STUDIES OF THERMOKINETICS IN AN ADIABATIC CALORIMETER
II. Calorimetric curve analysis methods for irreversible and reversible reactions

S. Zhan, J. Liu*, Z. Qin and Y. Deng

Department of Chemistry, Sichuan University, Chengdu 610064, P. R. China

Abstract

Thermokinetic research methods for irreversible and reversible reactions in the adiabatic calorimeter are proposed. Four reaction systems, including an endothermic reaction, have been studied with an adiabatic calorimeter and the validity of these methods is verified.

Keywords: calorimetry, irreversible reaction, reversible reaction, thermokinetics

Introduction

One of the objectives of thermokinetics is to study chemical and biochemical reaction kinetics by calorimetry; many kinds of calorimeters have been applied for this purpose [1]. Some approaches have been made to determine rate constants of chemical and biochemical reactions with adiabatic calorimeters [2–5].

Thermokinetic research methods for first-order, second-order and reversible reactions in the adiabatic calorimeter are proposed in this paper, and their validity has been verified by the results of calorimetric analysis of some reaction systems, in the adiabatic calorimeter reported in Part I. The adiabatic calorimeter is considered suitable for thermokinetic studies of chemical and biochemical reactions.

Theory and methods

Relationships between extent of reaction and calorimetric curve peak height

Let us consider a closed adiabatic calorimeter system with constant volume, in which a homogeneous reaction is taking place at constant temperature and

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* Author to whom correspondence should be addressed.

pressure. If there are no other heat effects except the heat effect generated by the chemical reaction, and if the temperature gradients, the concentration gradients, and the change in the total capacity of the calorimeter system are small enough to be ignored while the reaction is proceeding, then the calorimetric curve peak-height Δ at time t is proportional to the extent of reaction χ, and the rate of temperature change, i.e. the slope of the calorimetric curve at time t, $(d\Delta/dt)$, is proportional to the reaction rate at time t, $(d\chi/dt)$:

$$\Delta = \lambda\chi \tag{1}$$

and

$$(d\Delta/dt) = \lambda(d\chi/dt) \tag{2}$$

where λ is the proportionality constant.

When the reaction is complete, i.e. $t \to \infty$, we have

$$\Delta_\infty = \lambda\chi_\infty \tag{3}$$

and

$$(d\Delta_\infty/dt) = 0 \tag{4}$$

where Δ_∞ is the final calorimetric curve peak-height and χ_∞ is the final extent of reaction. Equation (4) shows that when the reaction is complete, the part of a curve corresponding to this period is a line parallel to the time axis and is called the end period of the curve.

According to Eqs (1–3), we have

$$\Delta/\Delta_\infty = \chi/\chi_\infty \tag{5}$$

$$(d\Delta_\infty/dt)/\Delta_\infty = (d\chi_\infty/dt)/\chi_\infty \tag{6}$$

Equations (5) and (6) are the relationships between the extent of reaction and the curve's peak-height in the adiabatic calorimetric system.

Calorimetric curve analysis methods

Reversible reactions

A. Calorimetric equation

For reversible reactions of the type m-n, where m and n are the orders of the forward and backward reactions, if the initial concentrations of the reactants are A_o and B_o, respectively, and the initial concentrations of the products are equal

to zero, then it can be proved that they obey a general differential kinetic equation:

$$d\chi/dt = k_I(\chi_E - \chi) + k_{II}(\chi_E - \chi)^2 \qquad (7)$$

where χ_E is the extent of reaction when the reaction reaches equilibrium, i.e. $\chi_E = \chi_\infty$, and is known as the final extent of the reversible reactions, while k_I and k_{II} are called the kinetic parameters of the reversible reactions, whose values depend only on the kinetic properties and initial concentrations of the reaction systems, as shown in Table 1, where k_f and k_b are the rate constants of the forward and backward reactions, respectively.

Table 1 Expressions of the kinetic parameters k_I and k_{II} for reversible reactions

Reaction type	Kinetic equation $(d\chi/dt)$	k_I	k_{II}
2–1	$k_f(A_o - \chi)(B_o - \chi) - k_b\chi$	$k_f(A_o + B_o - 2\chi_E) + k_b$	k_f
2–2	$k_f(A_o - \chi)(B_o - \chi) - k_b\chi^2$	$k_f(A_o + B_o - 2\chi_E) + 2k_b\chi_E$	$k_f - k_b$
1–2	$k_f(A_o - \chi) - k_b\chi^2$	$k_f + 2k_b\chi_E$	$-k_b$

Next, we define a dimensionless parameter ψ as

$$\Psi = k_I/(k_{II} \chi_E) \qquad (8)$$

where $k_{II} \neq 0$. From Eqs (5–8), it can be proved that

$$\Delta = \Delta_\infty \frac{(\Psi + 1)(e^{k_I t} - 1)}{(\Psi + 1)e^{k_I t} - 1} \qquad (9)$$

Equation (9) is called the calorimetric equation of reversible reactions.

