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Application of thermogram reconstruction to thermokinetic studies with conduction calorimeters

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Abstract

The application of thermogram reconstruction and the reduced extent method to thermokinetic studies of chemical reactions is proposed in this paper. The reliability of this has been verified by experimental results.

INTRODUCTION

Conduction calorimeters have been largely used for thermokinetic studies [1-3]. Because of thermal inertia in the calorimeter system, the recorded thermogram, i.e. the curve of the temperature difference signal, Δ versus time t, cannot represent the true thermokinetic curve, i.e. the curve of the thermal generation rate Ω versus time t; this phenomenon is called "thermogram distortion". In order to analyse the kinetic character of the investigated change process, it is necessary to reconstruct the recorded thermogram properly. In previous studies [3, 4], many methods have been proposed for the reconstruction of the recorded thermogram into the true thermokinetic curve on the basis of theoretical models of the calorimeter systems; this is called reconstruction or deconvolution of the thermokinetic curve. Thermokinetic curves can be used to describe the kinetic behaviour of the investigated change process both precisely and vividly; they are especially suitable for studies on the thermokinetics of bacterial growth, materials engineering, etc.

However, in studies on the thermokinetics of chemical and biochemical reactions, it is not convenient to determine kinetic parameters by means of the thermokinetic curve [5, 6]. For this application, thermogram reconstruction and the reduced extent method for calculating kinetic parameters are proposed; their reliabilities are verified by experimental results.

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THEORY AND METHOD

Theoretical model of a conduction calorimeter and thermogram reconstruction

When a thermal change, for example a chemical reaction, takes place in a batch conduction calorimeter, according to Calvet and Prat [1], the relation between the input function Ω and the output function Δ can be described with Tian's equation

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

where K and Λ are the heat loss coefficient and heat capacity constant, respectively. In a recorded thermogram, Δ is the peak height at time t.

On integration of eqn. (1) with respect to t, we obtain

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

and

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

where Q is the heat liberated before time t, Q_∞ is the total heat effect, a is the peak area up to time t, and A is the total area under the thermogram.

From eqns. (1) and (2), it is apparent that the peak height Δ at time t in the recorded thermogram is proportional neither to the heat power Ω, nor to the heat effect Q; hence Δ is proportional to neither the reaction rate $\mathrm{d}x/\mathrm{d}t$ nor the reaction extent x. Therefore, it is not convenient to determine directly the kinetic parameters of a chemical reaction from the recorded thermogram.

We define

$$\bar{\Delta} = Q/\Lambda = \Delta + ka \tag{4}$$

and

$$\bar{\Delta}_\infty = Q_\infty/\Lambda = kA \tag{5}$$

where $k = K/\Lambda$, is called the cooling constant.

According to eqns. (4) and (5), a thermogram measured with a conduction calorimeter can be reconstructed into an "ideal adiabatic thermogram". This kind of processing method is called "thermogram reconstruction"; $\bar{\Delta}$ is the peak height at time t in the reconstructed adiabatic thermogram, and $\bar{\Delta}_\infty$ is the final peak height, corresponding to the end period of this adiabatic thermogram.

Thus, the adiabatic peak height $\bar{\Delta}$ at time t is proportional to the heat liberated before t, Q, and hence, it is proportional to the extent of reaction x. The slope at time t, $\mathrm{d}\bar{\Delta}/\mathrm{d}t$, is proportional to the heat generation rate Ω, and hence, it is proportional to the reaction rate $\mathrm{d}x/\mathrm{d}t$. Therefore, it is convenient to study the thermokinetics of chemical and biochemical reactions by means of the reconstructed thermogram.

