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Thermo-kinetic research method for simple-order reactions: Time-parameter method

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Abstract

On the basis of thermo-kinetic theories, a novel thermo-kinetic research method, the time-parameter method for simple-order reactions, has been proposed in this paper. In order to test the validity of this method, the saponification of ethyl buryate and ethyl benzoate in aqueous ethanol solvent and the formation of hexamethylenetetramine in aqueous solution have been studied. The rate constants calculated with this method are in agreement with those in the literature. Therefore, the time-parameter method is believed to be correct. © 1998 Elsevier Science B.V.

Keywords: Thermo-kinetic research method; Thermo-kinetics; Time-parameter method; Simple-order reaction

1. Introduction

The thermoanalytical curve of a chemical reaction implies the kinetic and thermodynamic information which the reaction has. It is an important purpose of thermo-kinetics to establish a research method for obtaining such valuable information. So far, many kinds of thermo-kinetic research methods [1–4] have been established and used to investigate the thermo-kinetics of chemical and biochemical reactions [5–8]. All these methods do not involve the time parameter when calculating the kinetic parameters of studied reactions. In order to perfect the thermo-kinetic research method, based on the fundamental theory of thermo-kinetics and regarded time as a known parameter, a novel research method for simple-order reactions, the time-parameter method, has been suggested in this paper. Its validity is tested by comparison with experimental results.

2. Theory and method

2.1. Thermo-kinetic equations of simple-order reactions

When a chemical reaction takes place in a batch conduction calorimeter, the rate of heat production Φ can be calculated using Tian's equations [9]

$$\Phi = K\Delta + \Lambda(\mathrm{d}\Delta/\mathrm{d}t) \tag{1}$$

where Δ is the peak height of thermoanalytical curve of time t, K and Λ are the apparatus constants of the calorimeter.

Integrating Eq. (1) with respect to time t, we have

$$Q = Ka + \Lambda\Delta \tag{2}$$

$$Q_\infty = KA \tag{3}$$

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Rearrangement of Eqs. (1)–(3) leads to

$$(Q_\infty - Q)/Q_\infty = (Ka^* - \Lambda\Delta)/KA \qquad (4)$$

$$\Phi/Q_\infty = [K\Delta + \Lambda(\mathrm{d}\Delta/\mathrm{d}t)]/KA \qquad (5)$$

where Q is the heat produced before time t, Q_∞ is the total heat effect, 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.

According to the principle of chemical kinetics, it can be proved that the kinetic equations of simple-order reactions can be describe as:

$$(x_\infty - x)/x_\infty = \mathrm{F}(t) \qquad (6)$$

$$(\mathrm{d}x/\mathrm{d}t)/x_\infty = \mathrm{G}(t) \qquad (7)$$

where x and x_∞ are the extent of reaction at time t and t_∞, respectively. F(t) and G(t) are the function with respect to time t. For different order reactions, F(t) and G(t) have different expressions (as shown in Table 1)

In the previous article [1], we proved that

$$(Q_\infty - Q)/Q_\infty = (x_\infty - x)/x_\infty \qquad (8)$$

$$\Phi/Q_\infty = (\mathrm{d}x/\mathrm{d}t)/x_\infty \qquad (9)$$

So, from Eqs. (6)–(9), it turns to

$$(Ka^* - \Lambda\Delta)/KA = \mathrm{F}(t) \qquad (10)$$

$$[K\Delta + \Lambda(\mathrm{d}\Delta/\mathrm{d}t)]/KA = \mathrm{G}(t) \qquad (11)$$

Eqs. (10) and (11) are called the thermo-kinetic equations of simple-order reactions.

2.2. Mathematical models of time-parameter method

The time-parameter method includes three methods with which we can analyse the thermoanalytical curve, namely one-, two- and three-point methods, respectively.

2.2.1. One-point method

When $t=t_\mathrm{m}$, then $\Delta = \Delta_\mathrm{m}, \mathrm{d}\Delta/\mathrm{d}t = 0, \mathrm{G}(t) = \mathrm{G}(t_\mathrm{m})$, from Eq. (11), we obtain

$$\Delta_\mathrm{m}/A = \mathrm{G}(t_\mathrm{m}) \qquad (12)$$

where t_m is the time corresponding to the maximum peak height Δ_m of the curve.

Eq. (12) is the mathematical model of one-point method. From the thermoanalytical curve, we know the values of Δ_m, t_m and A, respectively. Therefore, Eq. (12) involves only one unknown kinetic parameter K_n which can be calculated by a computer.

