

CHARACTERISTIC PARAMETER METHOD FOR STUDYING KINETICS OF OPPOSING REACTIONS IN CALORIMETER

Y. Chen^{1*}, H. Yan¹, B. Zhang¹ and X. C. Zeng²

¹Department of Applied Oil Engineering, Logistical Engineering University, Chongqing 400016, P. R. China

²Department of Chemistry, Sichuan University, Chengdu 610064, P. R. China

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Abstract

According to the theoretical basis of thermokinetics, the integral and differential thermokinetic equations of opposing reactions have been derived, and a novel thermokinetic research method, the characteristic parameter method for opposing reactions which taking place in a batch conduction calorimeter under isothermal condition, has been proposed in this paper. Only needing the characteristic thermoanalytical data corresponding to t_m and $2t_m$ from the same curve, the rate constants of forward and backward reactions and equilibrium constant can be calculated 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 trihydroxymethyl aminomethane (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 characteristic parameter method for opposing reaction is believed to be correct.

Keywords: calorimetry, characteristic parameter method, opposing reactions, thermokinetics

Introduction

The calorimeter is an important tool for the thermokinetic investigation and has been applied widely to study reaction involving thermal change processes in many fields [1–8]. When a chemical reaction was taking place in a batch conduction calorimeter, the thermoanalytical curve measured with a calorimeter implies kinetic and thermodynamic information that the reaction has. It is an important aim of the thermokinetics to establish a research method for obtaining such valuable information. In our previous article [9, 10], based on the fundamental theory of thermokinetics and regarding time as a known parameter, the time-parameter method for simple order reactions and consecutive first order reaction were suggested and applied to study

* Author for correspondence: E-mail: cydoc@sohu.com

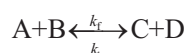
thermokinetics for several kinds of simple order reactions and consecutive reactions successfully.

Opposing reactions form a particular class of composite reactions. Owing to the complexity of the thermokinetic equation of opposing reaction, it is very difficult to determine the rate constants of forward and backward reactions and equilibrium constant simultaneously. So far, several thermokinetic research methods for opposing reactions have been reported [11–13]. Of these, the mathematical model of the reduced-extent method [11] was much more complex and there existed a lower degree of precision in evaluating the kinetic parameter. In the dimensionless parameter method for opposing reactions [12], the kinetic parameter must be calculated from two thermoanalytical curves, which is inconvenient for users. In order to enrich and perfect the thermokinetic research method for opposing reactions, the integral and differential thermokinetic equations of opposing reaction have been derived, and the mathematical models of the characteristic parameter method for opposing reactions have been established in this paper. Needing only the characteristic time parameter t_m and $2t_m$ and corresponding thermoanalytical data from the same curve, both rate constants and equilibrium constant can be determined simultaneously. The validation of the theory and method of the characteristic parameter method for opposing reactions is verified by the experimental results.

Theory and method

Thermokinetic equation for opposing reactions

When 2-2 type opposing reaction which behavior can be written as follows is taking place in a homogeneous closed system with a constant volume



its rate equation is

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

where x is the extent of reaction at time t , A_0 and B_0 are the initial concentrations of reactant A and B, k_f and k_b are the rate constants of forward and backward reactions, respectively.

When $t \rightarrow \infty$ and then $dx/dt=0$, $x=x_E$, from Eq. (1), we have

$$k_f(A_0 - x_E)(B_0 - x_E) = k_b x_E^2 \quad (2)$$

where x_E is the final extent of reaction.

From Eqs (1) and (2), it can be proved that

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

where

$$k_I = k_f(A_0 + B_0 - 2x_E) + 2k_b x_E \quad (4)$$

$$k_{II} = k_f - k_b \quad (5)$$

k_I and k_{II} are called as the kinetic parameters of 2-2 type opposing reaction, here having dimensions of first-order and second-order reaction rate constants respectively.

Derived in the same way as stated above, it can be proved that Eq. (3) can also be suitable for 1-2 type or 2-1 type opposing reactions, in which k_I and k_{II} have different expressions (as shown in Table 1).