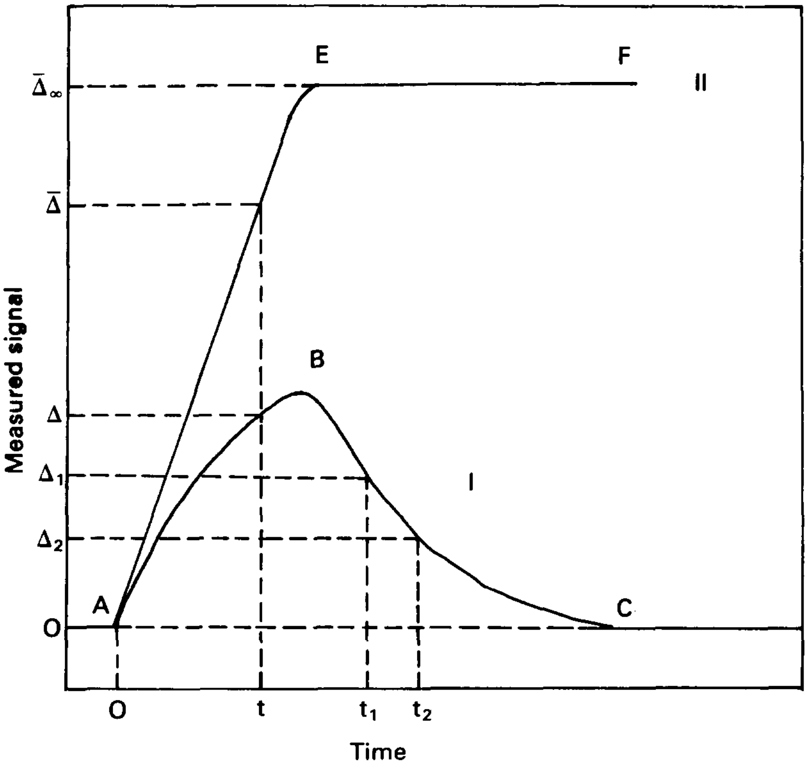

Fig. 1. Thermogram reconstruction for constant-power heating (schematic).

Determination of the cooling constant

For thermogram reconstruction, the cooling constant k is an important parameter of the calorimeter system. From eqn. (4), it can be found that the value of the cooling constant determines whether the experimental conditions approach more closely either the isothermal or the adiabatic type. The value of the cooling constant k can usually be determined from the electrical calibration.

From Newton's law of cooling

$$d\Delta/dt = -k\Delta \tag{6}$$

According to eqn. (6), it is easy to obtain

$$k = \ln(\Delta_1/\Delta_2)/(t_2 - t_1) \tag{7}$$

Thus, we can determine the cooling constant k from the data of two measured signals (Δ_1, Δ_2) in a cooling curve, as shown in Fig. 1.

Mathematical models for thermokinetics of chemical reactions

Second-order reaction with unequal initial concentrations

For a second-order reaction with unequal initial concentrations, the kinetic equation is

$$\mathrm{d}x/\mathrm{d}t = k_2(A_0 - x)(B_0 - x) \tag{8}$$

where A_0 and B_0 are the initial concentrations of the reactants, x is the extent of the reaction at time t, and k_2 is the rate constant of the second-order reaction.

If $A_0 > B_0$, we define

$$r = A_0/B_0 \tag{9}$$

and

$$K_2 = k_2(A_0 - B_0) \tag{10}$$

From eqn. (8), we obtain

$$1 - x/x_\infty = (r - 1)/[r\exp(K_2 t) - 1] \tag{11}$$

where $x_\infty = B_0$, is the final extent of reaction.

We define a dimensionless function Φ as

$$\Phi = x/x_\infty \tag{12}$$

where Φ is the ratio of reaction extent at time t to the final extent of reaction, and is called the reduced extent of reaction.

Inserting eqn. (12) into eqn. (11), we obtain

$$(r - \Phi)/(1 - \Phi) = r\exp(K_2 t) \tag{13}$$

According to the literature [7], we have

$$x/x_\infty = Q/Q_\infty \tag{14}$$

Because $\bar{\Delta}$ and $\bar{\Delta}_\infty$ are proportional to Q and Q_∞, respectively, then, from eqns. (4), (5) and (14), we have

$$\Phi = \bar{\Delta}/\bar{\Delta}_\infty \tag{15}$$

Thus Φ can be called the thermokinetic reduced extent in thermokinetics studies, and eqn. (13) is known as the thermokinetic equation of a second-order reaction with unequal initial concentrations. If we reconstruct the measured thermogram into an ideal adiabatic thermogram, according to eqn. (15) the reduced extent Φ_i at any time t_i can be determined.