2.2.2. Two-point method

From the thermoanalytical curve, it can be seen that each peak height (except Δ_m) corresponds to two time points, t_i and t_i'. Thus, according to Eq. (10), we get:

$$(Ka_i^* - \Lambda\Delta_i)/KA = \mathrm{F}(t_i) \qquad (13)$$

$$(Ka_i^{*\prime} - \Lambda\Delta_i)/KA = \mathrm{F}(t_i') \qquad (14)$$

From Eqs. (13) and (14) and letting

$$R_i = \frac{a_i^* - a_i^{*\prime}}{A}$$

we have

$$R_i = \mathrm{F}(t_i) - \mathrm{F}(t_i') \qquad (15)$$

R_i is ratio of peak area between t_i and t_i' to the total area of the thermoanalytical curve.

Eq. (15) represents the mathematical model of two-point method. a_i^*, $a_i^{*\prime}$, A, t_i and t_i' can be obtained from

Table 1
Formulae of F(t) and G(t)[a]

Reaction type	F(t)	G(t)
First-order reaction	$e^{-k_1 t}$	$k_1 e^{-k_1 t}$
Second-order reaction with equal concentrations	$\dfrac{1}{1+K_2 t}$	$\dfrac{K_2}{(1+K_2 t)^2}$
Second-order reaction with unequal concentrations	$\dfrac{r-1}{re^{k_2' t}-1}$	$\dfrac{r(r-1)K_2' e^{K_2' t}}{(re^{K_2' t}-1)^2}$
*N*th-order reaction with equal concentrations	$\dfrac{1}{[1+(n-1)K_n t]^{\frac{1}{n-1}}}$	$\dfrac{K_n}{[1+(n-1)K_n t]^{\frac{n}{n-1}}}$

[a] $K_2 = k_2 C_0$, $K_2' = k_2(A_0 - B_0)$, $r = A_0/B_0$, $K_n = k_n C_0^{n-1}$, $n \neq 1$. A_0, B_0, C_0 are initial concentrations of reactants.

the thermoanalytical curve. In this way, the kinetic parameter K_n, which is the only unknown parameter in Eq. (15), can be calculated by a computer.

2.2.3. Three-point method

Rearrangement of Eq. (12) leads to

$$A = \Delta_m / G(t_m) \tag{16}$$

thus

$$R_i = \frac{a_i^* - a_i^{*\prime}}{\Delta_m} \times G(t_m) \tag{17}$$

Inserting Eq. (17) into Eq. (15), and defining $\Psi_i = \frac{a_i^* - a_i^{*\prime}}{\Delta_m}$, we have

$$\Psi_i = \frac{F(t_i) - F(t_i')}{G(t_m)} \tag{18}$$

The mathematical model of three-point method can be expressed by Eq. (18). Ψ_i can be calculated using values of Δ_m and the peak area between t_i and t_i'. Meanwhile, t_i and t_i' can be obtained from the thermoanalytical curve. Therefore, K_n which is only unknown parameter in Eq. (18), can be calculated by a computer.

3. Experimental

3.1. Reaction systems

In order to test the validity of the time-parameter method, the thermo-kinetics of different order reactions as shown below, have been studied.

- Pseudo-first-order reaction: Saponification of ethyl butyrate in aqueous ethanol solvent at 30°C. If $C_{KOH} > C_{ester}$, $k_1^* = k_2 C_{ester}$.
- Second-order reaction with equal reactant concentrations: Saponification of ethyl benzoate in aqueous ethanol solvent at 25°C.
- Second-order reaction with unequal reactant concentrations: Saponification of ethyl butyrate in aqueous ethanol solvent at 30°C.
- Third-order reaction: The reaction of formaldehyde with ammonia in water to form hexamethylenetetramine at 20°C. The kinetic parameter of this reaction is $K_3 = 144 k_3 C_0^2$.

3.2. 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 deionized water. The concentrations of potassium hydroxide and sodium hydroxide in solutions were standardized with potassium hydrogen phthalate.

3.3. Apparatus

All the thermoanalytical curves of the above-mentioned reactions were measured with a twin conduction calorimeter which has been described in detail in a previous article [10].

4. Results and discussion

According to the time-parameter method, the calculated results and examples of analysis of thermoanalytical curve are given in Tables 2–9.

