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Thermo-kinetic research methods for simple order reactions: Analog curve and characteristic parameter methods

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Abstract

In order to simplify the thermo-kinetic research method and study faster reactions, two novel thermo-kinetic research methods, namely the thermo-analytical analog curve and characteristic parameter methods, have been proposed in this paper. The general formulae for calculating kinetic parameter K_n and rate constant k_n have been derived.

The thermo-kinetics of five reactions with first, second, third, and fractional orders, respectively, have been studied with these methods, and their validity has been verified by the experimental results. © 1997 Elsevier Science B.V.

Keywords: Analog thermo-analytical curve method; Characteristic parameter method; Simple order reactions; Thermo-kinetic research method

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1. Introduction

Based on the fundamental theory of thermo-kinetics, the dimensionless parameter method of different order reactions had been developed in literature [1–7], and it can be applied to study slower reactions as well as faster ones when the ratio of the thermo-analytical curve characteristic data a^*_m/A is beyond its critical value. In addition, different order reactions have different forms of the dimensionless parameter method. This is inconvenient for the users. In practice, many chemical and biochemical reactions are rapid and, consequently, it is necessary to develop a thermo-kinetic research method applicable to these faster reactions.

In this paper, two novel research methods for studying slower and faster reactions, the analog thermo-analytical curve and characteristic parameter methods, have been proposed. The formulae for calculating the kinetic parameters and rate constants are very simple when these methods are followed. In order to test the validity of these methods, we have studied the saponifications of ethyl butyrate and ethyl propionate in aqueous ethanol and water, respectively, the formation of hexamethylenetetramine in water, and the polymerization of acrylamide. The rate constants calculated by the proposed methods are in agreement with those in the literature, and therefore, the analog thermo-analytical curve and characteristic parameter methods were validated.

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2. Theory and method

2.1. The analog thermo-analytical curve equation and the thermo-kinetic characteristic equations of simple order reactions

The thermo-analytical curve for a chemical reaction occurring in a conduction calorimeter is shown in Fig. 1. It varies with the reaction order, the rate constant and initial concentrations of reactants. However, it can be approximately simulated by the following relationship:

$$\Delta = at\mathrm{e}^{-k\beta t} \tag{1}$$

Eq. (1) is called the analog thermo-analytical curve equation. Therein, k is the cooling constant of a thermo-kinetic system, t the reaction time, Δ the peak height at time t, α and β the analog parameters related to the thermo-kinetic system. When $t = 0$, $\Delta = 0$, and when $t \rightarrow \infty$, $\Delta \rightarrow 0$; thus, it is clear that the analog thermo-analytical curve satisfies the boundary conditions of the real thermo-analytical curve.

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

$$\frac{\mathrm{d}\Delta}{\mathrm{d}t} = \alpha(1 - k\beta t)\mathrm{e}^{-k\beta t} \tag{2}$$

At $t = t_\mathrm{m}$, $\mathrm{d}\Delta/\mathrm{d}t = 0$, and $\Delta = \Delta_\mathrm{m}$, from Eq. (2) we have

$$\beta = 1/(kt_\mathrm{m}) \tag{3}$$

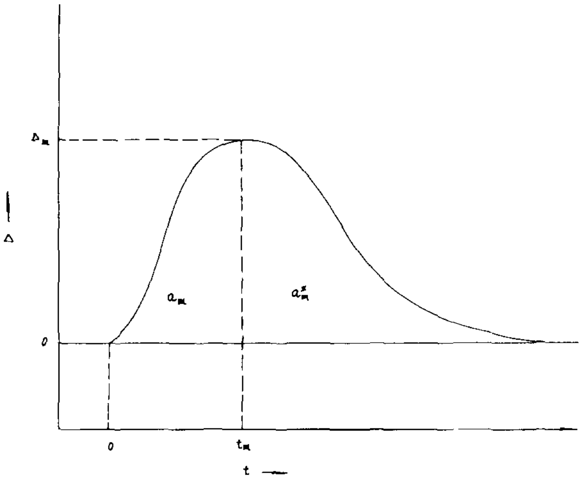

Fig. 1. Thermo-analytical curve of a chemical reaction (schematic).

At $t=t_\mathrm{m}$, from Eq. (1), and taking into account Eq. (3), we have

$$\alpha = \mathrm{e}\Delta_\mathrm{m}/t_\mathrm{m} \tag{4}$$

Inserting Eqs. (3) and (4) into Eq. (1), we have

$$\Delta = t/t_{\mathrm{m}\Delta_\mathrm{m}}\mathrm{e}^{(1-t/t_\mathrm{m})} \tag{5}$$

Eq. (5) is the characteristic expression of the analog thermo-analytical curve.

