

Thermokinetic research method for first-order reactions

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Abstract

This paper presents a novel data processing method for thermokinetics of first-order reactions, in which the rate constant of a first-order reaction can be calculated from only three characteristic peak-height data without using any peak-area, rate of temperature rise, or functional table of dimensionless parameters. The saponification of ethyl benzoate and ethyl acetate in aqueous ethanol have been studied with a twin conduction calorimeter and the rate constants calculated with this method are in fair agreement with those in the literature; hence the validity of this method is demonstrated.

INTRODUCTION

It is very interesting and advantageous to study kinetics of chemical and biochemical reactions by calorimetry, because thermokinetic research of reaction systems may be undertaken in any solvent, and the spectral, electrochemical or other properties of the substances involved in the reacting system need not be considered. Conduction calorimeters have been largely used for thermokinetic investigation; the data processing method for the thermogram of a first-order reaction measured with a conduction calorimeter has been an attractive subject for a long time [1–7], because most chemical and biochemical reactions can be treated as pseudo-first-order reactions under certain conditions.

A novel method is proposed in this paper, by which the rate constant of a first-order reaction can be calculated from only three characteristic peak-height data; its validity is tested by comparison with experimental results.

PRINCIPLE OF THE METHOD

Thermogram equation of a first-order reaction

When a chemical reaction is taking place in a batch conduction calorimeter, a thermogram, as shown in Fig. 1, can be recorded.

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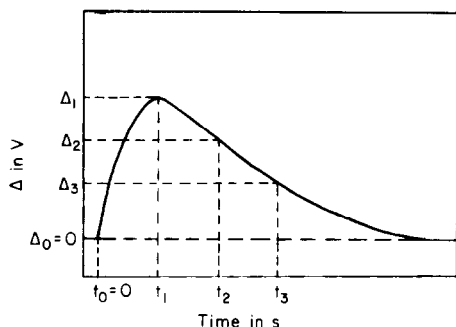


Fig. 1. Thermogram of a first-order reaction.

According to Calvet and Prat [3], the rate of heat production Ω , can be calculated using Tian's equation

$$\Omega = K\Delta + \Lambda(d\Delta/dt) \quad (1)$$

where Δ is peak-height at time t ; K and Λ are the apparatus constants of the calorimeter.

According to eqn. (1), 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 [7]

$$\Delta = A \left(\frac{kk_1}{k - k_1} \right) (e^{-k_1t} - e^{-kt}) \quad (2)$$

where A is the total area under the thermogram, k_1 is the rate constant of the first-order reaction and $k = K/\Lambda$, is the cooling constant of the calorimeter. Equation (2) is called thermogram equation of a first-order reaction, from which it can be seen that peak-height $\Delta(t)$ is an exponential function of time t .

Based on eqn. (2), we can show that the n th order derivation of function $\Delta(t)$ with respect to time t is

$$\Delta^{(n)} = (-1)^n \left(\frac{kk_1A}{k - k_1} \right) (k_1^n e^{-k_1t} - k^n e^{-kt}) \quad (3)$$

If $\Delta^{(n)} = 0$, then

$$t_n = \frac{n \ln R}{k - k_1} \quad (4)$$

where $R = k/k_1$ is called the dimensionless parameter of a first-order reaction.

These special times t_n , corresponding to $\Delta^{(n)} = 0$ in a thermogram, are defined as the characteristic time of the first-order reaction. Inserting eqn.

(4) into eqn. (2) gives

$$\Delta_n = \left(\frac{kk_1A}{k - k_1} \right) R^{nR/(1-R)} (R^n - 1) \tag{5}$$

where Δ_n is called the characteristic peak-height in the thermogram of a first-order reaction.