Table 2
Saponification of ethyl butyrate at 30°C (solvent: 85% (w/w) EtOH–H_2O; $C_{KOH} = 0.5298$ mol l^{-1})

No.	C_0 (ester)/ mol l^{-1}	$k_1^* \times 10^3$/ s^{-1}			$k_2 \times 10^3$/ l mol^{-1} s^{-1}		
1	0.5594	1.51[a]	1.52[b]	1.57[c]	2.70[a]	2.72[b]	2.80[c]
2	0.5827	1.64	1.63	1.66	2.81	2.80	2.85
3	0.5885	1.56	1.60	1.59	2.65	2.72	2.70
4	0.6054	1.70	1.66	1.65	2.81	2.74	2.73
5	0.6303	1.74	1.72	1.75	2.76	2.73	2.78
				Average:	2.84	2.77	2.75
				[11]:	2.79		

[a] With the one-point method.
[b] With the two-point method.
[c] With the three-point method.

Table 3
Example of thermoanalytical curve analysis (No. 4)

i	t_i/ s	t_i'/ s	$10^{-4}(a_i^* - a_i^{*\prime})$/ mm s	R_i	$\Psi_i \times 10^{-3}$	$K_1^* \times 10^3$ s^{-1}	
1	70	2007	10.5	0.8537	1.207	1.60[b]	1.70[c]
2	99	1710	9.72	0.7902	1.117	1.68	1.63
3	126	1467	8.93	0.7260	1.026	1.71	1.61
4	171	1287	7.80	0.6341	0.897	1.64	1.65
5	212	1107	6.69	0.5439	0.769	1.67	1.68
					average:	1.66	1.65

[b] Same as in Table 2.
[c] Same as in Table 2.
Δ_m=87.0 mm, t_m=513 s, $A=1.23\times10^5$ mm s.

Table 4
Saponification of ethyl benzoate at 25°C (solvent: 50% (w/w) EtOH–H_2O, C_0 (ester)=C_0 (NaOH)

No.	C_0 mol l^{-1}	$K_2\times10^4$/ s^{-1}			$k_2\times10^3$/ l mol^{-1} s^{-1}		
1	0.1485	2.03[a]	2.07[b]	1.90[c]	1.37[a]	1.39[b]	1.28[c]
2	0.1651	2.21	2.21	2.23	1.34	1.34	1.35
3	0.1857	2.51	2.40	2.44	1.35	1.29	1.31
4	0.2063	2.79	2.76	2.81	1.35	1.34	1.36
5	0.2269	3.15	3.11	3.03	1.39	1.37	1.33
				Average:	1.36	1.35	1.33
				[12]:	1.32		

[a] Same as in Table 2.
[b] Same as in Table 2.
[c] Same as in Table 2.

Table 5
Example of a thermoanalytical curve analysis (No. 1)

i	t_i/ s	t_i'/ s	$10^{-4}(a_i^* - a_i^{*\prime})$/ mm s	R_i	$\Psi_i \times 10^{-3}$	$K_2\times10^4$/ s^{-1}	
1	180	4800	1.71	0.4647	3.226	2.09[b]	1.92[c]
2	240	3900	1.47	0.3994	2.774	2.07	1.94
3	270	3210	1.27	0.3451	2.396	2.06	1.96
4	306	2700	1.10	0.2989	2.075	2.07	1.86
5	396	2280	0.90	0.2446	1.698	2.05	1.82
					Average:	2.07	1.90

[b] Same as in Table 2.
[c] Same as in Table 2.
Δ_m=53.0 mm, t_m=930 s, $A=3.68\times10^5$ mm s.

From Tables 2–9, it can be seen that the rate constants of different order reactions calculated with our novel method are in agreement with those in the literature. The results show that calculations of the rate constants are quite reproducible and self-consistent. Therefore, the time-parameter method for simple-order reactions is believed to be correct.

The time-parameter method for simple-order reactions is to be conveniently dealt with, because its principle is simple and its expressions have concise form. It does not require the functional table of dimensionless parameter and calibration of the cooling constant. There are three data-collecting methods which are listed as one-, two- and three-point methods.