The peak area of the analog thermo-analytical curve is given by

$$A = \int_0^{+\infty} \Delta \mathrm{d}t \tag{6}$$

Inserting Eq. (5) into Eq. (6) we have

$$t_\mathrm{m} = A/(\mathrm{e}\Delta_\mathrm{m}) \tag{7}$$

Let the peak area and the characteristic peak height of the analog thermo-analytical curve be equal to those of the real thermo-analytical curve, respectively. From Eq. (7), t_m can be calculated with A and Δ_m of the real thermo-analytical curve. From Eqs. (5) and (7), it can be seen that the analog thermo-analytical curve can be determined according to the real thermo-analytical curve.

Inserting Eq. (7) into Eq. (3), we obtain the cooling constant of the thermo-kinetic system:

$$k = \mathrm{e}\Delta_\mathrm{m}/(\beta A) \tag{8}$$

Based on the fundamental theory of thermo-kinetics [1], the thermo-kinetic characteristic equations of simple-order reactions are given by

$$\Delta_\mathrm{m}/A = \varphi(K_\mathrm{n}, t_m) \tag{9}$$

and

$$a^*_\mathrm{m}/A - \Delta_\mathrm{m}/(kA) = \psi(K_\mathrm{n}, t_\mathrm{m}) \tag{10}$$

Here, A, Δ_m, t_m and a^*_m are the thermo-analytical curve characteristic data representing the total area, maximum peak height, time corresponding to Δ_m and the peak area after t_m of a thermo-analytical curve, respectively, (see Fig. 1); $\varphi(K_\mathrm{n}, t_\mathrm{m})$ and $\psi(K_\mathrm{n}, t_\mathrm{m})$ are functions with respect to K_n and t_m which reflect the kinetic characteristics of the thermo-kinetic system and have different forms for different order reactions, K_n being the kinetic parameter.

Let

$$\Phi_m = a_m^*/A - \Delta_m/(kA) \tag{11}$$

Combining Eq. (11) with Eq. (10), we have

$$\Phi_m = \psi(K_n, t_m) \tag{12}$$

According to Eq. (11), there are two ways of calculating Φ_m; hence, two thermo-kinetic research methods can be derived, as described in the following sections.

2.2. Analog thermo-analytical curve method

One way to calculate Φ_m is to determine the cooling constant with Eq. (8). Inserting Eq. (8) into Eq. (11), we have

$$\Phi_m = a_m^*/A - \beta/e \tag{13}$$

From Eq. (12) and corresponding rate equations of different order reactions, the formulae for calculating kinetic parameters K_n and rate constants k_n for different order reactions can be obtained (shown in Table 1)

2.3. Characteristic parameter method

Another way to calculate Φ_m is to calibrate the cooling constant according to an already described procedure [8]. From Eqs. (9) and (12) and correspond-

Table 1
Formulae for calculating K_n and k_n

Reaction type	K_n [a]	K_n [b]	k_n
First-order reaction	$K_1 = -\frac{1}{t_m}\ln\Phi_m$	$K_1 = \frac{\Delta_m/A}{\Phi_m}$	$k_1 = K_1$
Second-order reaction with unequal concentrations	$K_2^* = \frac{1}{t_m}\ln\left[\frac{1+(r-1)/\Phi_m}{r}\right]$	$K_2^* = \frac{\Delta_m/A}{\Phi_m + \Phi_m^2/(r-1)}$	$k_2 = K_2^*/(A_0 - B_0)$ [c]
*n*th-order reaction with equal concentrations	$K_n = \frac{1}{(n-1)t_m}\left[\Phi_m^{(1-n)} - 1\right]$	$K_n = \frac{\Delta_m/A}{\Phi_m^n}$	$k_n = K_n/C_0^{(n-1)}$ [c]
Reaction with fractional-order 1/2	$K_{1/2} = \frac{2}{t_m}\left[1 - \Phi_m^{1/2}\right]$	$K_{1/2} = \frac{\Delta_m/A}{\Phi_m^{1/2}}$	$k_{1/2} = K_{1/2}C_0^{1/2}$
3/2	$K_{3/2} = \frac{2}{t_m}[\Phi_m^{-1/2} - 1]$	$K_{3/2} = \frac{\Delta_m/A}{\Phi_m^{3/2}}$	$k_{3/2} = K_{3/2}C_0^{-1/2}$
5/2	$K_{5/2} = \frac{2}{3t_m}[\Phi_m^{-3/2} - 1]$	$K_{5/2} = \frac{\Delta_m/A}{\Phi_m^{5/2}}$	$k_{5/2} = K_{5/2}C_0^{-3/2}$

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[a] Analog thermo-analytical curve method.