B. Calculation formulae for dimensionless parameter ψ and kinetic parameter k_I

We can obtain three peak-height data, Δ_1, Δ_2 and Δ_3, from a calorimetric curve of a reversible reaction under investigation, in a fixed time-interval, i.e. $\Delta t = t_3 - t_2 = t_2 - t_1 = $ constant, as shown in Fig. 2. And then, according to Eq. (9), we can prove that

$$\Psi = \frac{(\Delta_\infty - \Delta_1)(\Delta_3 - \Delta_2) - (\Delta_\infty - \Delta_3)(\Delta_2 - \Delta_1)}{(\Delta_\infty - \Delta_1)(\Delta_\infty - \Delta_3) - (\Delta_\infty - \Delta_2)^2} \frac{(\Delta_\infty - \Delta_2)}{\Delta_\infty} \qquad (10)$$

$$k_I = \frac{1}{\Delta t} \ln \frac{(\Delta_\infty - \Delta_1)(\Delta_3 - \Delta_2)}{(\Delta_\infty - \Delta_3)(\Delta_2 - \Delta_1)} \qquad (11)$$

From Eqs (10) and (11), we can calculate the dimensionless parameter ψ and the kinetic parameter k_I from calorimetric data (Δ_1, Δ_2, Δ_3 and Δ_∞).

C. Calculation formulae for final extent of reaction χ_E, the kinetic parameter k_{II}, the rate constant k_f and k_b, and the equilibrium constant K.

Using k_I and ψ, we can calculated the final reaction extent χ_E, as shown in Table 2, and the kinetic parameter k_{II} as shown below:

$$k_{II} = k_I/(\chi_E \Psi) \tag{12}$$

Then, the rate constants k_f and k_b can be calculated as shown in Table 2. Finally, equilibrium constant K can be obtained:

$$K = k_f \ / \ k_b \tag{13}$$

Table 2 Formulas for calculating the final reaction extent χ_E, and the rate constants, k_f and k_b

Reaction type	χ_E	k_f	k_b
2–1	$[A_o B_o/(\Psi + 1)]^{\frac{1}{2}}$	k_{II}	$k_I(A_o + B_o - 2\chi_E) \, k_{II}$
2–2	$\dfrac{A_o B_o}{(A_o + B_o)} \dfrac{(\Psi + 2)}{(\Psi + 1)}$	$\dfrac{k_I + 2k_{II} \chi_E}{(A_o + B_o)}$	$\dfrac{k_I - (A_o + B_o - 2\chi_E)K_I}{(A_o + B_o)}$
1–2	$A_o(\Psi + 2)/(\Psi + 1)$	$k_I + 2k_{II}\chi_E$	$- k_{II}$

Therefore, from Eqs (8–13) and Table 2, we can determine the rate constants and the equilibrium constant of a reversible reaction simultaneously by analysing a calorimetric curve.

Second-order reactions

For a 2–2 type or 2–1 type reversible reaction, if k_b is equal to zero, then it will actually be a second-order reaction, whose rate constant is k_2. If $A_o > B_o$ and defining

$$r = A_o/B_o \tag{14}$$

we have $\chi_E = B_o$, $k_{II} = k_f = k_2$

$$k_I = (A_o - B_o)k_2 \tag{15}$$

and

$$\Psi = r - 1 \tag{16}$$

From Eqs (10) and (16), it can be proved that

$$r = \frac{(\Delta_\infty - \Delta_1)(\Delta_3 - \Delta_2) - (\Delta_\infty - \Delta_3)(\Delta_2 - \Delta_1)}{(\Delta_\infty - \Delta_1)(\Delta_\infty - \Delta_3) - (\Delta_\infty - \Delta_2)^2} \frac{(\Delta_\infty - \Delta_2)}{\Delta_\infty} + 1 \qquad (17)$$

From Eqs (11) and (15), we can also prove that

$$k_2 = \frac{1}{(A_o - B_o)\,\Delta t} \ln \frac{(\Delta_\infty - \Delta_1)(\Delta_3 - \Delta_2)}{(\Delta_\infty - \Delta_3)(\Delta_2 - \Delta_1)} \qquad (18)$$

Equation (18) is known as the formula for determining the rate constant of a second-order reaction with unequal initial concentrations by analysing its calorimetric curve.