Table 6
Saponification of ethyl butyrate at 30°C (solvent: 85% (w/w) EtOH–H_2O)

No.	C_0 (ester)/ $mol\,l^{-1}$	C_0 (KOH)/ $mol\,l^{-1}$	r	$K_2' \times 10^4$/ s^{-1}			$k_2 \times 10^3$/ $l\,mol^{-1}\,s^{-1}$		
1	0.3333	0.1169	2.851	6.05[a]	6.10[b]	6.05[c]	2.79[a]	2.82[b]	2.79[c]
2	0.2651	0.06667	3.976	5.82	5.67	5.48	2.93	2.86	2.76
3	0.3333	0.06275	5.312	7.75	7.63	7.56	2.86	2.82	2.75
4	0.3005	0.04706	6.385	7.02	7.15	6.96	2.77	2.82	2.75
5	0.5650	0.06275	9.004	14.2	13.5	13.8	2.83	2.69	2.75
					Average:		2.84	2.80	2.77
					[10]:		2.79		

[a] Same as in Table 2.
[b] Same as in Table 2.
[c] Same as in Table 2.

Table 7
Example of a thermoanalytical curve analysis (No. 3)

i	t_i/ s	t'_i/ s	$10^{-4}(a_i^* - a_i^{*\prime})$/ mm s	R_i	$\Psi_i \times 10^{-3}$	$K_2' \times 10^4$/ s^{-1}	
1	81	2610	10.9	0.8134	1.603	7.63[b]	7.68[c]
2	126	2106	9.63	0.7187	1.416	7.56	7.60
3	198	1701	8.03	0.5992	1.181	7.64	7.49
4	279	1359	6.24	0.4657	0.918	7.65	7.52
5	333	1206	5.20	0.3880	0.765	7.66	7.50
					Average:	7.63	7.56

[b] Same as in Table 2.
[c] Same as in Table 2.
Δ_m=68.0 mm, t_m=594 s, A=1.33×10^5 mm s.

Table 8
Formation of hexamethylenetetramine at 20°C (solvent: H_2O)

No.	C_0 (HCHO)/ $mol\,l^{-1}$	C_0 (NH_3)/ $mol\,l^{-1}$	$K_3 \times 10^4$/ s^{-1}			$k_3 \times 10^2$/ $l\,mol^{-2}\,s^{-1}$		
1	0.0450	0.0300	3.83[a]	3.82[b]	3.85[c]	4.73[a]	4.72[b]	4.75[c]
2	0.0450	0.0300	3.81	3.88	3.80	4.70	4.79	4.69
3	0.0450	0.0300	3.85	3.80	3.88	4.75	4.69	4.73
4	0.0420	0.0280	3.35	3.38	3.30	4.75	4.79	4.68
5	0.0420	0.0280	3.44	3.34	3.38	4.87	4.73	4.79
					Average:	4.76	4.74	4.73
					[7]:	4.71		

[a] Same as in Table 2.
[b] Same as in Table 2.
[c] Same as in Table 2.

From Eq. (18), it is made explicit that kinetic parameter K_n can be calculated by three-point method without the completion of a reaction. Therefore, the three-point method is extremely useful to the two kinds of reactions, i.e. one is the reaction having very low rate. Long reaction time of such kinds of reactions results in drift of zero-point base line of the thermoanalytical curve which causes error in calculated results; the other has side reaction at the final stage of the reaction. The heat effects produced in the side reaction influences the calculated results of the studied reactions.

Table 9
Example of a thermoanalytical curve analysis (No. 1)

i	t_i/ s	t_i'/ s	$10^{-4}(a_i^* - a_i^{*\prime})$/ mm s	R_i	$\Psi_i \times 10^{-3}$	$K_3 \times 10^4$/ s^{-1}	
1	120	6870	9.21	0.5582	3.070	3.85[b]	3.80[c]
2	288	5280	7.58	0.4594	2.527	3.81	3.85
3	390	4020	6.31	0.3824	2.103	3.83	3.87
4	450	3420	5.54	0.3358	1.847	3.79	3.88
5	528	300	4.84	0.2933	1.613	3.84	3.84
					Average:	3.82	3.85

[b] Same as in Table 2.
[c] Same as in Table 2.
Δ_m=30.0 mm, t_m=840 s, A=1.65×10^5 mm s.

Time-parameter method is also suitable for investigating the kinetics of an unknown reaction. For an unknown reaction, its kinetic parameter and reaction order can be determined with heuristic method. Rate constant of the studied reaction may be calculated with a supposed reaction order by Eqs. (12), (15) and (18) in the present paper. If the rate constants are in agreement with each other at different initial concentrations of reactants, then the supposed reaction order is the order of the unknown reaction.

As stated above, the time-parameter method for simple-order reactions further perfect the thermo-kinetic research method. It can be applied to the investigation on the thermo-kinetics of both chemical and biochemical reactions.

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