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THERMOKINETIC RESEARCH METHOD FOR SIMPLE-ORDER REACTIONS

Double-thermoanalytical curve method

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Abstract

A novel thermokinetic research method for determination of the rate constant of a reaction taking place in a batch conduction calorimeter under isothermal conditions is proposed: the double-thermoanalytical curve method. The method needs only the characteristic time parameter t_m, the peak height Δ_m at time t_m and the peak area a^*_m after time t_m for two thermoanalytical curves measured with different initial concentrations of the reactants: it conveniently calculates the rate constants. The thermokinetics of four reaction systems were studied with this method, and its validity was verified by the experimental results.

Keywords: calorimetry, double-thermoanalytical curve method, simple-order reactions, thermokinetics

Introduction

The calorimetric study of chemical kinetics is a very interesting and valuable technique. For chemical reactions which take place in solution, many calorimetric techniques have been created and are of considerable importance in a wide range of applications in the investigation of chemical kinetics, involving such equipment as the flow calorimeter [1–3], the batch conduction calorimeter [4–7], the titration calorimeter [8, 9], the differential scanning calorimeter [10, 11], etc. The thermoanalytical curve of a chemical reaction, measured with a calorimeter, implies kinetic and thermodynamic information on the reaction. It is an important aim of thermokinetics to establish a research method to obtain such valuable information. On the basis of the fundamental theory of thermokinetics, several thermokinetic research methods have been proposed to determine the rate constants of chemical reactions in a batch conduction calorimeter, including the dimensionless parameter method [4, 5], the reduced-extent parameter method [12] and the analogue thermoanalytical curve method [13]. In a previous article [14], we developed the time pa-

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rameter method for simple-order reactions and successfully applied it to study the thermokinetics for several kinds of simple-order reactions. The principle of this method is simple and its expressions have a concise form. However, the mathematical models of this method do not have explicit formulae and the kinetic parameters are obtained only by using a numerical method with the aid of a computer. In order to enrich the thermokinetic research method and further improve the time parameter method, a novel thermokinetic research method is proposed in this paper: the double-thermoanalytical curve method. This method uses the characteristic time parameter t_m, the peak height Δ_m at time t_m and the peak area a^*_m after time t_m for two thermoanalytical curves with different initial concentrations of the reactants to obtain the kinetic parameters. The thermokinetics of the saponifications of ethyl butyrate and ethyl benzoate in aqueous ethanol as solvent, the ring opening of epichlorohydrin with hydrobromic acid in aqueous solution and the polymerization of acrylamide in aqueous solution have been studied with this method. The experimental results suggest that this novel method is correct.

Theory and method

Thermokinetic transformation equation for simple-order reactions

When a chemical reaction is taking place in a batch conduction calorimeter under isothermal conditions, it is well known that the relation between the reaction rate r and the thermal power of reaction Ω can be described as

$$\Omega=rV\Delta H \tag{1}$$

where ΔH is the molar enthalpy of this reaction and V is the reaction volume.

If we define the derivative of the reaction extent χ with respect to time t as the rate of the reaction, i.e. $r=\mathrm{d}\chi/\mathrm{d}t$, we have

$$\Omega=\frac{\mathrm{d}\chi}{\mathrm{d}t}V\Delta H \tag{2}$$

On integrating Eq. (2) with respect to time t, we obtain

$$Q=\chi V\Delta H \tag{3}$$

$$Q_\infty=\chi_\infty V\Delta H \tag{4}$$

where Q and Q_∞ are the heat evolved before time t and the total heat evolved by the reaction studied, respectively, while χ and χ_∞ are the reaction extents at times t and t_∞.

Then, from Eqs (1)–(4), it can be proved that

$$\frac{Q_\infty-Q}{Q_\infty}=\frac{\chi_\infty-\chi}{\chi_\infty} \tag{5}$$

$$\frac{\Omega}{\Omega_\infty}=\frac{\frac{\mathrm{d}\chi}{\mathrm{d}t}}{\chi_\infty} \tag{6}$$

Equations (5) and (6) are the thermokinetic transformation equations for simple-order reactions, which are the bridges linking thermochemistry and kinetics.

