the characteristic time parameter  $t_m$ .

## Experimental

### *Reaction system*

The thermokinetics of reaction systems shown below have been studied:

- Pseudo-first-order reaction: the saponification of ethyl propionate in aqueous ethanol solvent at 25°C. The saponification of the esters in aqueous ethanol solvent is a second-order reaction. If  $C_0(\text{ester}) > C_0(\text{KOH})$ , the saponification may be treated as a pseudo-first-order reaction, and then  $k_1^* = k_2 C_0(\text{ester})$ , where  $k_2$  is the second-order rate constants.
- Second-order reaction: the saponification of ethyl acetate in aqueous ethanol solvent at 25°C.
- Third-order reaction: the ring opening reaction of epichlorohydrin with hydrobromic acid in aqueous solution at 20°C.
- Fractional-order reaction: the polymerization of acrylamide in aqueous solution at 30°C. According to the mechanism of polymerization of acrylamide initiated by sodium sulfite [17], it is known that this reaction is of order 1.5 with respect to acrylamide and of order 0.5 with respect to sodium sulfite. The polymerization is overall of second-order. The concentration of sodium sulfite exhibits no appreciable change during the course of polymerization, and hence, this reaction can be regarded as a pseudo-1.5-order reaction,  $k_{1.5} = k_2 [\text{HSO}_3^-]^{1/2}$ .

### *Reactants*

Chemical pure ethyl propionate was obtained from Shanghai Chemicals Co. (China) and purified further by distillation under reduced pressure. The other reactants were analytically pure and purchased from Chongqing Chemicals Co. (China). The solutions of reactants were prepared in deionized water by mass. The concentration of potassium hydroxide was standardized with potassium hydrogenphthalate.

### *Reactants apparatus*

All the thermoanalytical curves of the reaction systems mentioned above were measured with a batch conduction calorimeter, which basic construction was similar to that of the Calvet calorimeter [18]. The reaction cell and reference cell were placed into an isothermal block and thermopiles were located between the measuring system and the block according to the twin principle. The effects of mixing, dilution, stirring and evaporation in the reaction cell should be compensated for by the corresponding effects produced in the reference cell. The thermoanalytical curves were sampled and recorded by a computer and the measured curves were printed out.

## Results and discussion

The cooling constants of reaction systems studied are determined by using electrical calibration. After the thermoanalytical curve has been measured in a batch conduction calorimeter, the characteristic time parameter  $t_m$  can be obtained from the thermoanalytical curve, and then the values of  $R_m$  and  $r_m$  can be calculated via Eqs (20) and (21). The rate constants of reaction studied can therefore be calculated with the mathematical models of the characteristic parameter method for simple-order reactions. The experimental results for system studied are given in Tables 2–5.

From Tables 2–5, it can be seen that the rate constants calculated with our novel method are in agreement with those in the literature. The experimental results show that the mathematical models of the characteristic parameter method for simple-order reaction are correct.

**Table 2** Experimental results on saponification of ethyl propionate in aqueous ethanol solvent at 25°C

$C_0(\text{ester})/\text{mol L}^{-1}$	$t_m/\text{s}$	$R_m$	$10^4 r_m/\text{s}^{-1}$	$10^3 k_1^*/\text{s}^{-1}$	$10^3 k_2/\text{L mol}^{-1} \text{s}^{-1}$
0.380	486	0.534	7.57	1.42	3.74
0.430	457	0.521	8.05	1.55	3.60
0.456	436	0.511	8.44	1.65	3.62
0.498	405	0.494	9.08	1.84	3.69
0.531	378	0.476	9.73	2.04	3.84
				Average	3.70
				Literature value [19]	3.65

$C_0(\text{KOH})=0.0125 \text{ mol L}^{-1}$

**Table 3** Experimental results of polymerization of acrylamide at 30°C

$C_0/\text{mol L}^{-1}$	$t_m/\text{s}$	$R_m$	$10^4 r_m/\text{s}^{-1}$	$10^4 K_{1.5}\text{s}^{-1}$	$10^4 k_1 s / \text{mol}^{-1/2} \text{s}^{-1}$
0.345	3242	0.705	1.13	1.91	3.24
0.418	2973	0.703	1.24	2.10	3.25
0.495	2802	0.701	1.32	2.25	3.20
0.568	2640	0.699	1.39	2.38	3.16
0.597	2470	0.696	1.49	2.57	3.33
				Average	3.24