If $r \to 1$, then the reaction can be treated as a second-order reaction with equal initial concentrations, and from Eq. (17) we have

$$\Delta_\infty = \frac{\Delta_1\Delta_2 + \Delta_2\Delta_3 - 2\Delta_1\Delta_3}{2\Delta_2 - \Delta_1 - \Delta_3} \qquad (19)$$

and $B_o \to A_o$. Combining Eqs (18) and (19) and according to the L'hopital rule, it can be proved that

$$k_2 = \frac{1}{2A_o\,\Delta t} \ln \frac{(2\Delta_2 - \Delta_1 - \Delta_3)^2 \Delta_\infty}{(\Delta_3 - \Delta_1)(\Delta_3 - \Delta_2)(\Delta_2 - \Delta_1)} \qquad (20)$$

Equation (20) is known as the formula for determining the rate constant of a second-order reaction with equal initial concentrations by analysing its calorimetric curve.

First-order reactions

If $r \to \infty$, then the reaction can be treated as a pseudo-first-order reaction. From Eq. (17), we have

$$\Delta_\infty = \frac{\Delta_2^2 - \Delta_1\Delta_3}{2\Delta_2 - \Delta_1 - \Delta_3} \qquad (21)$$

and $(A_o - B_o) \to A_o$. Defining k_1^* as $(k_2 A_o)$, and combining Eqs (16) and (18), we obtain

$$k_1^* = \frac{1}{\Delta t} \ln \frac{\Delta_2 - \Delta_1}{\Delta_3 - \Delta_2} \qquad (22)$$

Equation (22) is known as the formula for determining the rate constant of a first-order reaction by analysing its calorimetric curve.

Experimental

Reaction systems

In order to test the reliability of the adiabatic calorimeter designed and established in our laboratory (see part I) for thermokinetic studies, and to test the validation of the calorimetric analysis methods proposed in the present paper, four reaction systems were studied: the alkaline hydrolysis of benzyl chloride, the saponification of ethyl benzoate, the proton transfer reaction between tris(hydroxymethyl)-aminomethane and nitroethane, and the esterification between acetic acid and ethanol.

All reagents were analytically or chemically pure, and the chemically pure reagents were purified by distillation under reduced pressure.

Experimental condition control and calorimetric measurements

The assembly of the calorimetric vessel, the glass-tube for injection, the gals-tube for stirring and the glass-tube for air-pressure adjustment are shown in Fig. 1. The glass-tube for stirring is connected to an air-compression micropump, which circulates once every 6 s.

Reactant solutions were made with the same solvent to eliminate the mixing heat, the initial concentration ratios of the reactant solutions were adjusted to eliminate the dilution heat, the reaction systems were stirred throughout the reaction and adiabatic compensation was applied to reduce the effect of the stirring heat to a minimum. Therefore, the heat effects (except for the reaction heat) were eliminated on the whole, and thus the recorded curve as shown in Fig. 2 is believed to be the curve of the reaction. For the experiments in this paper, the final temperature changes of the calorimetric system were about 0.10~0.20°C.

Results and discussion

Alkaline hydrolysis of benzyl chloride

The alkaline hydrolysis of benzyl chloride in 80% (v/v) DMSO–H_2O is a second-order reaction, of first order in each reactant. If benzyl chloride is present in large excess, this reaction may be treated as a pseudo-first-order reaction and $k_1^* = k_2 C_o$ (benzyl chloride).