[b] Characteristic parameter method.

[c] A_0, B_0, C_0 are the initial concentrations of reactants; $r = A_0/B_0 (> 1)$

ing rate equations of different order reactions, the formulae for calculating kinetic parameters, K_n, and rate constants k_n for different order reactions can also be obtained (shown in Table 1).

From Table 1, it is seen that the mathematical models of our two novel thermo-kinetic research methods, in the present paper, are very simple, especially for the *n*th-order reactions with equal concentrations of reactants there are general mathematical models.

3. Experimental

3.1. Reactions and reactants

In order to test the validity of the analog thermo-analytical curve and characteristic parameter methods, the thermo-kinetics of five different order reactions as shown below, have been studied.

- Pseudo-first-order reaction: saponification of ethyl butyrate in aqueous ethanol solvent at 30°C.
- Second-order reaction with equal reactant concentrations: saponification of ethyl propionate in water at 25°C.
- Second-order reaction with unequal reactant concentrations: saponification of ethyl benzoate in aqueous ethanol solvent at 25°C.
- Third-order reaction: the reaction of formaldehyde with ammonia in water to form hexamethylenetetramine at 15°C.
- Fractional-order reaction: the polymerization of acrylamide at 30°C.

All the reagents of the above reactions were analytically pure. The mixed solvents were prepared from analytically pure ethanol and deionized water.

3.2. Apparatus

All the thermo-analytical curves of the above-mentioned reactions were measured with a twin conduction calorimeter, described in detail in the previous article [8]. In an earlier paper, we have described a method for measuring the cooling constant of a thermo-kinetic system [9].

4. Results and discussion

4.1. Verification of the analog thermo-analytical curve and characteristic parameter methods.

According to the formulae for calculating K_n and k_n in Table 1 and Eq. (11), or Eqs. (7) and (13), the rate constants can be calculated with the thermo-analytical curve characteristic data a^*_{m}, Δ_{m} and A. The results of the above-mentioned different order reactions are listed in Tables 2–6, in which, $K^*_1 = K_1$ for a pseudo-first-order reaction, $k_{3/2} = K_2 C_0^{1/2}$ (Na_2SO_3) for the polymerization of acrylamide. The reaction equation of formaldehyde with ammonia in water is given below

$$6HCHO + 4NH_3 \xrightarrow{k_3} (CH_2)_6N_4 + 6H_2O$$

Table 2
Saponification of ethyl butyrate at 30°C (Solvent: 85% (w/w) E_tOH-H_2O; C_0 (KOH)=0.5298 mol l^{-1}; k=2.12×10^{-3} s^{-1})

C_0 (ester)/ (mol l^{-1})	Δ_m/ mm	$a^*_m \times 10^{-4}$/ (mm s)	$A\times10^{-5}$/ (mm s)	$k^*_1 \times 10^3$/ s^{-1}		$k_2\times10^3$/ (l mol^{-1} s^{-1})		
0.6054	86.8	9.23	1.19	1.26a[a]	1.68[b]	2.08[a]	2.78[b]	2.12[c]
0.5884	88.5	9.65	1.27	1.26	1.62	2.14	2.75	2.30
0.5827	80.0	8.60	1.15	1.30	1.66	2.23	2.85	2.39
0.5504	82.5	9.42	1.27	1.24	1.49	2.25	2.71	2.25
0.5897	89.2	9.63	1.29	1.30	1.64	2.20	2.78	2.36
					Average:	2.18	2.77	2.34
					[10]:	2.79		

[a] Results calculated according to the analog thermo-analytical curve method.
[b] Results calculated according to the characteristic parameter method.
[c] Results calculated according to the dimensionless parameter method.

Table 3
Saponification of ethyl propionate at 25°C (Solvent: H_2O; C_0 (NaOH)=C_0 (ester); k=3.55×10^{-3} l^{-1})

C_0 (ester)/ (mol l^{-1})	Δ_m/ mm	$a^*_m \times 10^{-4}$/ (mm s)	A×10^{-4}/ (mm s)	k_2×10^3/ (l mol^{-1} s^{-1})		
0.0550	78.5	5.65	7.45	8.14[a]	8.99[b]	Not applicable[c]
0.0550	77.5	5.62	7.40	8.05	8.83	
0.0495	68.5	5.12	6.62	8.33	9.00	
0.0495	69.0	5.22	6.70	8.10	8.70	
0.0450	61.0	4.78	6.10	8.49	8.82	
			Average:	8.22	8.87	
			[11]:	8.7		