Therefore, we can obtain three reduced extent values (Φ_1, Φ_2, Φ_3) from fixed time intervals, i.e. $\Delta t = t_3 - t_2 = t_2 - t_1$. According to eqn. (13), we can prove that

$$\gamma = \frac{(1-\Phi_1)(1-\Phi_2)(\Phi_3-\Phi_2)-(1-\Phi_2)(1-\Phi_3)(\Phi_2-\Phi_1)}{(1-\Phi_1)(1-\Phi_3)-(1-\Phi_2)^2}+1 \qquad (16)$$

$$k_2 = \frac{1}{(A_0-B_0)\Delta t}\ln\left[\frac{(1-\Phi_1)(\Phi_3-\Phi_2)}{(1-\Phi_3)(\Phi_2-\Phi_1)}\right] \qquad (17)$$

Equation (17) is a mathematical model for the thermokinetics of a second-order reaction with unequal initial concentrations.

Second-order reaction with equal initial concentrations

When $A_0 \to B_0$, i.e. $r \to 1$, according to eqns. (16) and (17), and to L'Hôpital's rule, it can be proved that

$$k_2 = \frac{1}{2A_0\Delta t}\frac{[(\Phi_2-\Phi_1)-(\Phi_3-\Phi_2)]^2}{(\Phi_3-\Phi_2)(\Phi_3-\Phi_1)(\Phi_2-\Phi_1)} \qquad (18)$$

Equation (18) is a mathematical model for the thermokinetics of a second-order reaction with equal initial concentrations.

First-order reaction

If $r \to \infty$ and we define $k_1^* = k_2A_0$, then, according to eqns. (16) and (17), it can be proved that

$$k_1^* = \frac{1}{\Delta t}\ln\frac{\Phi_2-\Phi_1}{\Phi_3-\Phi_2} \qquad (19)$$

Equation (19) is a mathematical model for the thermokinetics of a first-order reaction.

In the same way, mathematical models for the thermokinetics of other chemical reactions can be derived: this method of calculating kinetic parameters is called the reduced extent method.

EXPERIMENTAL

Thermogram reconstructions for constant-power heating and chemical reactions have been undertaken. The thermokinetics of the saponification of ethyl butyrate, ethyl propionate and ethyl benzoate in 85% (w/w) EtOH–H_2O have been studied with the method proposed in this paper.

Reagents

Chemically pure esters were purified further by distillation under reduced pressure. The mixed solvent 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.