It is clear that when $n = 0$, $t_0 = 0$ and $\Delta^{(0)} = \Delta = 0$. It means that the characteristic time t_0 is the initial time of a thermogram. According to eqn. (4) it is easy to prove that

$$t_{n+1} - t_n = \Delta t = \ln R / (k - k_1) \tag{6}$$

Because the right-side of eqn. (6) is a constant for the reaction system under investigation, the interval between two characteristic times t_{n+1} and t_n is fixed. This is an important characteristic of a first-order reaction and it is clear that

$$\Delta t = t_1 - t_0 = t_1$$

so, any characteristic time t_n can be determined by the characteristic time t_1 , which corresponds to the maximum peak-height Δ_1 in a thermogram, as shown in Fig. 1, i.e.

$$t_2 = 2t_1; \quad t_3 = 3t_1; \quad \dots; \quad t_n = nt_1$$

Calculation of rate constant k_1 and cooling constant k

From eqn. (6), it can be seen that

$$k_1 = (1/\Delta t) \ln R^{1/(R-1)} \tag{7}$$

Defining

$$X = R^{1/(R-1)} \tag{8}$$

we have

$$k_1 = (1/\Delta t) \ln X \tag{9}$$

Writing

$$m = \Delta_3/\Delta_1 \quad n = \Delta_2/\Delta_1$$

and according to eqn. (5), it can be shown that

$$m = (1 + R + R^2)R^{2R/(1-R)} \tag{10}$$

$$n = (1 + R)R^{R/(1-R)} \tag{11}$$

Combining eqns. (8), (10) and (11), we can prove that

$$(n^2 - m)X^2 - nX + 1 = 0 \quad (12)$$

The solution of eqn. (12) is

$$X = \frac{n \pm \sqrt{4m - 3n^2}}{2(n^2 - m)} \quad (13)$$

From eqn. (6), it can be shown that

$$k = (1/\Delta t) \ln R^{R/(R-1)} \quad (14)$$

Defining

$$W = R^{R/(R-1)} \quad (15)$$

we have

$$k = (1/\Delta t) \ln W \quad (16)$$

In the same way as above, it can be proved that

$$(n^2 - m)W^2 - nW + 1 = 0 \quad (17)$$

and

$$W = \frac{n \pm \sqrt{4m - 3n^2}}{2(n^2 - m)} \quad (18)$$

From eqns. (13) and (18), it can be found that the dimensionless parameters X and W of a first-order reaction system are the two positive real roots of the same algebraic equation of the second degree in one unknown. This is another important and interesting characteristic of a first-order reaction.

Now we provide an algebraic equation of the second degree in one unknown y of the form

$$(n^2 - m)y^2 - ny + 1 = 0 \quad (19)$$

and the two positive real roots of this equation are

$$y^{\oplus} = \frac{n + \sqrt{4m - 3n^2}}{2(n^2 - m)} \quad y^{\ominus} = \frac{n - \sqrt{4m - 3n^2}}{2(n^2 - m)}$$

and then, when $R > 1$; i.e. $k > k_1$, we have

$$W = y^{\oplus} \quad \text{and} \quad X = y^{\ominus}$$

when $R < 1$; i.e. $k < k_1$, we have

$$X = y^{\oplus} \quad \text{and} \quad W = y^{\ominus}$$

so it can be seen that in order to calculate k_1 and k , it is a prerequisite to judge whether k is larger or smaller than k_1 .

Comparison of cooling constant k with rate constant k_1

According to eqn. (6) we have

$$\Delta tk = t_1 k = R \ln R / (R - 1) \quad (20)$$

Writing

$$\tau = 1/k \quad \text{and} \quad \delta = t_1/\tau$$

where τ is known as time constant of the calorimeter, we can obtain

$$\delta = R \ln R / (R - 1) \quad (21)$$

so, δ is a function of R and its domains of definition are $(0, 1)$ and $(1, +\infty)$. We can prove that function $\delta(R)$ is a monotonic increasing function in its domains of definition, and then we have $0 < \delta < 1$ when $0 < R < 1$; and $1 < \delta < +\infty$ when $1 < R < +\infty$.