Thermokinetic equation for simple-order reactions

If the calorimeter is regarded as a uniform, isotropic body of homogeneous temperature which changes only with time *t*, the dynamic properties of a calorimetric system can be described by Tian's equation [15], and then we have

$$\Omega=K\Delta+\Lambda\frac{\mathrm{d}\Delta}{\mathrm{d}t} \tag{7}$$

where Δ is the peak height of the thermoanalytical curve at time *t*, while *K* and Λ are the coefficient of heat losses and the effective capacity of the calorimetric system. On integrating Eq. (7) with respect to time *t*, we get

$$Q=Ka+\Lambda\Delta \tag{8}$$

$$Q_\infty=KA \tag{9}$$

Rearrangement of Eqs (7)–(9) leads to

$$\frac{Q_\infty-Q}{Q_\infty}=\frac{a^*}{A}-\frac{\Delta}{kA} \tag{10}$$

$$\frac{\Omega}{Q_\infty}=\frac{\Delta}{A}+\frac{\frac{\mathrm{d}\Delta}{\mathrm{d}t}}{kA} \tag{11}$$

where *a* is the peak area before time *t, A* is the total area under the thermoanalytical curve, $a^*=A-a$, which is the peak area after time *t*, and $k=K/\Lambda$, which is called the cooling constant of the 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

$$\frac{\chi_\infty-\chi}{\chi_\infty}=F(t) \tag{12}$$

$$\frac{\frac{\mathrm{d}\chi}{\mathrm{d}t}}{\chi_\infty}=G(t) \tag{13}$$

where *F*(*t*) and *G*(*t*) are functions with respect to time *t.* For different reaction orders, *F*(*t*) and *G*(*t*) have different expressions (as shown in Table 1). Thus, from Eqs (5), (6) and (10)–(13), we have

$$\frac{a^*}{A}-\frac{\Delta}{kA}=F(t) \tag{14}$$

$$\frac{\Delta}{A}+\frac{\frac{\mathrm{d}\Delta}{\mathrm{d}t}}{kA}=G(t) \tag{15}$$

Equations (14) and (15) are the thermokinetic equations of simple-order reactions.

Table 1 The expressions for $F(t)$ and $G(t)$ for reactions with different order*

Reaction type	$F(t)$	$G(t)$
First-order reaction	e^{-k_1t}	$k_1e^{-k_1t}$
Second-order reaction with equal concentrations	$\frac{1}{1+K_2t}$	$\frac{K_2}{(1+K_2t)^2}$
n^{th}-order reaction with equal concentrations	$\frac{1}{[1+(n-1)K_nt]^{1/(n-1)}}$	$\frac{K_n}{[1+(n-1)K_nt]^{n/(n-1)}}$

* $K_2=k_2C_0$, $K_n=k_nC_0^{n-1}$, $n\neq1$. C_0 is the initial concentration of the reactant

Mathematical model of double-thermoanalytical curve method

The time corresponding to the maximal peak height of the curve, t_m, is called the characteristic time parameter of the thermoanalytical curve. When $t=t_m$, then $\Delta=\Delta_m$, $\mathrm{d}\Delta/\mathrm{d}t=0$, $a^*=a^*_m$, and from Eqs (14) and (15) we obtain

$$\frac{a^*_m}{A}-\frac{\Delta_m}{kA}=F(t_m) \tag{16}$$

$$\frac{\Delta_m}{A}=G(t_m) \tag{17}$$

We define

$$\Phi_m=\frac{a^*_m}{\Delta_m}+(1-n)t_m \tag{18}$$

where Φ_m is called the comprehensive characteristic datum of the thermoanalytical curve. Its value varies with the initial concentration of the reactant.

On inserting Eq. (17) into Eq. (16), according to Table 1, we get

$$\Phi_m=\frac{1}{K_n}+\frac{1}{k} \tag{19}$$

where $K_n=k_nC_0^{n-1}(n\neq1)$, k_n is the rate constant of the reaction studied, and C_0 is the initial concentration of the reactant.

For a reaction system, we can get Φ_{m1} and Φ_{m2} from two thermoanalytical curves with different initial concentrations C_{01} and C_{02}. Then, according to Eq. (19), we have

$$\Phi_{m1}=\frac{1}{K_{n1}}+\frac{1}{k} \tag{20}$$

$$\Phi_{m2}=\frac{1}{K_{n2}}+\frac{1}{k} \tag{21}$$

From Eqs (20) and (21), it can be proved that

$$k_n=\frac{C_{01}^{1-n}-C_{02}^{1-n}}{\Phi_{m1}-\Phi_{m2}} \tag{22}$$

Equation (22) is the mathematical model of the double-thermoanalytical curve method for simple-order reactions. For a known reaction, the rate constant can be easily calculated from a_m^*, Δ_m and t_m for two thermoanalytical curves with different initial concentrations.