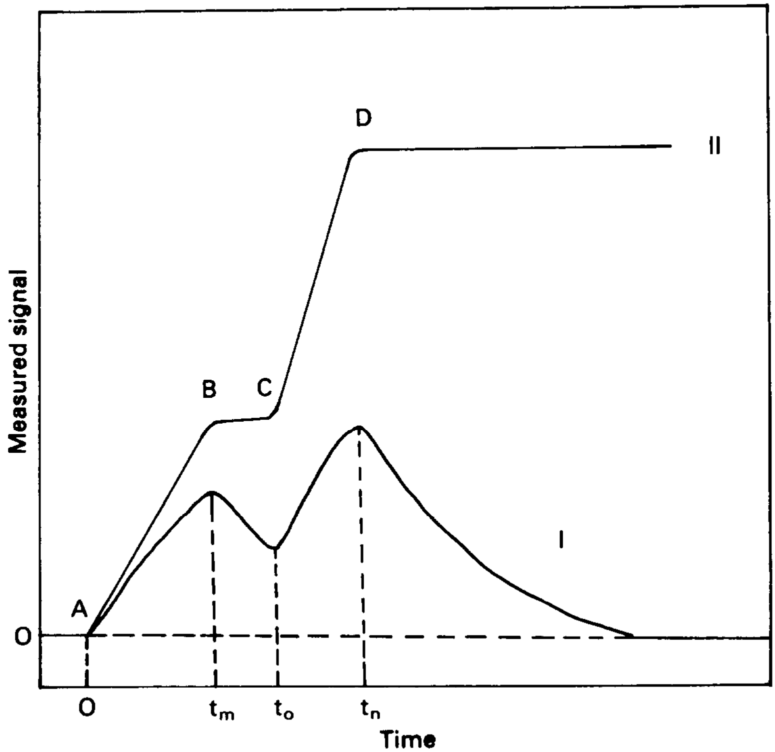

Fig. 2. Thermogram reconstruction for consecutive constant-power heating (schematic).

Apparatus

The experiments were carried out in a conduction calorimeter, which has been described in a previous article [8]. The heat effects of mixing, dilution, stirring and evaporation produced in the reacting cell of the calorimeter should be compensated with the same heat effects produced in the reference cell.

RESULTS AND DISCUSSION

Thermogram reconstruction for constant-power heating and determination of the cooling constant

As shown in Fig. 1, curve I is a recorded thermogram of constant-power heating and curve II is the ideal reconstructed adiabatic thermogram. AB in curve I is the heating period which corresponds to the main period in the reconstructed adiabatic thermogram II, i.e. the line AE, whose slope is equal to the ratio of heat power Ω_0 to the heat capacity constant Λ. BC in curve I is the cooling curve which corresponds to the end period of the recon-

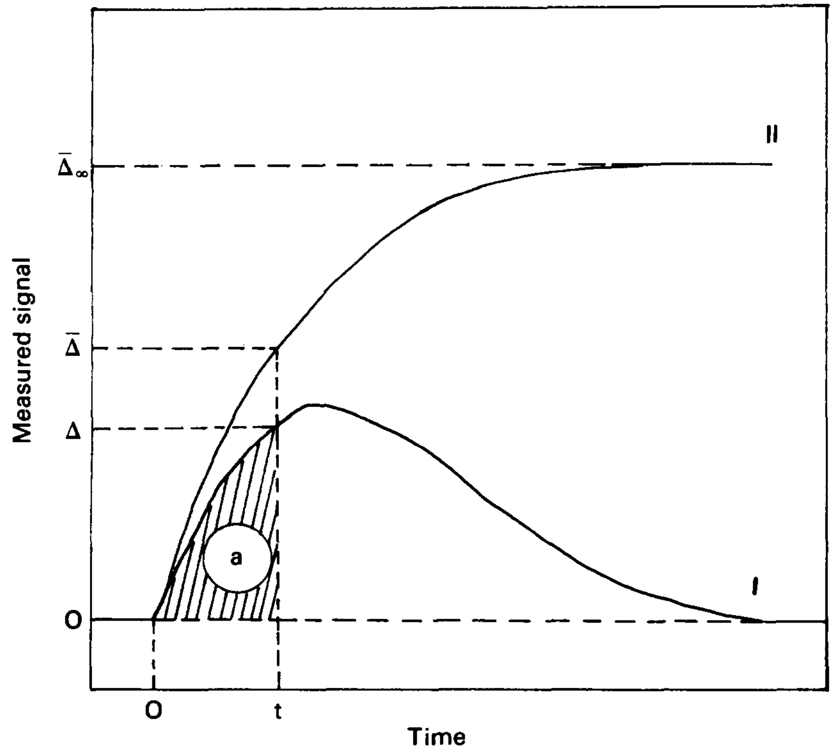

Fig. 3. Thermogram reconstruction for a chemical reaction.

structed adiabatic thermogram II, i.e. line EF, which is parallel to the time axis. According to eqn. (7), we can calculate the cooling constant k using data from two peak heights (Δ_1, Δ_2) in the cooling curve BC.