$C_0(\text{NaHSO}_3)=0.000688 \text{ mol L}^{-1}$ ,  $k_2(\text{calculated})=1.23 \cdot 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ ,  
 $k_2(\text{Literature [17]})=1.13 \cdot 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$

**Table 4** Experimental results on saponification of ethyl acetate in aqueous ethanol solvent at 25°C

$C_0(\text{ester})/\text{mol L}^{-1}$	$t_m/\text{s}$	$R_m$	$10^4 r_m/\text{s}^{-1}$	$10^3 K_2/\text{s}^{-1}$	$10^3 k_2/\text{L mol}^{-1} \text{s}^{-1}$
0.220	689	0.593	5.34	1.52	6.91
0.278	600	0.572	6.13	1.87	6.73
0.315	546	0.556	6.74	2.18	6.92
0.343	506	0.542	7.27	2.47	7.20
0.380	472	0.528	7.79	2.79	7.34
				Average	7.02
				Literature value [19]	6.98

$$C_0(\text{ester})=C_0(\text{KOH})$$

**Table 5** Experimental results on ring opening reaction of epichlorohydrin with hydrobromic acid at 20°C

$C_0/\text{mol L}^{-1}$	$t_m/\text{s}$	$R_m$	$10^4 r_m/\text{s}^{-1}$	$10^4 K_3/\text{s}^{-1}$	$10^3 k_3/\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$
0.140	2450	0.696	1.50	4.45	2.27
0.140	2404	0.695	1.53	4.56	2.33
0.155	2106	0.689	1.75	5.35	2.23
0.155	2165	0.690	1.70	5.17	2.15
0.168	1858	0.683	1.98	6.21	2.20
				Average	2.24
				Literature value [20]	2.15

The same as the thermokinetic characteristic parameter method for opposing reactions [21], the mathematical models to calculate the kinetic parameter of our novel method are established according to the integral and differential thermokinetic equations of simple-order reaction, which are concise and need a little computing effort and work. Only needing the characteristic time parameter  $t_m$  from the thermoanalytical curve, the characteristic parameter  $R_m$  and  $r_m$  can be determined and the rate constants of reaction studied are calculated conveniently, which simplify greatly the kinetic analyzing procedure. This not only applies when studying known reaction, but also for investigating the kinetics of an unknown reaction. For an unknown reaction, we can get  $R_m$ ,  $r_m$ ,  $R_{m1}$  and  $r_{m2}$  from two thermoanalytical curves with different initial concentrations  $C_{01}$  and  $C_{02}$ , respectively. And then, according to Eq. (16), we have

$$k_n C_{01}^{n-1} = \frac{r_{m1}}{R_{m1}^n} \quad (22)$$

$$k_n C_{02}^{n-1} = \frac{r_{m2}}{R_{m2}^n} \quad (23)$$

Therefore, from Eqs (22) and (23), it turns to

$$n = \frac{\ln(r_{m1}/r_{m2}) + \ln(C_{01}/C_{02})}{\ln(R_{m1}/R_{m2}) + \ln(C_{01}/C_{02})} \quad (24)$$

Equation (24) is the formula for determination of the reaction order of the reaction studied.

In contrast to the dimensionless method, the reduced extent method and the analog thermoanalytical curve method, the characteristic parameter method does not need the thermokinetic reaction to be completed. Therefore, it can be extremely useful for two kinds of reactions: reaction with very low rate, the long reaction times of such reactions result in drift of the baseline of the thermoanalytical curve, which causes error in the calculated results; and reactions involving the side-reactions in the final stage of the reaction, in which the heat of the side-reactions produced will influence the calculated results of the reaction studied.