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

Table 4
Saponification of ethyl benzoate at 25°C (Solvent: 50% (w/w) E$_t$OH-H_2O; k=1.96×10^{-3} s^{-1})

C_0 (ester)/ (mol l^{-1})	C_0 (NaOH)/ (mol l^{-1})	r	Δ_m/ mm	$a^*_m \times 10^{-5}$/ (mm s)	A×10^{-5}/ (mm s)		k_2×10^3/ (l mol^{-1} s^{-1})	
0.300	0.100	3	67.8	2.19	2.66	1.38[a]	1.37[b]	1.35[c]
0.500	0.100	5	135	2.82	3.58	1.30	1.38	1.37
0.350	0.0500	7	89.2	2.38	2.90	1.37	1.39	1.31
0.397	0.0460	8.63	95.0	2.39	2.95	1.30	1.31	1.30
0.451	0.0464	9.72	76.5	1.75	2.29	1.36	1.30	1.32
					Average:	1.34	1.35	1.33
					Ref. [12]:	1.33		

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

Table 5
Formation of hexamethylenetetramine at 15°C (Solvent: H_2O; k=1.83×10^{-3} s^{-1})

C_0 (HCHO)/ (mol l^{-1})	C_0 (NH_3)/ (mol l^{-1})	Δ_m/ mm	$a^*_m \times 10^{-5}$/ (mm s)	A×10^{-5}/ (mm s)		k×10^2/ (l^2 mol^{-2} s^{-1})	
0.0600	0.0400	37.6	1.73	1.95	2.60[a]	2.80[b]	2.90[c]
0.0600	0.0400	34.9	1.66	1.86	2.46	2.64	2.71
0.0540	0.0360	27.2	1.57	1.76	2.50	2.51	2.76
0.0540	0.0360	27.5	1.49	1.68	2.73	2.77	2.96
0.0540	0.0360	24.5	1.44	1.63	2.56	2.52	2.80
				Average:	2.57	2.65	2.79
				[13]:	2.84[d]		

[a] Same as in Table 2.
[b] Same as in Table 2.
[c] Same as in Table 2.
[d] Obtained from the half-life in [13].

$$\begin{array}{llllll} t=0 & 6C_0 & 4C_0 & 0 & 0 \\ t=\mathrm{t} & 6(C_0-\mathrm{x}) & 4(C_0-\mathrm{x}) & \mathrm{x} & 6\mathrm{x} \end{array}$$

$$\frac{dx}{dt} = 144(C_0 - x)^3$$

Thus, the kinetic parameter of this reaction is $K_3 = 144k_3C_0^2$.

From Tables 2–6, it can be seen that the rate constants of different order reactions calculated with our two novel methods are in agreement with those in the

Table 6
Polymerization of acrylamide at 30°C (Solvent: H_2O; k=1.88×10^{-3} s^{-1})

C_0 (A)/ ($mol\ l^{-1}$)	C_0 (B)×10^4/ ($mol\ l^{-1}$)	Δ_m/ mm	a_M^* × 10^{-5}/ (mm s)	A×10^{-5}/ (mm s)	$k_{3/2}$×10^4/ ($l^{1/2}\ mol^{-1/2}\ s^{-1}$)		k_2×10^2/ ($l\ mol^{-1}\ s^{-1}$)		
0.2017	1.651	35.8	5.94	6.39	1.41 [a]	1.47 [b]	1.10 [a]	1.15 [b]	1.13 [c]
0.4946	6.447	78.2	4.85	5.64	2.94	2.83	1.16	1.11	1.15
0.5675	6.050	85.8	5.13	5.78	2.65	2.71	1.08	1.10	1.07
0.5974	6.175	95.0	5.50	6.38	2.86	2.78	1.15	1.12	1.14
0.3432	3.295	74.0	6.84	7.46	2.05	2.11	1.14	1.16	1.13
0.3448	4.606	76.0	6.05	6.68	2.43	2.49	1.13	1.15	1.13
0.3473	5.226	77.2	5.61	6.17	2.63	2.74	1.15	1.19	1.15
						Average:	1.13	1.14	1.14
						[7]:	1.13		

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

literature and, therefore, the analog thermo-analytical curve and characteristic parameter methods are believed to be correct.