As shown in Fig. 2, the reaction cell was heated with constant power Ω_1 to time t_m and cooled to time t_0; then it was heated again with constant-power Ω_2 from t_0 to t_n, and cooled to the base line. Curve I is the recorded thermogram and curve II is the reconstructed adiabatic thermogram, in which the slopes of AB and CD are proportional to heat power Ω_1 and Ω_2 respectively.

Thermogram reconstruction for chemical reactions and studies on thermokinetics

In order to test the reliability of the application of thermogram reconstruction to thermokinetic studies of chemical reactions, three reaction systems have been studied with the conduction calorimeter. As shown in Fig. 3, curve I is a thermogram of a reaction measured with the conduction calorimeter and curve II is the reconstructed adiabatic thermogram.

For the saponification of ethyl butyrate, with A_0(KOH) > B_0(ester), this is a second-order reaction with unequal initial concentrations. After the

TABLE 1

Saponification of ethyl butyrate in 85% (w/w) $CH_3CH_2OH-H_2O$ at 30.0°C

No.	A_0(KOH)/ (mol l^{-1})	B_0(ester)/ (mol l^{-1})	$r(A_0/B_0)$	$k_2 \times 10^3$/ (l mol^{-1} s^{-1})
1	0.4812	0.0685	7.02	2.68
2	0.4812	0.0685	7.02	2.79
3	0.4430	0.0886	5.00	2.71
4	0.4430	0.0886	5.00	2.67
5	0.4647	0.1545	3.01	2.81
			Average value	2.73
			Literature value [9]	2.79

ideal adiabatic thermogram has been reconstructed from the recorded thermogram, the reduced extent Φ_i at any time t_i can be obtained, and then the rate constant can be calculated with the mathematical model for the thermokinetics of a second-order reaction with unequal initial concentrations (eqn. (17)). Experimental results are listed in Table 1, and Table 2 is an example of thermogram analysis.

For the saponification of ethyl propionate, $A_0(\text{KOH}) = B_0(\text{ester}) = C_0$; thus, this is a second-order reaction with equal initial concentrations. Experimental results are listed in Table 3, and Table 4 is an example of thermogram analysis.

For the saponification of ethyl benzoate, if $A_0(\text{KOH}) \gg B_0(\text{ester})$, this reaction may be treated as a pseudo-first-order reaction and $k_1^* = k_2 A_0$. Experimental results are listed in Table 5, and Table 6 is an example of thermogram analysis.

From these tables, it can be observed that the rate constants calculated with the methods proposed in this paper are in fair agreement with those given in the literature. Therefore, the reliability of the application of thermogram reconstruction to thermokinetic studies can be verified.

TABLE 2

Example of a thermogram analysis (No. 1 in Table 1): $A = 2976$ V s; $k = 2.091 \times 10^{-3}$ s^{-1}

i	Δ_i/V	a_i/V s	$\bar{\Delta}_i$/V	Φ_i	Data group	Δt/s	$k_2 \times 10^3$/(l mol^{-1} s^{-1})
1	1.685	473.9	2.676	0.4301	(Φ_1, Φ_2, Φ_3)	400	2.76
2	1.623	1159	4.048	0.6506	(Φ_2, Φ_3, Φ_4)	400	2.70
3	1.243	1736	4.873	0.7831	(Φ_3, Φ_4, Φ_5)	400	2.80
4	0.8662	2156	5.375	0.8638	(Φ_1, Φ_3, Φ_5)	800	2.75
5	0.5826	2441	5.690	0.9144	(Φ_2, Φ_4, Φ_6)	800	2.63
6	0.3769	2630	5.877	0.9445	(Φ_1, Φ_4, Φ_7)	1200	2.45
7	0.2345	2750	5.984	0.9617	Average value		2.68

TABLE 3

Saponification of ethyl propionate in 85% (w/w) $CH_3CH_2OH{-}H_2O$ at 30.0°C: $A_0(KOH) = B_0(ester) = C_0$