In practice, the approximate value of time constant τ (or cooling constant k) of the calorimeter is known by means of calibration. Thus we can judge whether k is larger or smaller than k_1 through comparison of the characteristic time $t_1 (= \Delta t)$ with time constant τ . If $t_1 > \tau$, then $R > 1$ and $k > k_1$. If $t_1 < \tau$, then $R < 1$ and $k < k_1$.

Finally, the rate constant k_1 can be determined with three characteristic peak-height data $(\Delta_1, \Delta_2, \Delta_3)$ according to those formulae above. This method is called the characteristic peak-height method.

Fundamental characteristics of dimensionless functions $X(R)$ and $W(R)$

From the fundamental formulae of the characteristic peak-height method for a first-order reaction, we know that the dimensionless functions $X(R)$ and $W(R)$ are the keys to calculate rate constant and cooling constant from thermogram data. It is necessary to discuss their fundamental characteristics.

Equations (8) and (15) give the domains of definition of both functions $X(R)$ and $W(R)$ as $(0, 1)$ and $(1, +\infty)$. We can prove that $X(R)$ is a monotonic decreasing function and $W(R)$ is a monotonic increasing function in the domains of definition. The domains of value of these functions are $e < X < +\infty$, $1 < W < e$ when $0 < R < 1$; and $1 < X < e$, $e < W < +\infty$ when $1 < R < +\infty$.

We can give the plots of X and W versus $\lg R$, as shown in Fig. 2, and it can be found that these two plots are fully symmetrical.

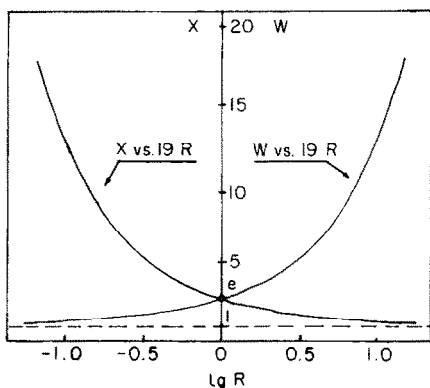


Fig. 2. Plots of X and W versus $\lg R$.

EXPERIMENTAL

Reagents

The saponifications of ethyl benzoate and ethyl acetate in aqueous alcohol were studied to test the validity of the characteristic peak-height method proposed in this paper. Chemically pure ethyl benzoate and ethyl acetate were purified under reduced pressure. The mixed solvent, 85 wt.% $\text{CH}_3\text{CH}_2\text{OH}-\text{H}_2\text{O}$, was prepared from analytically pure ethanol and deionized water. The potassium hydroxide used was of guaranteed grade and its concentration in solution was standardized with potassium hydrogen phthalate.

Apparatus

The experiments were carried out in a twin conduction calorimeter, which has been described in detail in a previous paper [8]. The heat effect of mixing, dilution, stirring and evaporation in the reacting cell can be compensated for by the same effects produced in the reference cell.

RESULTS AND DISCUSSION

If the initial concentrations of reactions are unequal and $C_0(\text{ester}) \ll C_0(\text{KOH})$, the saponification may be treated as a pseudo-first-order reaction and $k_1^* = k_2 C_0(\text{KOH})$. For the saponification of ethyl benzoate at 25.0 and 35.0°C, $\Delta t = t_1 > \tau$, so $k > k_1^*$. For the saponification of ethyl acetate at 20.0 and 30.0°C, $\Delta t = t_1 < \tau$, so $k < k_1^*$. The characteristic thermogram data, the rate constant k_1^* (and k_2) and the cooling constant k calculated with the method suggested in this paper are summarized in Tables 1 and 2 from which it may be seen that rate constants calculated with