We define

$$\beta = \frac{k_{II} x_E}{k_I} \quad (6)$$

Table 1 Expressions of k_I and k_{II} for opposing reactions

Reaction type $m-n$	Rate equation (dx/dt)	k_I	k_{II}
2-2	$k_f(A_0-x)(B_0-x) - k_b x^2$	$k_f(A_0 + B_0 - 2x_E) + 2k_b x_E$	$k_f - k_b$
2-1	$k_f(A_0-x)(B_0-x) - k_b x$	$k_f(A_0 + B_0 - 2x_E) + k_b$	k_f
1-2	$k_f(A_0-x) - k_b x^2$	$k_f + 2k_b x_E$	$-k_b$

From Eqs (3) and (6), it follows that

$$\frac{dx}{dt} = k_{II}(x_E - x) \left(\frac{1+\beta}{\beta} x_E - x \right) \quad (7)$$

Integrating Eq. (7) with respect to time t , we obtain

$$\frac{x_E - x}{x_E} = \frac{1}{(1+\beta)e^{k_I t} - \beta} \quad (8)$$

Differentiating Eq. (8) with respect to time t , we get

$$\frac{dx/dt}{x_E} = \frac{k_I(1+\beta)e^{k_I t}}{[(1+\beta)e^{k_I t} - \beta]^2} \quad (9)$$

If the calorimeter is regarded as a uniform, isotropic body of homogeneous temperature that changes only with time t , the dynamic properties of a calorimetric system can be described by Tian's equation [14], and then we have

$$\Omega = K\Delta + \Lambda \frac{d\Delta}{dt} \quad (10)$$

where Ω is the thermal power of reaction, Δ is the peak height of thermoanalytical curve at time t , K and Λ are the coefficient of heat losses and the effective capacity of the calorimetric system. On integrating Eq. (10) with respect to time t , we get

$$Q = Ka + \Lambda \Delta \quad (11)$$

$$Q_{\infty} = KA \quad (12)$$

Rearrangement of Eqs (10)–(12) leads to

$$\frac{Q_{\infty} - Q}{Q_{\infty}} = \frac{a^*}{A} - \frac{\Delta}{kA} \quad (13)$$

$$\frac{\Omega}{Q_{\infty}} = \frac{\Delta}{A} + \frac{(d\Delta/dt)}{kA} \quad (14)$$

where Q and Q_{∞} are the heat evolved before time t and the total heat evolved by the reaction studied respectively, a and a^* are the peak areas before and after time t respectively, and $A = a + a^*$, which is the total area under the curve, $k (= K/\Lambda)$ is called the cooling constant of thermokinetic system.

When an opposing reaction is taking place in a batch conduction calorimeter under isothermal conditions, it is well known that the relationship between the reaction rate (dx/dt) and the thermal power of reaction (Ω) can be described as

$$\Omega = \frac{dx}{dt} V \Delta H \quad (15)$$

where ΔH is the molar enthalpy of this reaction and V is the reaction volume.

On integrating Eq. (15) with respect to time t , we obtain

$$Q = xV\Delta H \quad (16)$$

$$Q_{\infty} = x_E V \Delta H \quad (17)$$

Then, from Eqs (15)–(17), it can be proved that

$$\frac{Q_{\infty} - Q}{Q_{\infty}} = \frac{x_E - x}{x_E} \quad (18)$$

$$\frac{\Phi}{Q_{\infty}} = \frac{dx/dt}{x_E} \quad (19)$$

So, from Eqs (8), (9) and Eqs (18), (19), it turns to

$$\frac{a^*}{A} - \frac{\Delta}{kA} = \frac{1}{(1+\beta)e^{k_1 t} - \beta} \quad (20)$$

$$\frac{\Delta}{A} + \frac{(d\Delta/dt)}{kA} = \frac{k_1(1+\beta)e^{k_1 t}}{[(1+\beta)e^{k_1 t} - \beta]^2} \quad (21)$$

Equations (20) and (21) are the integral and differential thermokinetic equations of opposing reactions.