The calculated results at 20.0°C are summarized in Table 3, and Table 4 presents an example of the calorimetric analysis. These results shown that the calculated values of the rate constant k_2 are self-consistent for a single curve and
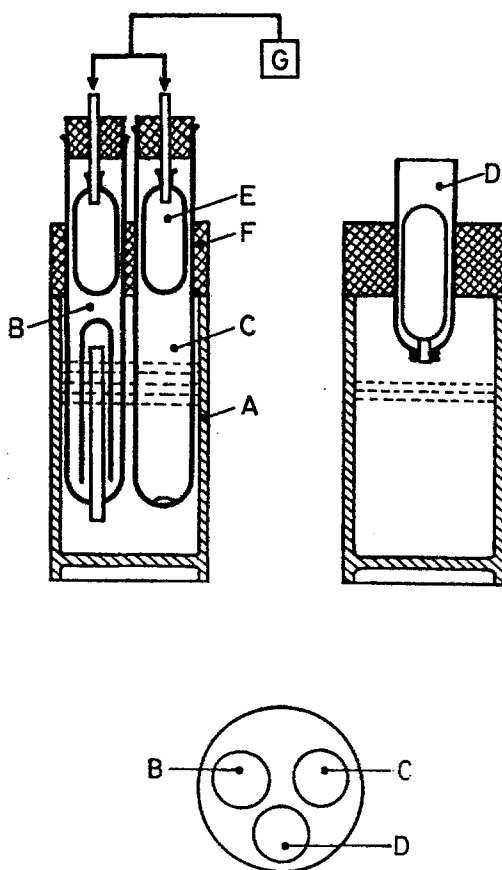
Fig. 1 Assembly of calorimeter vessel, injection tube, stirring tube and air-pressure adjust-
ing tube. A. calorimeter vessel; B. glass-tube for injection; C. glass-tube for stirring;
D. glass-tube for air-pressure adjustment; E. balloon; F. connecting tube; G. air-com-
pression pump

reproducible for various curves, and the average value is in fair agreement with
that given in the literature [6]. Therefore, the validity of the curve analysis
method for first-order reactions should be tested.

Saponification of ethyl benzoate

The saponification of ethyl benzoate in 50% (v/v) $CH_3CH_2OH-H_2O$ is a
second-order reaction. The calculated results at 25.0°C are summarized in Ta-
ble 5, and the correctness of the calorimetric analysis method for second-order
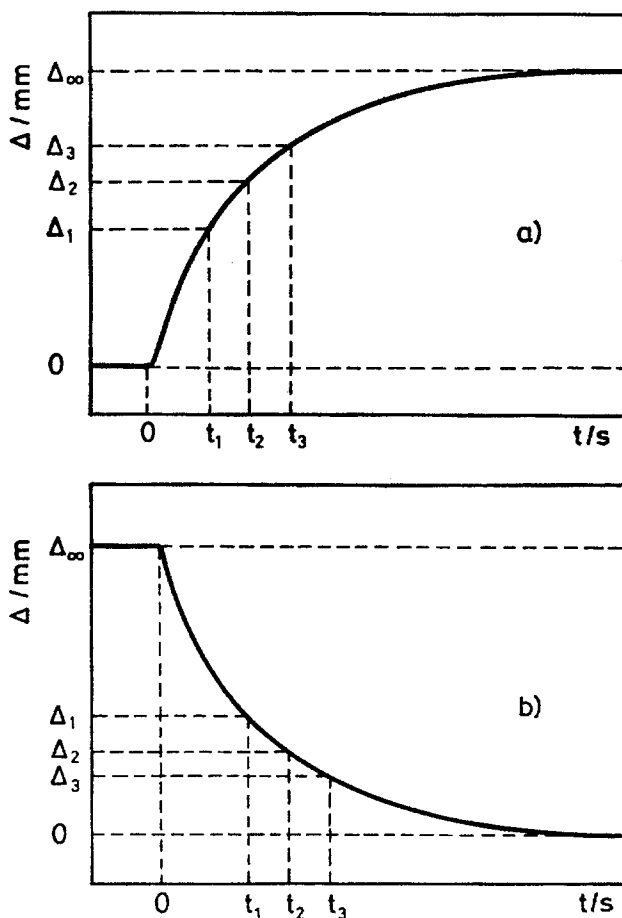reactions should be demonstrated.

Fig. 2 Calorimetric curve of an exothermic reaction (a); Calorimetric curve of an endother-
mic reaction (b)

Proton transfer reaction between tris(hydroxymethyl)aminomethane and nitroethane

The proton transfer reaction between Tris and nitroethane in water ($\mu = 1.0$) is a 2–2 type reversible reaction. The calculated results are summarized in Table 6. The calculated values of the rate constants of the forward and backward reactions (k_f and k_b) are in fair agreement with those given in literature [8], and thus the validity of the calorimetric analysis method for reversible reactions has been verified.

