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Studies on the thermokinetics of reversible reactions

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Abstract

Some new mathematical models of reversible reacton kinetics, using which both rate constants and equilibrium constants can be calculated simultaneously, are suggested and a reduced-extent method for studies of thermokinetics of reversible reactions is proposed. In the light of these models, two reversible reaction systems have been studied using a conduction calorimeter. The rate constants and equilibrium constants calculated are in fair agreement with those given in the literature.

INTRODUCTION

One of the objects of thermokinetics is to study chemical reaction kinetics by calorimetry. Because of high sensitivity possible in calorimetric measurements, it can be used to study very many chemical reactions involving enthalpy change, even at fairly high dilutions. Calorimetry should be applicable to reactions of any kind in any solvent irrespective of the spectral, electrochemical, or other properties of the substances involved. Because of these advantages, thermokinetics has received increasing attention from calorimetricists, chemists, biologists and others. Many reports [1–8] have been presented since 1908, when Duclaux first investigated the kinetics of a chemical reaction using a calorimeter. But most have been confined to studies of reactions with simple orders. It is much more difficult to obtain the kinetic parameters of composite reactions by analysing their thermograms, because they have two or more kinetic parameters. Only recently has some attempt been made to resolve this [9, 10].

Reversible reactions are a particular type of composite reaction. In this paper, a general kinetic equation for several kinds of reversible reaction has been deduced, and some new mathematical models for calculating both rate

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constants and the equilibrium constant are suggested. A reduced-extent method for studies of thermokinetics is first reported. We also present the analyses of thermogram data obtained from studies of two reversible reaction systems applying this method. The validity of this method and the correctness of its theoretical basis have been verified by the results.

THEORETICAL

The general kinetic equation of reversible reactions

For a homogeneous closed system with a constant volume, in which a 2–2-type reversible reaction is taking place, the kinetic equation is

$$\frac{dx}{dt} = k_f(A_0 - x)(B_0 - x) - k_b x^2 \tag{1}$$

where x is the extent of reaction, k_f and k_b are the rate constants of the forward and backward reactions respectively, and A_0 and B_0 are the initial concentrations of the reactants.

When the reaction is complete, i.e. $dx/dt = 0$, $x = x_E$ and eqn. (1) becomes

$$k_f(A_0 - x_E)(B_0 - x_E) = k_b x_E^2 \tag{2}$$

From eqns. (1) and (2) we can prove that

$$\frac{dx}{dt} = k_I(x_E - x) + k_{II}(x_E - x)^2 \tag{3}$$

and

$$\frac{dx}{dt} = k_{II}(x_E - x)(r x_E - x) \tag{4}$$

where

$$k_I = k_f(A_0 + B_0 - 2x_E) + 2k_b x_E \tag{5}$$

$$k_{II} = k_f - f_b \tag{6}$$

$$r = k_I/(k_{II} x_E) + 1 \qquad (k_I \neq 0) \tag{7}$$

Likewise, we can prove that the kinetic equations of other types of reversible reactions can be expressed similarly to eqns. (3) and (4), but with

TABLE 1

Expressions of k_I and k_II for reversible reactions

Reaction type	Rate equation (dx/dt)	k_I	k_II
2–1	$k_f(A_0-x)(B_0-x)-k_bx$	$k_f(A_0+B_0-2x_E)+k_b$	k_f
2–2	$k_f(A_0-x)(B_0-x)-k_bx^2$	$k_f(A_0+B_0-2x_E)+2k_bx_E$	k_f-k_b
1–2	$k_f(A_0-x)-k_bx^2$	$k_f+2k_bx_E$	$-k_b$

different expressions for k_I and k_II, as shown in Table 1. The terms k_I and k_II are the kinetic parameters of reversible reactions, having dimensions of first-order and second-order rate constants respectively. They depend only on the kinetic properties and the initial conditions of the investigated reaction system.

Equation (3) or (4) can then be defined as the general differential equation of reversible reactions.

Integrating eqn. (4) with respect to time t, we obtain

$$\frac{x_E-x}{x_E}=\frac{r-1}{r\exp(k_\mathrm{I}t)-1} \tag{8}$$

Now we define

$$\Phi=\frac{x}{x_E} \tag{9}$$

where Φ is the ratio of the extent of reaction at time t to that at equilibrium and can be called the reduced extent of reaction at time t.

Then, eqn. (8) becomes

$$\frac{r-\Phi}{1-\Phi}=r\exp(k_\mathrm{I}t) \tag{10}$$

where eqn. (10) is the general reduced-extent equation of reversible reactions.

The thermokinetic equation of reversible reactions

When a chemical reaction takes place in a batch conduction calorimeter, the rate of heat production Ω can be calculated using Tian's equation [11]

$$\Omega=K\Delta+\Lambda(\mathrm{d}\Delta/\mathrm{d}t) \tag{11}$$

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

Integrating eqn. (11) with respect to time t

$$Q = Ka + \Lambda\Delta \tag{12}$$

$$Q_\infty = KA \tag{13}$$

where Q is the heat produced before time t, Q_∞ is the total heat effect, a is the peak area before time t and A is the total area under the curve.