Mathematical models of characteristic parameter method for opposing reactions

We define

$$R = \frac{Q_\infty - Q}{Q_\infty} \quad (22)$$

where R is the ratio of the heat evolved after time t to the total heat evolved by the reaction studied, and then from Eqs (13) and (20), we get

$$(1+\beta)e^{k_1 t} = \frac{1+\beta R}{R} \quad (23)$$

On inserting Eq. (23) into Eq. (21) and defining $r = \Phi/Q_\infty$, it follows that

$$k_1 = \frac{r}{R + \beta R^2} \quad (24)$$

The time corresponding to the maximal peak height of the curve, t_m , is called as the characteristic time parameter of thermoanalytical curve. When $t = t_m$ and $t = 2t_m$, we can get R_m , R_{2m} , r_m , and r_{2m} using the corresponding thermoanalytical data. Therefore, from Eq. (24), it can be proved that

$$\beta = \frac{R_{2m} r_m - R_m r_{2m}}{R_m^2 r_{2m} - R_{2m}^2 r_m} \quad (25)$$

$$k_1 = \frac{r_m}{R_m + \beta R_m^2} = \frac{r_{2m}}{R_{2m} + \beta R_{2m}^2} \quad (26)$$

From Eq. (6), we obtain

$$k_{II} = \frac{k_1 \beta}{x_E} \quad (27)$$

Equations (25), (26) and (27) are the mathematical models of the characteristic parameter method for determination of the kinetic parameter β , k_1 and k_{II} of opposing reactions.

For an m - n type opposing reaction, the formula for calculating x_E , k_p , k_b and K can be derived easily according to Table 1, which are listed in Table 2.

In the previous paper [10], we have proved that the formulae to determine values of R and r at characteristic time t_m and $2t_m$ using the corresponding thermoanalytical data are

$$R_m = \frac{a_m^*}{A} - \frac{\Delta_m}{kA}, \quad r_m = \frac{\Delta_m}{A} \quad (28)$$

$$R_{2m} = \frac{a_{2m}^*}{A} - \frac{2\Delta_m}{e k A}, \quad r_{2m} = \frac{\Delta_m}{e A} \left(2 - \frac{1}{k t_m} \right) \quad (29)$$

where e is the base of natural logarithm.

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

Reaction type	x_E	k_f	k_b	K
2-2	$\frac{A_0 B_0 (1+2\beta)}{(A_0 + B_0)(1+\beta)}$	$\frac{k_1 + 2x_E k_{II}}{A_0 + B_0}$	$\frac{k_1 - (A_0 + B_0 - 2x_E)k_{II}}{A_0 + B_0}$	$\frac{x_E^2}{(A_0 - x_E)(B_0 - x_E)}$
2-1	$\left(\frac{A_0 B_0 \beta}{1+\beta}\right)^{\frac{1}{2}}$	k_1	$k_1 - (A_0 + B_0 - 2x_E)k_{II}$	$\frac{x_E}{(A_0 - x_E)(B_0 - x_E)}$
1-2	$\frac{A_0(1+2\beta)}{1+\beta}$	$k_1 + 2x_E k_{II}$	$-k_{II}$	$\frac{x_E^2}{(A_0 - x_E)}$

Therefore, after the thermoanalytical curve has been measured, the values of R_m , R_{2m} , r_m and r_{2m} are calculated according to Eqs (28) and (29), and then the kinetic parameter β , k_1 and k_{II} , the rate constants of forward reaction k_f and backward reactions k_b , and the equilibrium constant can be determined easily.

Experimental

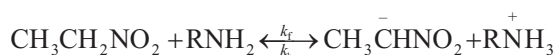
Reaction system

In order to test the characteristic parameter method for opposing reactions, the thermokinetics of the reaction systems shown below have been studied:

- Proton transfer reactions of nitroethane with ammonia in water at 15 and 25°C
- Proton transfer reactions of nitroethane with trihydroxymethyl aminomethane (Tris) in 1 mol L⁻¹ KCl solution at 15 and 30°C
- Proton transfer reactions of nitroethane with trihydroxymethyl aminomethane (Tris) in 1 mol L⁻¹ KCl solution at 30°C when nitroethane is excess reactant.

The reaction equation of proton transfer reactions of nitroethane with ammonia and Tris is given below

(ammonia, $R=H$; Tris, $R=C(CH_2OH)_3$)



Thus, it is regarded as the 2-2 type opposing reaction. If nitroethane is excessive reactant, i.e. $C_0(\text{Nitro}) \gg C_0(\text{Tris})$, it can be treated as the pseudo-1-2 type opposing reaction, and then $k_f^* k_f C_0(\text{Nitro})$.