TABLE 1
Saponification of ethyl benzoate in 85 wt. % CH₃CH₂OH-H₂O (*R* > 1) ^a

<i>T</i> /°C	No.	<i>C</i> ₀ (ester)/ mol l ⁻¹	<i>C</i> ₀ (KOH)/ mol l ⁻¹	Δ <i>t</i> /s	Δ ₁ / <i>V</i>	Δ ₂ / <i>V</i>	Δ ₃ / <i>V</i>	10 ³ <i>k</i> * ₁ /s ⁻¹	10 ³ <i>k</i> ₂ / l mol ⁻¹ s ⁻¹	10 ³ <i>k</i> /s ⁻¹
25.0	1	0.04394	0.9699	860	0.7972	0.5748	0.3478	0.642	0.662	2.24
	2	0.05126	0.9699	820	0.8698	0.6432	0.4041	0.617	0.636	2.43
	3	0.05493	0.9366	820	0.9279	0.7000	0.4437	0.615	0.657	2.31
	4	0.05126	0.9366	860	0.9027	0.6723	0.4122	0.646	0.690	2.05
	5	0.04760	0.9366	900	0.8189	0.6016	0.3651	0.625	0.667	2.01
							Average value	0.662		2.21
							Literature value [9]	0.621		
35.0	1	0.04394	0.9546	540	1.506	1.034	0.5460	1.53	1.60	2.58
	2	0.04760	0.8233	580	1.548	1.111	0.6202	1.27	1.54	2.47
	3	0.05146	0.8233	560	1.701	1.171	0.6279	1.38	1.68	2.65
	4	0.03808	0.7654	640	1.173	0.7043	0.3276	1.45	1.89	2.47
	5	0.04760	0.7654	540	1.407	1.045	0.5989	1.36	1.77	2.48
							Average value	1.70		2.53
							Literature value [9]	1.68		

^a 25.0°C: *k* = 2.09 × 10⁻³ s⁻¹, τ = 478 s; 35.0°C: *k* = 2.17 × 10⁻³ s⁻¹, τ = 461 s.

TABLE 2
Saponification of ethyl acetate in 85 wt.% CH₃CH₂OH-H₂O ($R < 1$)^a

T/°C	No.	C ₀ (ester)/ mol l ⁻¹	C ₀ (KOH)/ mol l ⁻¹	Δt/s	Δ ₁ /V	Δ ₂ /V	Δ ₃ /V	10 ³ k ₁ [*] /s ⁻¹	10 ³ k ₂ / l mol ⁻¹ s ⁻¹	10 ³ k/s ⁻¹
20.0	1	0.04516	0.8965	400	1.675	1.255	0.7576	4.05	4.52	1.49
	2	0.04516	0.8965	380	1.547	1.235	0.8069	4.36	4.87	1.31
	3	0.04086	0.8450	400	1.370	1.089	0.7118	4.23	5.01	1.23
	4	0.03656	0.7293	460	1.103	0.8274	0.5007	3.54	4.85	1.28
	5	0.03656	0.7293	380	1.359	1.076	0.6628	3.51	4.81	1.67
							Average value	4.81	4.81	1.39
							Literature value [10]	4.54		
30.0	1	0.04301	0.9140	240	2.564	1.867	1.187	9.25	10.12	1.99
	2	0.03226	0.8743	220	1.547	1.154	0.7313	9.01	10.31	2.26
	3	0.03871	0.8653	260	1.762	1.173	0.6660	8.18	9.46	2.32
	4	0.05377	0.9404	200	2.792	2.208	1.482	9.59	10.20	2.20
	5	0.04301	0.8653	200	1.727	1.515	1.112	8.57	9.90	1.81
							Average value	10.0	10.0	2.12
							Literature value [10]	10.9		

^a 20.0°C: $k = 1.93 \times 10^{-3} \text{ s}^{-1}$, $\tau = 518 \text{ s}$; 30.0°C: $k = 2.09 \times 10^{-3}$, $\tau = 478 \text{ s}$.

the method given in this paper are in fair agreement with those reported in the literature [9,10], and the cooling constants k calculated are in agreement with those determined by means of calibration, therefore demonstrating the validity of this method.

To calculate the rate constant with this novel method, it is not necessary to know the peak area [2, 4–7], the rate of temperature rise [2, 3], or the functional table of dimensionless parameters [7]. Therefore, this method can be widely applied for studies on thermokinetics of chemical and biochemical reactions.

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