No.	$C_0/(mol\ l^{-1})$	$k_2 \times 10^3/(l\ mol^{-1}\ s^{-1})$
1	0.0970	5.29
2	0.1394	5.70
3	0.1394	5.47
4	0.1443	5.35
5	0.1443	5.40
	Average value	5.44
	Literature value [9]	5.30

TABLE 4

Example of a thermogram analysis (No. 2 in Table 3): $A = 4439$ V s; $k = 2.091 \times 10^{-3}\ s^{-1}$

i	Δ_i/V	$a_i/V\ s$	$\bar{\Delta}_i/V$	Φ_i	Data group	$\Delta t/s$	$k_2 \times 10^3/(l\ mol^{-1}\ s^{-1})$
1	1.654	289.9	2.260	0.2435	(Φ_1, Φ_3, Φ_5)	800	5.90
2	2.020	1071	4.259	0.4588	(Φ_2, Φ_4, Φ_6)	800	5.58
3	1.672	18188	5.473	0.5897	(Φ_3, Φ_5, Φ_7)	800	5.66
4	1.274	2407	6.307	0.6795	(Φ_4, Φ_6, Φ_8)	800	5.51
5	0.9645	2852	6.928	0.7464	(Φ_1, Φ_4, Φ_7)	1200	5.71
6	0.7255	3187	7.390	0.7962	(Φ_2, Φ_5, Φ_8)	1200	5.67
7	0.5640	3444	7.766	0.8367	(Φ_1, Φ_5, Φ_9)	1600	5.88
8	0.4416	3644	8.062	0.8686	Average value		5.70
9	0.3474	3802	8.296	0.8938			

TABLE 5

Saponification of ethyl benzoate in 85% (w/w) $CH_3CH_2OH{-}H_2O$ at 35.0°C

No.	$A_0(KOH)/(mol\ l^{-1})$	$B_0(ester)/(mol\ l^{-1})$	$k_1^* \times 10^3/s^{-1}$	$k_2 \times 10^3/(l\ mol^{-1}\ s^{-1})$
1	0.9546	0.0439	1.64	1.72
2	0.9546	0.0439	1.61	1.69
3	0.8233	0.0476	1.49	1.81
4	0.8233	0.0516	1.43	1.74
5	0.9934	0.0516	1.53	1.54
			Average value	1.70
			Literature value [10]	1.68

TABLE 6

Example of a thermogram analysis (No. 3 in Table 5): $A = 2476$ V s; $k = 2.170 \times 10^{-3}\ \mathrm{s}^{-1}$

i	Δ_i/V	$a_i/\mathrm{V\ s}$	$\bar{\Delta}_i/\mathrm{V}$	Φ_i	Data group	$\Delta t/\mathrm{s}$	$k_1^* \times 10^3/\mathrm{s}^{-1}$	$k_2 \times 10^3/$ $(\mathrm{l\ mol^{-1}\ s^{-1}})$
1	1.098	126.1	1.418	0.2639	(Φ_1, Φ_2, Φ_3)	400	1.56	1.89
2	1.529	719.2	3.089	0.5749	(Φ_3, Φ_4, Φ_5)	400	1.53	1.86
3	1.214	1278	3.986	0.7418	(Φ_5, Φ_6, Φ_7)	400	1.15	1.40
4	0.7908	1697	4.474	0.8291	(Φ_1, Φ_3, Φ_5)	800	1.58	1.92
5	0.5050	1937	4.709	0.8764	(Φ_3, Φ_5, Φ_7)	800	1.55	1.88
6	0.2972	2092	4.838	0.9003	(Φ_1, Φ_4, Φ_7)	1200	1.56	1.89
7	0.1773	2185	4.919	0.9154	Average value		1.49	1.81

We believe that thermogram reconstruction, combined with the reduced extent method, can be widely applied to studies on the thermokinetics of chemical and biochemical reactions, especially composite reactions, such as reversible reactions, consecutive reactions, enzyme-catalysed reactions, etc.

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