Reactants

Chemically pure nitroethane was obtained from Chongqing Chemicals Co. (China) and purified further by distillation under reduced pressure. Analytically pure ammonia, trihydroxymethyl aminomethane (Tris) and potassium chloride were purchased from Shanghai Chemicals Co. (China). The solutions of reactants were prepared in

deionized water by mass. The concentration of the ammonia solution was standardized with potassium hydrogenphthalate (Chongqing Chemicals Co.).

Measurement of thermoanalytical curves

All the thermoanalytical curves of the reaction systems mentioned above were measured with a batch conduction calorimeter, whose basic construction was similar to that of the Calvet calorimeter [15]. Two equal systems (reaction cell and reference cell) were placed into an isothermal block according to the twin principle. The effects of mixing, dilution, stirring and evaporation in the reaction cell should be compensated for by the corresponding effects produced in the reference cell. The thermoanalytical data were collected and recorded by a computer and the measured curves were printed out.

Results and discussion

The cooling constants of reaction systems studied were determined by using electrical calibration. After the thermoanalytical curve had been measured, R_m , R_{2m} , r_m and r_{2m} can be obtained from the thermoanalytical data at times t_m and $2t_m$ respectively and then the rate constants and equilibrium constant can be calculated via the mathematical models of the characteristic parameter method for opposing reactions. The experimental results 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 results show that calculations are reproducible and self-consistent. Therefore, the characteristic parameter method for opposing reactions is believed to be correct.

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

The thermokinetic equations of opposing reactions are much more complex than those of simple order reactions, and so it is more difficult to determine the rate constants of forward and backward reactions simultaneously by analyzing the thermoanalytical curve. In the reduced extent method and the dimensionless parameter method for opposing reactions, the mathematical models were established only according to the integral thermokinetic equation, and hence they were much more complex to determine the kinetic parameter. The same as the thermokinetic time parameter method for consecutive first-order reaction [10], the mathematical models to calculating the kinetic parameter of our novel method reaction are established according to the integral and differential thermokinetic equations, which are concise and need a little computing effort and work.

The kinetic parameters of opposing reactions taking place in a calorimeter can also be determined by fitting the thermoanalytical curve to the corresponding analytical expressions directly. However, for the different reaction systems and the same re-

Table 3 Experimental results for the reaction between nitroethane and Tris at 30°C*

$A_0/$ mol L^{-1}	$B_0/$ mol L^{-1}	R_m	R_{2m}	$10^4 r_m/$ s^{-1}	$10^4 r_{2m}/$ s^{-1}	$10^3 k_r/$ s^{-1}	$10^3 k_f/$ $\text{L mol}^{-1} \text{s}^{-1}$	$10^3 k_b/$ $\text{L mol}^{-1} \text{s}^{-1}$	K
0.033	0.390	0.360	0.124	9.06	3.20	2.07	5.31	9.36	0.567
0.035	0.410	0.345	0.115	9.19	3.14	2.19	5.34	9.29	0.575
0.023	0.410	0.371	0.133	9.28	3.39	2.18	5.32	9.48	0.561
0.023	0.420	0.366	0.130	9.46	3.42	2.27	5.40	9.25	0.584
0.026	0.420	0.363	0.127	9.44	3.37	2.23	5.31	9.42	0.564
						average	5.34	9.36	0.570
						literature value	5.20	9.30	0.560 [16]

* A_0 = Tris, B_0 = nitroethane

Table 4 Experimental results for the reaction between nitroethane and ammonia at 15 and 25°C*

$T/$ °C	$A_0/$ mol L ⁻¹	$B_0/$ mol L ⁻¹	R_m	R_{2m}	$10^4 r_m/$ s ⁻¹	$10^4 r_{2m}/$ s ⁻¹	$10^3 k_p/$ L mol ⁻¹ s ⁻¹	$10^4 k_p/$ L mol ⁻¹ s ⁻¹	K
15	0.301	0.150	0.521	0.297	3.21	1.64	2.36	1.91	12.4
	0.301	0.192	0.519	0.302	3.19	1.61	2.38	1.98	12.0
	0.346	0.150	0.518	0.296	3.71	1.92	2.36	2.10	11.2
	0.346	0.192	0.515	0.298	3.51	1.80	2.25	2.13	10.6
	0.346	0.240	0.513	0.290	3.65	1.77	2.37	2.16	11.0
					average		2.34	2.06	11.4
					literature value		2.35	1.98	11.9 [17]
25	0.4210	0.253	0.440	0.224	4.23	1.89	3.91	5.91	6.62
	0.217	0.242	0.447	0.230	4.28	1.93	3.94	6.06	6.50
	0.222	0.253	0.429	0.217	4.40	1.95	4.14	6.16	6.72
	0.230	0.303	0.427	0.212	4.90	2.13	4.11	5.81	7.07
	0.248	0.303	0.421	0.207	5.15	2.22	4.24	6.26	6.77
					average		4.07	6.04	6.74
					literature value		4.00	6.03	6.63 [17]