Table 3 Rate constant of alkaline hydrolysis of benzyl chloride (solvent: 80% DMSO–H_2O; T: 25.0°C; $k_1^* = k_2A_0$)

No.	A_0 (benzyl chloride)/ mol l^{-1}	B_0(KOH)/ mol l^{-1}	$10^4 k_1^*$/ s^{-1}	$10^3 k_2$/ l mol^{-1} s^{-1}
1	0.2820	0.0124	3.42	1.22
2	0.2820	0.0124	3.38	1.20
3	0.3139	0.0124	3.84	1.22
4	0.3318	0.0138	4.09	1.24
5	0.3454	0.0124	4.20	1.22
			average value:	1.22
			literature value [6]	1.27

Table 4 Example of thermogram analysis (No.5 in Table 1)

Δ_1/ mm	Δ_2/ mm	Δ_1/ mm	Δ_1/ s	$10^4 k_1^*$ s^{-1}	$10^3 k_2$/ l mol^{-1} s^{-1}
93.3	118.9	134.5	1200	4.13	1.20
107.1	127.8	140.0	1200	4.41	1.28
118.9	134.5	144.1	1200	4.05	1.17
93.3	127.8	144.1	1800	4.17	1.21
				average value:	1.22

Table 5 Rate constant of saponification of ethyl benzoate (solvent: 85% $CH_3CH_2OH-H_2O$; T: 25.0°C; $r = A_0/B_0$

No.	A_0(ester)/ mol l^{-1}	B_0(KOH)/ mol l^{-1}	r	$10^3 k_2$/ l $mol^{-1}s^{-1}$
1	0.4006	0.0691	5.80	1.32
2	0.4302	0.0737	5.83	1.36
3	0.4476	0.0766	5.84	1.33
4	0.4512	0.0766	5.89	1.40
5	0.4512	0.0765	5.90	1.36
			average value:	1.35
			literature value [7]:	1.32

Esterification between acetic acid and ethanol

The esterification between acetic acid and ethanol was undertaken in 0.5 M H_2SO_4 solution. As water is present in large excess, this reaction system can be

Table 6 Rate constants of reaction between Tris. and nirtoethane (solvent: H_2O, $\mu = 1.0$; T: 30.0°C)

No.	A_o(nitroethane)/ mol l^{-1}	B_o(Tris.)/ mol l^{-1}	$10^3 k_f$ l mol^{-1} s^{-1}	$10^2 k_b$ l mol^{-1} s^{-1}
1	0.1450	0.1386	5.76	0.944
2	0.1692	0.1691	5.98	1.37
3	0.1933	0.1918	5.83	1.03
4	0.2174	0.2164	5.93	1.13
5	0.2416	0.2528	5.76	1.01
		average value:	5.85	1.09
		literature value [8]:	5.20	0.93

Table 7 Rate constants of acid-catalyzed esterification between acetic acid and ethanol (solvent: H_2O; T; 30.0°C)

No.	A_o(ethanol)/ mol l^{-1}	B_o(acetic acid)/ mol l^{-1}	$10^3 k_f$/ l mol^{-1} s^{-1}	$10^4 k_b$ s^{-1}
1	1.32	1.31	1.42	3.41
2	1.40	1.40	1.53	3.58
3	1.50	1.49	1.47	3.52
4	1.60	1.60	1.25	3.31
5	1.70	1.70	1.27	3.40
		average value:	1.39	3.44

treated as a 2–1 type reversible reaction. Further, this reaction is an endothermic reaction and its curve is recorded as shown in Fig. 2b. The calculated results at 30.0°C are presented in Table 7.

The rate constants of the acid-catalysed esterification of a fatty acid are much affected by the experimental conditions, and especially by the solvent and the catalyst. Under the experimental conditions applied in this paper, the values of the rate constants of the forward and backward reactions were not found in the literature. For the backward reaction, i.e. the acid-catalysed hydrolysis, the hydrolysis property of ethyl acetate is similar to that of methyl acetate [9], and the value of the rate constant of the hydrolysis of methyl acetate under the same experimental conditions as in this work, which was reported in [10], is close to the value measured in this work. Therefore, the calculated results in this work may be believed, and the adiabatic calorimeter designed in our laboratory should be suitable for thermokinetic studies of endothermic reactions.

In conclusion, the thermokinetics of two irreversible reaction systems and two reversible reaction systems have been studied with the adiabatic calorime-

ter. The calorimetric analysis methods proposed in this paper are valid and this calorimeter can be used to study the thermokinetics of both endothermic and exothermic reactions. This calorimeter and these research methods can be widely applied to studies on the thermokinetics of chemical and biochemical reactions.

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