We have demonstrated previously [12, 13] that

$$\frac{x}{x_\mathrm{E}} = \frac{Q}{Q_\infty} \tag{14}$$

From eqns. (9) and (14), we obtain

$$\Phi = \frac{Q}{Q_\infty} \tag{15}$$

In the batch conduction calorimetric system, according to eqns. (12), (13) and (15) we can say that

$$\Phi = \frac{ka + \Delta}{kA} \tag{16}$$

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

Thus Φ can be called the thermokinetic reduced extent in thermokinetic studies and may be regarded as a synthetic thermogram parameter. And eqn. (10) can be called the thermokinetic equation of reversible reactions.

Mathematical models of reversible reactions

For a reacting system, if the reduced extent of reaction at any time t_i can be measured, we can obtain three sets of data (Φ_1, Φ_2, Φ_3) at fixed time intervals, $\Delta t = t_3 - t_2 = t_2 - t_1$.

According to eqn. (10), we can prove that

$$k_\mathrm{I} = \frac{1}{\Delta t} \ln \frac{(1 - \Phi_1)(\Phi_3 - \Phi_2)}{(1 - \Phi_3)(\Phi_2 - \Phi_1)} \tag{17}$$

$$r = \frac{(1 - \Phi_1)(1 - \Phi_2)(\Phi_3 - \Phi_2) - (1 - \Phi_2)(1 - \Phi_3)(\Phi_2 - \Phi_1)}{(1 - \Phi_1)(1 - \Phi_3) - (1 - \Phi_2)^2} + 1 \tag{18}$$

From Table 1 and eqn. (7), we can calculate the final reaction extent x_E (see

TABLE 2

Formulae for calculating the final reaction extent, the rate constants and equilibrium constants

Reaction type	x_E	k_f	k_b	K
2–1	$\left(\frac{A_0B_0}{r}\right)^{1/2}$	k_{II}	$k_I-(A_0+B_0-2x_E)k_{II}$	$\frac{x_E}{(A_0-x_E)(B_0-x_E)}$
2–2	$\frac{A_0B_0}{(a_0+B_0)}\frac{(r-1)}{r}$	$\frac{k_I+2k_{II}x_E}{A_0+B_0}$	$\frac{k_I-(A_0+B_0-2x_E)k_{II}}{A_0+B_0}$	$\frac{x_E^2}{(A_0-x_E)(B_0-x_E)}$
1–2	$A\frac{(r+1)}{r}$	$k_I+2k_{II}x_E$	$-k_{II}$	$\frac{x_E^2}{(A_0-x_E)}$

Table 2) and the kinetic parameter k_{II}

$$k_{II}=\frac{k_I}{(r-1)x_E} \tag{19}$$

Finally, both rate constants and the equilibrium constant can be calculated from k_I, k_{II} and x_E (see Table 2).

According to eqns. (17), (18), (19) and Table 1, both rate constants and the equilibrium constant can be calculated simultaneously from an experimental thermogram.

EXPERIMENTAL

Reaction systems

Two proton-transfer reaction systems were studied to test the correctness of the models and the validity of this reduced-extent method. The reagents used were analytically pure. The mixed solvent was prepared from analytically pure ethanol and deionized water.

Calorimeter

The experiments were carried out in a conduction calorimeter whose constructional details have been reported previously [14]. The heat effects of mixing, dilution, stirring and evaporation were compensated with the same effects produced in the reference cell.

RESULTS AND DISCUSSION

The cooling constant k of calorimeter was measured by electrical calibration. After the reaction thermogram has been recorded with the conduction calorimeter, the data of the synthetic thermogram parameter

TABLE 3

Experimental results for the reaction between nitroethane and Tris in water ($\mu = 1.0$) at 30.0°C [a]

No.	A_0 [b] (mol l^{-1})	B_0 [b] (mol l^{-1})	x_E (mol l^{-1})	$k_f \times 10^3$ (l mol^{-1} s^{-1})	$k_b \times 10^3$ (l mol^{-1} s^{-1})	K
1	0.2801	0.2803	0.120	5.04	8.96	0.565
2	0.2662	0.2523	0.110	4.69	8.61	0.546
3	0.2028	0.1869	0.0847	5.34	8.99	0.598
4	0.2028	0.1869	0.0830	5.62	10.1	0.556
5	0.2028	0.1869	0.0821	5.09	9.54	0.534
Average				5.16	9.24	0.560
Literature				5.2	9.3	0.56

[a] $k = 1.813 \times 10^{-3}$ s^{-1}. [b] A_0 = Tris, B_0 = nitroethane.

Φ_i at any time t_i can be obtained from eqn. (16), and then the rate constants and equilibrium constant can be calculated with the reduced-extent method proposed in this paper. The experimental conditions and calculated results are given in Tables 3–6.