4.2. *Determination of β in the analog thermo-analytical curve method*

For a thermo-analytical curve, t_m is determinate. From Table 1, it can be seen that the key to calculate the rate constants accurately lies in the determination of the precise value of β. According to our experimental results, when the initial rate of a studied reaction is faster, the value of β is larger, otherwise, when the initial rate of a studied reaction is slower, the value of β is smaller. Generally speaking, when the initial rate of a reaction >10^{-4} $mol\ l^{-1}s^{-1}$, the value of β turns out to 1; however, when the initial rate of a studied reaction is <10^{-4} $mol\ l^{-1}s^{-1}$, the value of β is 2/3. When the initial rate is $\sim 10^{-4}$ $mol\ l^{-1}\ s^{-1}$, we can change the initial concentrations of reactants to make it far smaller than or larger than 10^{-4} $mol\ l^{-1}\ s^{-1}$, so that the experimental results will be credible.

For an unknown reaction, the value of β can be determined heuristically. First, the rate constants can be calculated with two values of β, namely 2/3 and 1; then the initial rate can be calculated. With this initial rate, the value of β can be determined with the above-mentioned method.

4.3. *The comparison of the analog thermo-analytical curve with the real thermo-analytical curve*

The analog thermo-analytical curves of saponification of ethyl benzoate and ethyl propionate are shown in Figs. 2 and 3, respectively. From the two figures, we can see that the real thermo-analytical curve can reasonably be well simulated by the analog thermo-analytical curve for a slower or faster reaction. Thus, the validity of Eq. (5) for simulating the real thermo-analytical curve has been verified.

4.4. *Comparison of the analog thermo-analytical curve and characteristic parameter methods with the dimensionless parameter method.*

From Tables 2–6, we can see that the rate constants of the slow reactions calculated with the analog thermo-analytical curve and characteristic parameter methods and the dimensionless parameter method are in agreement with those in the literature, but the dimensionless parameter method cannot be applied to faster reaction (see Table 3). The reason is that the thermo-analytical curve and characteristic parameter methods only require the thermal change process to satisfy the Tian equation, but the dimensionless parameter method not only requires the thermal change process to satisfy the Tian equation, but also stipulates that the ratio a_m^*/A must be greater than the critical

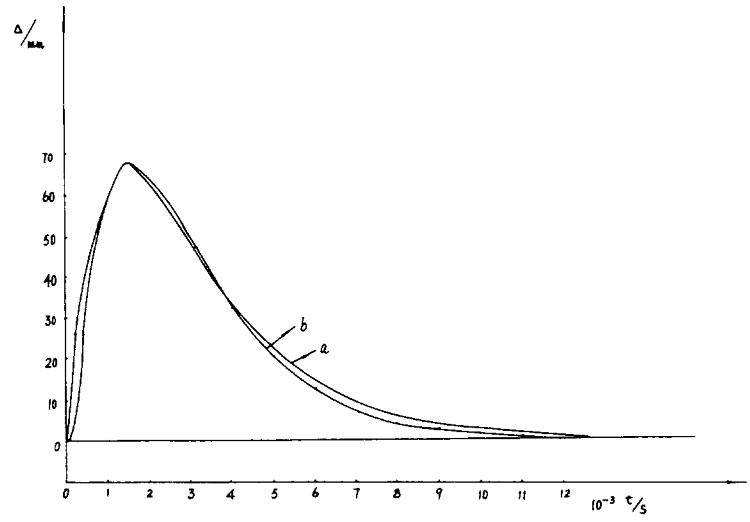

Fig. 2. Saponification of ethyl benzoate: (a) – real thermo-analytical curve (Table 4 No. 1); (b) – analog thermo-analytical curve ($\Delta = 0.0470te^{1-t/1443}$, $\beta = 2/3$).

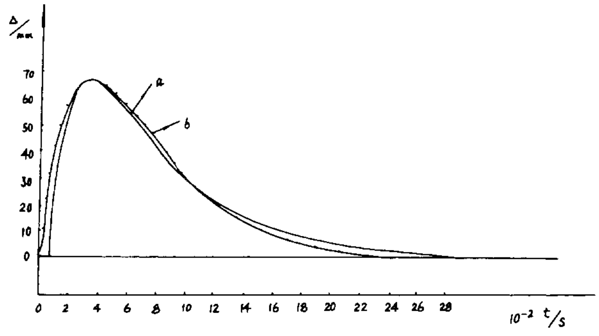

Fig. 3. Saponification of ethyl propionate: (a) – real thermo-analytical curve (Table 3, No. 1); and (b) – analog thermo-analytical curve ($\Delta = 0.192te^{1-t/356}$, $\beta = 1$).

value obtained by this method. Therefore, the analog thermo-analytical curve and characteristic parameter methods have a wider applicable range than the dimensionless parameter method. Thus, the two former methods can be more widely used to study chemical and biochemical reactions.

Acknowledgements

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