The characteristic time parameter  $t_m$  is an important parameter in our novel method. Its value depends on the reaction type and kinetic parameter of reaction studied. For different reactions, the characteristic time parameters and corresponding thermoanalytical data are different. Our novel method only needs  $t_m$  to calculate the kinetic parameters of a simple-order reaction, and hence, the precision in evaluating the kinetic parameters of our method depends on the accurate determination of  $t_m$ . In general,  $t_m$  is obtained from the measured thermoanalytical curve directly. So the distortion degree of the measured curve owing to thermal inertia will lead to an experimental error in kinetic evaluation. For a slower reaction, the thermal delay will decrease, and the influence of distortion can be neglected. But for a faster reaction, the distortion degree of the measured curve will obviously increase. In the case, the characteristic time  $t_m$  must be corrected. In our previous paper [22], we have established a method to modify the distorted thermoanalytical curve into the real thermoanalytical curve from which the kinetic parameter can be obtained directly. The relationship between the distorted curve and the ideal real thermoanalytical curve is:

$$\Delta_0 = \Delta + \frac{d\Delta/dt}{\beta} \quad (25)$$

where  $\beta$  is the cooling constant of the sensor,  $\Delta_0$  is the peak height at time  $t$  of the ideal real thermoanalytical curve.

Then, from Eqs (17) and (25), it can be proved

$$t_{0m} = \frac{2 - \beta t_m}{1 - \beta t_m} t_m \quad (26)$$

Equation (26) is the formula to determine the characteristic time  $t_{0m}$  using the  $t_m$  obtained from the distorted curve.



As stated above, as a novel method for the determination of rate constants, the characteristic parameter method further enriches and perfects the thermokinetic research method. It can be applied to investigations of the thermokinetics of both chemical and biochemical reactions taking place in a batch conduction calorimeter under isothermal condition.

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## References

- 1 J. J. Pysiak and Y. Albadwi, *J. Therm. Anal. Cal.*, 70 (2002) 423.
- 2 R. M. Vinnik and V. A. Roznyatovsky, *J. Therm. Anal. Cal.*, 71 (2003) 531.
- 3 J. Liu, X. Zeng and A. Tian, *J. Thermal Anal.*, 44 (1995) 617.
- 4 Y. Liang, C. X. Wang and S. S. Qu, *Thermochim. Acta*, 268 (1995) 27.
- 5 M. Beran and V. Panlicek, *J. Thermal Anal.*, 38 (1992) 1979.
- 6 A. A. Saboury, *J. Therm. Anal. Cal.*, 72 (2003) 93.
- 7 R. Vilcu and V. Meltze, *Rev. Chem.*, 41 (1991) 39.
- 8 R. Vilcu and V. Meltze, *J. Thermal Anal.*, 41 (1994) 1335.
- 9 Y. Deng, X. C. Zeng and Y. Q. Zhang, *Thermochim. Acta*, 169 (1990) 223.
- 10 J. S. Liu, X. C. Zeng and A. M. Tian, *Thermochim. Acta*, 231 (1994) 39.
- 11 X. C. Zeng, Y. Q. Zhang and X. G. Meng, *Chem. J. Chinese Univ.*, 17 (1996) 607.
- 12 X. C. Zeng, Y. Chen and Y. Q. Zhang, *Thermochim. Acta*, 317 (1998) 151.
- 13 Y. Chen, H. D. Wang and X. C. Zeng, *J. Therm. Anal. Cal.*, 61 (2000) 219.
- 14 E. Calvet and H. Prat, *Recent Progress in Microcalorimetry*, Pergamon Press, Oxford 1963.
- 15 Y. Deng, *Chem. J. Chinese Univ.*, 6 (1985) 621.
- 16 X. N. Chen and X. C. Zeng, *Acta Physico-Chimica Sinica*, 12 (1996) 1031.
- 17 K. M. Asharaf, X. C. Zeng and Q. Wang, *J. Dispersion Sci. Tech.*, 18 (1997) 389.
- 18 W. Hemminger and G. Hohne, *Calorimetry, Fundamentals and Practice*, Wehheim, Basel 1984.
- 19 C. H. Banford and C. F. H. Tipper, *Ester Formation and hydrolysis and related Reactions*, Elsevier, Amsterdam 1972.
- 20 Q. Z. Huang and H. Li, *Acta Chim. Sinica*, 51 (1993) 13.
- 21 Y. Chen, H. Yan and B. Zhang, *J. Therm. Anal. Cal.*, 69 (2002) 647.
- 22 X. C. Zeng, Y. Chen and X. N. Chen, *Thermochim. Acta*, 332 (1999) 97.