The results show that the calculations of the rate constants and equilibrium constants are quite reproduceable and self-consistent. For the

TABLE 4

Example of thermogram analysis (No. 1) [a]

Δ_i (V)	a_i (V s)	Φ_i	Δt (s)	x_E (mol l^{-1})	$k_f \times 10^3$ (l mol^{-1} s^{-1})	$k_b \times 10^3$ (l mol^{-1} s^{-1})	K
3.893	616.4	0.5356					
4.435	1036	0.6747	100.0	0.118	4.89	9.20	0.532
4.540	1488	0.7735					
4.223	819.8	0.6102					
4.532	1261	0.7287	100.0	0.117	4.84	9.50	0.510
4.472	1714	0.8122					
3.894	616.4	0.5356					
4.511	1171	0.7087	130.0	0.120	5.06	8.89	0.569
4.472	1759	0.8188					
4.041	695.8	0.5667					
4.525	1216	0.7190	120.0	0.124	5.32	8.38	0.635
4.472	1759	0.8188					
3.970	655.7	0.5513					
4.511	1171	0.7087	120.0	0.121	5.10	8.83	0.578
4.492	1714	0.8122					
			Average	0.120	5.04	8.96	0.565

[a] $A = 5161$ (V s).

TABLE 5

Experimental results for the reaction between 2-nitropropane and morpholine in 40% (v:v) EtOH/H_2O

T (°C)	No.	A_0 [a] (mol l^{-1})	B_0 [a] (mol l^{-1})	x_E (mol l^{-1})	$k_t \times 10^3$ (l mol^{-1} s^{-1})	$k_b \times 10^4$ (l mol^{-1} s^{-1})	K
25.0 [b]	1	0.3067	0.3381	0.2441	4.21	4.16	10.12
	2	0.2629	0.2898	0.2067	4.36	4.77	9.19
	3	0.2454	0.2705	0.1924	4.15	4.64	8.94
	4	0.2191	0.2416	0.1740	4.78	4.82	10.04
	5	0.1928	0.2116	0.1524	4.77	4.93	9.69
				Average	4.45	4.66	9.59
30.0 [b]	1	0.2191	0.2416	0.1609	5.49	9.96	5.51
	2	0.1928	0.2116	0.1411	5.67	10.4	5.45
	3	0.1753	0.1924	0.1259	5.38	11.1	4.84
	4	0.1578	0.1443	0.1005	5.09	12.6	4.03
	5	0.1314	0.1208	0.0864	5.64	11.8	4.78
				Average	5.45	11.2	4.92

[a] A_0 = 2-nitropropane, B_0 = morpholion. [b] 25.0°C: $k = 1.882 \times 10^{-3}$ s^{-1}; 30.0°C: $k = 1.861 \times 10^{-3}$ s^{-1}.

reaction between nitroethane and Tris, the calculated value of the rate constants and equilibrium constant are in fair agreement with those in the literature [15]. Therefore, it can serve as a check on the mathematical models in this paper.

TABLE 6

Example of thermogram analysis (No. 2 at 25.0°C) [a]

Δ_i (V)	a_i (V s)	Φ_i	Δt (s)	x_E (mol l^{-1})	$k_i \times 10^3$ (l mol^{-1} s^{-1})	$k_b \times 10^4$ (l mol^{-1} s^{-1})	K
1.378	2020	0.7732					
1.270	2151	0.7941	100.0	0.2038	4.14	5.06	8.18
1.169	2272	0.8128					
1.915	1015	0.5710					
1.869	1204	0.6173	100.0	0.2070	4.42	4.78	9.25
1.795	1386	0.6574					
1.598	1724	0.7231					
1.378	2020	0.7732	200.0	0.2102	4.54	4.31	10.53
1.169	2272	0.8128					
1.915	1015	0.5710					
1.795	1386	0.6574	200.0	0.2057	4.36	4.95	8.80
1.598	1724	0.7231					
			Average	0.2067	4.36	4.77	9.19

[a] A = 3559 (V s)

For the reaction between 2-nitropropane with morpholine, the changes in the values of the rate constants and equilibrium constants following changes in temperature are in conformity with the laws of kinetics and thermodynamics respectively. The activation energies of the forward and backward reactions are 30 kJ mol^{-1} (E_f) and 130.6 kJ mol^{-1} (E_b) respectively. This is in agreement with the experimental observation that in reactions that have large heat effects, E_f is much less than E_b. Compared with the rate constant of the reaction between nitroethane and morpholine [15], the results calculated in this paper should be correct considering the kinetic acidity of the nitroalkanes [16].

CONCLUSION

The correctness of the mathematical models for reversible reaction kinetics and the validity of the reduced-extent method for thermokinetics are verified by the results in this paper.

From the general differential equation, eqns. (3) and (4), we found that a reversible reaction can be regarded as a parallel reaction mixed with a first-order and second-order reaction, or a second-order reaction with unequal initial concentrations. This idea of regarding a composite reaction as a simple order reaction or the composition of several simple order reactions is very interesting and useful in studies of chemical kinetics.

The models suggested in this paper, using both rate constants and the equilibrium constant of a reversible reaction which can be calculated simultaneously, are simple and have clear physical sense. It is obvious that the reduced-extent method can be applied extensively to studies of chemical kinetics and thermokinetics.

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