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Thermo-kinetic time-parameter method for reversible reactions

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Abstract

According to the theoretical basis of thermo-kinetics, a novel thermo-kinetic research method, the time-parameter method for reversible reactions, has been proposed in this paper. The rate constants of forward and backward reactions and equilibrium constant can be calculated from the same thermoanalytical curve simultaneously with this method. In order to test the validity of this method, the proton-transfer reactions of nitroethane with ammonia at 15 and 25°C, and with Tris at 15 and 30°C have been studied, respectively. The results of rate constants and equilibrium constants calculated with this method are in agreement with those in the literature. Therefore, the time-parameter method for the reversible reaction is believed to be correct. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermo-kinetics; Thermo-kinetic research method; Time-parameter method; Reversible reactions

1. Introduction

In the previous article [1], based on the fundamental theory of thermo-kinetics and regarding time as a known parameter, the time-parameter method for simple-order reactions was suggested and applied to study thermo-kinetics for several kinds of simple-order reactions successfully. In practice, many chemical and biochemical reactions are composite, which usually have two or more kinetic parameters, and consequently, it is necessary to develop thermo-kinetic research methods applicable to these composite reactions.

Reversible reactions form a particular class of composite reactions. It would be useful to establish a thermo-kinetic research method applicable to reversible reactions. So far, several thermo-kinetic research methods for reversible reactions have been reported [2–4]. Of these, the mathematical model of the reduced-extent method [2] was much more complex and there existed a lower degree of precision in evaluating the kinetic parameter. In the dimensionless parameter method for reversible reactions [3], the kinetic parameter must be calculated from two thermo-analytical curves, which is inconvenient for users. In order to enrich the thermo-kinetic research method and enlarge the applicable range of the time-parameter method, mathematical models for the time-parameter method for reversible reactions have been established in this paper. Only needing the characteristic time parameter t_m and the thermo-analytical data corresponding to t_m and $2t_m$ from the same curve, both rate constants and the equilibrium constant can be determined simultaneously. The validation of the theory and method of the time-parameter method for reversible reactions is verified by experimental results.

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2. Theory and method

2.1. Thermo-kinetic equation of reversible reactions

For a homogeneous closed system with a constant volume, in which an *m–n* type reversible reaction is taking place, the general kinetic equation [2] is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1(x_\mathrm{E} - x) + k_2(x_\mathrm{E} - x)^2 \tag{1}$$

where x is the extent of reaction at time t, x_E is the final extent of reaction. k_1 and k_2 are the kinetic parameters of reversible reactions, here having dimensions of first-order and second-order reaction rate constants, respectively. They depend on the kinetic properties and the initial conditions of the reaction systems investigated. For the different types of reversible reactions, k_1 and k_2 have different expressions (as shown in Table 1). We define

$$r = \frac{k_1}{k_2 x_\mathrm{E}} + 1 \tag{2}$$

From Eqs. (1) and (2), we find

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_2(x_\mathrm{E} - x)(r x_\mathrm{E} - x) \tag{3}$$

Integrating Eq. (3) with respect to time t, we obtain

$$\frac{x_\mathrm{E} - x}{x_\mathrm{E}} = \frac{r-1}{r\mathrm{e}^{k_1 t} - 1} \tag{4}$$

Eq. (4) is called the integral kinetic equation of reversible reactions.

When an *m–n* type reversible reaction is taking place in the batch conduction calorimeter, according to Tian's equation [5], the thermo-kinetic transformation equation [6] and Eq. (4), it can be proved that the thermo-kinetic equation for reversible reactions can be described as

$$\frac{a^*}{A} - \frac{\Delta}{kA} = \frac{r-1}{r\mathrm{e}^{k_1 t} - 1} \tag{5}$$

where k is the cooling constant of thermo-kinetic system. α^* is the peak area after time t, Δ is the peak height at time t, and A is the total area under the curve.