In fact, Eq. (22) is not suitable for a first-order reaction. For a pseudo-first-order reaction system, we define

$$\psi_m=\frac{a_m^*}{\Delta_m} \tag{23}$$

It is still proved that

$$\psi_m=\frac{1}{k_1^*}+\frac{1}{k} \tag{24}$$

where $k_1^*=k_nC_0^{n-1}$, which is the pseudo-first-order reaction rate constant. k_n is the rate constant of the real-order reaction, and C_0 is the initial concentration of the excess reactant.

Therefore, if the concentration of the excess reactant is varied, the rate constant of the real-order reaction can be calculated by using Eq. (25), which is derived in the same way as stated above:

$$k_n=\frac{C_{01}^{1-n}-C_{02}^{1-n}}{\psi_{m1}-\psi_{m2}} \tag{25}$$

where ψ_{m1} and ψ_{m2} are the value of ψ_m with different initial concentrations C_{01} and C_{02} of excess reactant, respectively.

Experimental

Reaction system

In order to test the validity of the double-thermoanalytical curve method for simple-order reactions, the thermokinetics of the different-order reactions shown below were studied:

- Pseudo-first-order reaction: the saponification of ethyl butyrate in aqueous ethanol as solvent at 30°C.
- Second-order reaction: the saponification of ethyl benzoate in aqueous ethanol as solvent at 25°C.

- Third-order reaction: the ring opening of epichlorohydrin with hydrobromic acid in aqueous solution at 20°C.
- Fractional-order reaction: the polymerization of acrylamide in aqueous solution at 30°C.

Reactants

Chemical pure ethyl benzoate was purified further by distillation under reduced pressure. The other reactants were analytically pure. The mixed solvents were prepared from analytically pure ethanol and de-ionized water. The concentration of potassium hydroxide in solution was standardized with potassium hydrogenphthalate.

Measurement of thermoanalytical curves

All the thermoanalytical curves of the reaction systems mentioned above were measured with a batch conduction calorimeter, whose basic construction was similar to that of the Calvet calorimeter [16]. Two equal systems (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 data were collected and recorded by a computer and the measured curves were printed out.

Results and discussion

Experimental results

If C_0(ester)>C_0(KOH), the saponification of ethyl butyrate may be tested as a pseudo-first-order reaction. Hence, through variation of the concentration of the ester, the rate constant of the second-order reaction can be calculated directly with our novel method (Table 2). The experimental results on the saponification of ethyl benzoate and the ring opening reaction of epichlorohydrin are presented in Tables 3 and 4, respectively. 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; hence, this reaction can be regarded as a pseudo-1.5-order reaction, $k_{1.5}=k_2[HSO_3^-]^{1/2}$. The experimental results and the second-order rate constants are listed in Table 5.

Table 2 Experimental results on saponification of ethyl butyrate at 30°C; (solvent: 85% (m/m) EtOH–H_2O; C_0(KOH)=0.05298 mol l^{-1})

No.	C_0(ester)/mol l^{-1}	Δ_m/v	$10^{-3}\cdot a_m^*$/ vs	$10^3\cdot k_2$/l mol^{-1} s^{-1}
1	0.6303	2.264	2.392	2.77
	0.6054	2.184	2.359	
2	0.6303	2.264	2.392	2.73
	0.5827	2.096	2.314	
3	0.6303	2.264	2.392	2.78
	0.5594	1.981	2.235	
4	0.6054	2.184	2.359	2.69
	0.5827	2.096	2.314	
5	0.6054	2.184	2.359	2.79
	0.5594	1.981	2.235	
6	0.5827	2.096	2.314	2.88
	0.5594	1.981	2.235	
			Average	2.77
			Literature value	2.76 [18]

Table 3 Experimental results on saponification of ethyl benzoate at 25°C; (solvent: 50%(m/m) EtOH–H_2O; C_0(ester)=C_0(KOH))

No.	C_0(ester)/mol l^{-1}	Δ_m/v	$10^{-3}\cdot a_m^*$/ vs	t_m/s	$10^3\cdot k_2$/l mol^{-1} s^{-1}
1	0.4434	2.171	3.790	684	1.37
	0.3561	1.493	3.263	720	
2	0.4434	2.171	3.790	684	1.38
	0.3044	1.138	2.912	750	
3	0.4434	2.171	3.790	684	1.36
	0.2585	0.891	2.686	768	
4	0.3561	1.493	3.263	720	1.39
	0.3044	1.138	2.912	750	
5	0.3561	1.493	2.263	720	1.36
	0.2585	0.891	2.686	768	
6	0.3044	1.138	2.912	750	1.33
	0.2585	0.891	2.686	768	
				Average	1.37
				Literature value	1.34 [19]

Verification of the double-thermoanalytical curve method

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, and the results with different initial concentrations of reactant are quite reproducible. The double-thermoanalytical curve method for simple-order reactions is therefore believed to be correct.