* A_0 =nitroethane, B_0 =ammonia

Table 5 Experimental results for the reaction between nitroethane and Tris at 15 and 30°C*

$T/$ °C	$A_0/$ mol L ⁻¹	$B_0/$ mol L ⁻¹	R_m	R_{2m}	$10^4 r_m/$ s ⁻¹	$10^4 r_{2m}/$ s ⁻¹	$10^3 k_f/$ L mol ⁻¹ s ⁻¹	$10^3 k_b/$ L mol ⁻¹ s ⁻¹	K
15	0.186	0.193	0.512	0.271	2.57	1.31	1.63	0.915	1.78
	0.186	0.205	0.509	0.268	2.52	1.28	1.54	0.890	1.73
	0.214	0.228	0.490	0.249	2.81	1.38	1.57	0.930	1.69
	0.239	0.225	0.496	0.253	2.98	1.47	1.56	0.937	1.66
	0.299	0.281	0.483	0.240	3.40	1.64	1.45	0.891	1.63
					average		1.55	0.913	1.70
					literature value		1.51	0.917	1.65 [18]
30	0.093	0.067	0.488	0.231	5.12	2.50	5.28	9.03	0.585
	0.099	0.088	0.480	0.223	6.09	2.92	5.48	9.43	0.581
	0.111	0.112	0.447	0.192	6.77	3.00	5.48	9.41	0.582
	0.131	0.133	0.423	0.171	7.45	3.11	5.31	9.32	0.570
	0.152	0.153	0.417	0.166	8.39	3.45	5.21	9.29	0.561
					average		5.35	9.30	0.575
					literature value		5.20	9.30	0.560 [16]

* A_0 =nitroethane, B_0 =Tris

action with different initial concentrations of reactants, the analytical expressions are different, which is inconvenient for users. In contrast to the direct fit method, the mathematical methods of our novel method (Eqs (25)–(27)) have been derived from Tian equation and the general kinetic equations of opposing reactions, which have universality in the thermokinetic investigation for different reaction systems. Only needing the thermoanalytical data at the characteristic time parameters t_m and $2t_m$ from the same curve, both rate constants (k_f and k_b) and equilibrium constant can be obtained simultaneously, which simplify greatly the kinetic analyzing procedure. This not only applies when studying known opposing reactions, but also for unknown opposing reactions. For an unknown opposing reaction, the reaction type can be determined heuristically, and then the kinetic parameter can be calculated with the above mathematical models.

For the reaction between nitroethane and Tris in 1 mol L⁻¹ KCl solution at 30°C, the root-mean-square errors and relative errors for the values of rate constants (k_f and k_b) calculated with our method and other methods in literatures [11, 19] are given as follow according to the theory of error:

$$k_f: (5.34 \pm 0.04) \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}, 0.52\%; (5.16 \pm 0.35) \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}, 0.77\% [11]; \\ (5.36 \pm 0.13) \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}, 3.0\% [19].$$

$$k_b: (9.36 \pm 0.09) \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}, 0.77\%; (9.24 \pm 0.58) \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}, 0.65\% [11]; \\ (9.44 \pm 0.14) \cdot 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}, 1.5\% [19].$$

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 [16]. However, the root-mean-square errors with the characteristic 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.

Equation (3) is the general kinetic equation for an m-n opposing reaction. For different types of reactions, k_f and k_{II} in Eq. (3) have different expressions. However, for a 1-1 type opposing reaction, k_{II} is equal to zero, and then $r \rightarrow 0$. Therefore, the thermokinetic equation for opposing reaction and the mathematical models of the characteristic parameter method established in this paper are not suitable for 1-1 type opposing reaction.

As stated above, the characteristic parameter method for opposing reactions further enriches and perfects the thermokinetic research method. It can be applied to investigations of the thermokinetics for both chemical and biochemical reactions.

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