2.2. Mathematical model of time-parameter method for reversible reactions

We define

$$R = \frac{Q_\infty - Q}{Q_\infty} \tag{6}$$

where R is the ratio of the heat evolved after time t to the total heat evolved by the reaction studied.In the previous article [1], we have proved that

$$\frac{Q_\infty - Q}{Q_\infty} = \frac{a^*}{A} - \frac{\Delta}{kA} \tag{7}$$

So from Eqs. (5)–(7), it follows that

$$\frac{r - 1 + R}{rR} = \mathrm{e}^{k_1 t} \tag{8}$$

t_m is the time corresponding to the maximum peak height Δ_m of the curve, which is called the characteristic time parameter. When $t = t_\mathrm{m}$ and $t = 2t_\mathrm{m}$, we can get R_m and $R_{2\mathrm{m}}$ using the corresponding thermoanalytical data according to Eqs. (6) and (7).

Therefore, from Eq. (8), we have

$$\frac{r - 1 + R_\mathrm{m}}{rR_\mathrm{m}} = \mathrm{e}^{k_1 t_\mathrm{m}} \tag{9}$$

$$\frac{r - 1 + R_{2\mathrm{m}}}{rR_{2\mathrm{m}}} = \mathrm{e}^{2k_1 t_\mathrm{m}} \tag{10}$$

From Eqs. (9) and (10), it can be proved that

$$r = \frac{R_{2\mathrm{m}}(1 - R_\mathrm{m})^2}{R_{2\mathrm{m}} - R_\mathrm{m}^2} \tag{11}$$

$$k_1 = \frac{1}{t_\mathrm{m}} \ln \frac{R_\mathrm{m} - R_{2\mathrm{m}}}{R_{2\mathrm{m}}(1 - R_\mathrm{m})} \tag{12}$$

Table 1
Expressions of k_1 and k_2 for reversible reactions

Reaction type *m–n*	Rate equation (d*x*/d*t*)	k_1	k_2
2–1	$k_\mathrm{f}(A_0 - x)(B_0 - x) - k_\mathrm{b}x$	$k_\mathrm{f}(A_0 + B_0 - 2x_\mathrm{E}) + k_\mathrm{b}$	k_f
2–2	$k_\mathrm{f}(A_0 - x)(B_0 - x) - k_\mathrm{b}x^2$	$k_\mathrm{f}(A_0 + B_0 - 2x_\mathrm{E}) + 2k_\mathrm{b}x_\mathrm{E}$	$k_\mathrm{f} - k_\mathrm{b}$
1–2	$k_\mathrm{f}(A_0 - x) - k_\mathrm{b}x^2$	$k_\mathrm{f} + 2k_\mathrm{b}x_\mathrm{E}$	$-k_\mathrm{b}$

Table 2
Formulae for calculating x_E, k_f, k_b and K

Reaction type	x_E	k_f	k_b	K
2–2	$(A_0B_0(1+r))/((A_0+B_0)r)$	$(k_1+2x_Ek_2)/(A_0+B_0)$	$(k_1-(A_0+B_0-2x_E)k_2)/(A_0+B_0)$	$x_E^2/(A_0-x_E)(B_0-x_E)$
2–1	$((A_0B_0)/r)^{1/2}$	k_1	$k_1-(A_0+B_0-2x_E)k_2$	$x_E/(A_0-x_E)(B_0-x_E)$
1–2	$(A_0(1+r))/r$	$k_1+2x_Ek_2$	$-k_2$	$x_E^2/(A_0-x_E)$

Eqs. (11) and (12) are the mathematical models for the time-parameter method for reversible reactions. From Eq. (2), we have

$$k_2 = \frac{k_1}{(r-1)x_E} \tag{13}$$

For an *m–n* type reversible reaction, the formula for calculating x_E is proved easily (see Table 2). Finally, both rate constants of the forward reaction and the backward reaction, k_f and k_b, respectively, and the equilibrium constant K can be calculated from k_1, k_2 are x_E (see Table 2).

3. Experimental

3.1. Reaction system

In order to test the time-parameter method for reversible reactions, the thermo-kinetics of the reaction systems shown below have been studied:

- Pseudo-1–2 type reversible reaction: proton transfer reaction between nitroethane and Tris in 1 mol l^{-1} KCl solution at 30°C. If $C_0(\text{Nitro}) > C_0(\text{Tris})$, $k_f^* = k_fC_0(\text{Nitro})$.
- 2–2 type reversible reaction: proton transfer reaction between nitroethane and ammonia in water at 15 and 25°C. Proton transfer reaction between nitroethane and Tris in 1 mol l^{-1} KCl solution at 15 and 30°C.