Table 4 Experimental results on ring opening of epichlorohydrin with hydrobromic acid at 20°C; (solvent: H_2O)

No.	C_0/mol l^{-1}	Δ_m/v	$10^{-3}\cdot a^*_m$ / vs	t_m/s	$10^2\cdot k_3$/l^2 mol^{-2} s^{-1}
1	0.1546	1.581	5.961	930	2.27
	0.1392	1.336	5.773	990	
2	0.1546	1.581	5.961	930	2.20
	0.1089	0.941	5.648	1080	
3	0.1546	1.581	5.961	930	2.18
	0.0967	0.518	3.778	1200	
4	0.1392	1.336	5.778	990	2.18
	0.1089	0.941	5.648	1080	
5	0.1392	1.336	5.773	990	2.17
	0.0967	0.518	3.778	1200	
6	0.1089	0.941	5.648	1080	2.15
	0.0967	0.518	3.778	1200	
				Average	2.19
				Literature value	2.15 [20]

Table 5 Experimental results on polymerization of acrylamide at 30°C; (solvent: H_2O; $C_0(NaHSO_3)=6.58\cdot10^{-4}$ mol l^{-1})*

No.	C_0/mol l^{-1}	Δ_m/v	$10^{-4}\cdot a^*_m$ / vs	t_m/s	$10^4\cdot k_{1.5}$/l$^{-1/2}$ mol$^{-1/2}$ s^{-1}
1	0.5974	2.385	1.380	2400	2.81
	0.5675	2.159	1.288	2560	
2	0.5974	2.385	1.380	2440	2.93
	0.4946	1.926	1.218	2640	
3	0.5974	2.385	1.380	2440	3.07
	0.3478	1.682	1.215	2700	
4	0.5675	2.159	1.288	2560	2.97
	0.4946	1.926	1.218	2640	
5	0.5675	2.159	1.288	2560	3.10
	0.3478	1.682	1.215	2700	
6	0.4946	1.926	1.218	2640	3.15
	0.3478	1.682	1.215	2700	
				Average	3.01

* k_2(calculated)=$1.17\cdot10^{-2}$ l mol^{-1} s^{-1}, k_2(literature [21])=$1.13\cdot10^{-2}$ l mol^{-1} s^{-1}

The double-thermoanalytical curve method

In order to lessen the experimental errors in studies on the thermokinetics of chemical reactions, the thermoanalytical curves are generally measured at a series of initial concentrations of the reactants. The thermoanalytical curves at different initial concentrations are not independent: there is a relationship between them which is described by Eq. (22). The double-thermoanalytical curve method is therefore reasonable.

The double-thermoanalytical curve method does not require the functional table of the dimensionless parameter and calibration of the cooling constant in the kinetic evaluation. If merely the characteristic data a^*_m, Δ_m and t_m of two thermoanalytical curves measured at different initial concentrations are available, the rate constant can be calculated directly by using the simple explicit formula (Eq. (22)).

Determination of reaction order of an unknown reaction

This method is also suitable for an unknown reaction. For an unknown reaction, the thermoanalytical curves are measured at different initial concentration and the reaction order can be obtained via Eq. (26), derived according to the basic idea of our novel method, and the rate constant of the reaction studied can then be calculated via Eq. (22).

$$\frac{C_{01}^{1-\mathrm{n}}-C_{02}^{1-\mathrm{n}}}{C_{02}^{1-\mathrm{n}}-C_{03}^{1-\mathrm{n}}}=\frac{\Phi_{\mathrm{m}1}-\Phi_{\mathrm{m}2}}{\Phi_{\mathrm{m}2}-\Phi_{\mathrm{m}3}} \tag{26}$$

As stated above, the double-thermoanalytical curve method enriches the thermokinetic research method and improves the time parameter method for simple-order reactions. It can be applied to investigations of the thermokinetics of both chemical and biochemical reactions taking place in a batch conduction calorimeter under isothermal conditions.

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