3.2. Reactants

Chemically pure nitroethane was purified further by distillation under reduced pressure. The other reactants were analytically pure. The solutions of reactants and potassium chloride were prepared in deionized water by mass. The concentration of the ammonia solution was standardized with potassium hydrogenphthalate.

3.3. Apparatus

All the thermoanalytical curves of the above-mentioned reactions were measured with a twin conduction calorimeter, which has been described in detail in the previous article [7]. The data for thermoanalytical curves were sampled, recorded, and analyzed by computer.

4. Results and discussion

The cooling constants of the reaction systems studied were determined by using electrical calibration. After the thermoanalytical curve has been measured, R_m and R_{2m} can be obtained from the themoanalytical data at times t_m and $2t_m$, respectively, and then the rate constants and the equilibrium constant can be calculated according to the time-parameter method for reversible reactions. The experimental results for the systems studied here are given in Tables 3–5.

From Tables 3–5, it can be seen that the rate constants and equilibrium constants calculated by this novel method are in agreement with those in the literature. The experimental results indicate that the mathematical models of the time-parameter method for reversible reactions are correct.

From Tables 4 and 5, it can be seen that, with increasing temperature, the rate constants of both the forward reaction and the backward reaction of the reactions studied increase, but the equilibrium constants decrease, which are in conformity with the laws of kinetics and thermodynamics.

The time-parameter method for reversible reactions proposed in this paper is a simple mathematical model and has a concise form of expression. Only needing

Table 3
Experimental results for the reaction between nitroethane and Tris in 1 mol l^{-1} KCl solution at 30°C[a]

A_0 (mol l^{-1})	B_0 (mol l^{-1})	R_m	R_{2m}	t_m (s^{-1})	$10^3k_f^*$ (s^{-1})	10^3k_f (l mol^{-1}s^{-1})	10^3k_b (l mol^{-1}s^{-1})	K
0.4000	0.03289	0.3599	0.1236	418	2.07	5.18	9.46	0.548
0.4097	0.02302	0.3707	0.1330	406	2.17	5.30	9.43	0.562
0.4204	0.02302	0.3362	0.1299	396	2.26	5.38	9.36	0.574
0.4204	0.02631	0.3629	0.1270	399	2.23	5.30	9.36	0.566
0.5000	0.03289	0.3315	0.1145	370	2.60	5.21	9.32	0.559
					Average:	5.27	9.39	0.562
					[8]	5.20	9.30	0.560

[a] A_0: nitroethane, B_0: Tris.

Table 4
Experimental results for the reaction between nitroethane and ammonia in water at 15 and 25°C[a]

T (°C)	A_0 (mol l^{-1})	B_0 (mol l^{-1})	R_m	R_{2m}	t_m (s^{-1})	10^3k_f (l mol^{-1} s^{-1})	10^4k_b (l mol^{-1} s^{-1})	K
15	0.3028	0.1557	0.5210	0.2989	1018	2.19	1.96	11.2
	0.3028	0.2115	0.5195	0.3032	988	2.23	2.01	11.1
	0.3114	0.1557	0.5182	0.2960	970	2.28	2.00	11.4
	0.3114	0.2018	0.5152	0.2983	964	2.27	2.05	11.1
	0.3114	0.3028	0.5068	0.2953	900	2.22	1.85	12.0
					Average:	2.24	1.97	11.4
					[8]	2.35	1.98	11.9
25	0.2104	0.2523	0.4399	0.2238	755	3.92	5.92	6.62
	0.2171	0.2422	0.4468	0.2297	746	3.90	6.17	6.32
	0.2215	0.2523	0.4295	0.2170	722	4.07	5.97	6.82
	0.2326	0.3028	0.4268	0.2118	650	4.07	6.02	6.76
	0.2481	0.3028	0.4207	0.2074	624	4.26	6.19	6.88
					Average:	4.04	6.05	6.68
					[8]	4.00	6.03	6.63

[a] A_0: nitroethane, B_0: ammonia.

Table 5
Experimental results for the reaction between nitroethane and Tris in 1 mol l^{-1} KCl solution at 15 and 30°C[a]

T (°C)	A_0 (mol l^{-1})	B_0 (mol l^{-1})	R_m	R_{2m}	t_m (s^{-1})	10^3k_f (l mol^{-1} s^{-1})	10^3k_b (l mol^{-1} s^{-1})	K
15	0.1858	0.2092	0.5092	0.2678	1269	1.58	0.926	1.71
	0.1859	0.1933	0.5120	0.2711	1295	1.61	0.923	1.74
	0.2143	0.2282	0.4904	0.2486	1200	1.57	0.946	1.66
	0.2392	0.2245	0.4955	0.2534	1143	1.54	0.942	1.63
	0.2990	0.2807	0.4819	0.2398	1005	1.45	0.904	1.60
					Average	1.55	0.928	1.67
					[9]	1.51	0.917	1.65
30	0.0933	0.1667	0.4384	0.1842	496	5.19	9.36	0.554
	0.0989	0.0879	0.4802	0.2226	592	5.53	9.45	0.585
	0.1111	0.1120	0.4472	0.1920	547	5.45	9.44	0.577
	0.1307	0.1333	0.4233	0.1710	505	5.27	9.41	0.560
	0.1519	0.1525	0.4169	0.1658	450	5.23	9.27	0.564
					Average	5.33	9.39	0.568
					[10]	5.20	9.30	0.560

[a] A_0: nitroethane, B_0: Tris.

the thermoanalytical data for the characteristic time parameters t_m and $2t_m$ from a single thermoanalytical curve, both rate constants (k_f and k_b) and the equilibrium constant K can be obtained simultaneously, which is convenient for users. This not only applies when studying known reversible reactions, but also for unknown reversible reactions. For an unknown reversible reaction, the reaction type can be determined heuristically, and then the kinetic parameter can be calculated with the above mathematical model.

The characteristic time t_m is an important parameter in our method. Its value depends on the reaction type and kinetic parameter of the reaction studied. For different reactions, the characteristic time parameters and corresponding thermoanalytical data are different. Our novel method only need t_m and thermoanalytical data corresponding to t_m and $2t_m$ to calculate the kinetic parameters of a reversible reaction, and hence, the precision in evaluating the kinetic parameters of our method depends on the accurate determination of t_m. In general, t_m is obtained from the measured thermoanalytical curve directly. So the distortion degree of the measured curve owing to thermal inertia will lead to an experimental error in kinetic evaluation. For a slower reaction, the thermal delay will decrease, and the influence of distortion can be neglected. But for a faster reversible reaction, the distortion degree of the measured curve will obviously increase. In this case, the measured curve must be modified by the method proposed in the previous paper [11] before kinetic evaluation.

For the reaction between nitroethane and Tris in $1\ \mathrm{mol\,l^{-1}}$ KCl solution at 30°C, the value of rate constants (k_f and k_b) calculated with our method and other methods in the literature [2,12], the root-mean-square errors and relative errors for experimental results obtained according to the theory of error are

k_f: $(5.27 \pm 0.05) \times 10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$, 1.3%; $(5.16 \pm 0.35) \times 10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$, 0.77% [2]; $(5.36 \pm 0.13) \times 10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$, 3.0% [12].
k_b: $(9.39 \pm 0.06) \times 10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$, 1.0%; $(9.24 \pm 0.58) \times 10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$, 0.65% [2]; $(9.44 \pm 0.14) \times 10^{-3}\ \mathrm{l\,mol^{-1}\,s^{-1}}$, 1.5% [12].

It can be seen that the relative errors of three methods are less than 3.0% and the kinetic parameters calculated with these methods are in fair agreement with those in the literature [8]. However, the root-mean-square errors with the time parameter method are obviously smaller than those obtained with the other methods. Therefore, the degree of precision in calculating kinetic parameters with our novel method will increase.

Eq. (1) is the general kinetic equation for an m–n reversible reaction. For different types of reactions, k_1 and k_2 in Eq. (1) have different expressions. However, for a 1–1 type reversible reaction, k_2 is equal to 0, and then, $r \rightarrow \infty$; therefore, the thermo-kinetic equation for reversible reaction and the mathematical models of the time-parameter method established in this paper are not suitable for the 1–1 type reversible reaction.

As stated above, the time-parameter method for reversible reactions further enriches and perfects the thermo-kinetic research method. It can be applied to investigations of the thermo-kinetics for both chemical and biochemical reactions.

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