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Thermo-kinetic research method for faster reactions: modifier method of distorted thermoanalytical curve

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Abstract

Due to the thermal delay of calorimeter, the measured thermoanalytical curve was distorted. A method to modify the distorted thermoanalytical curve into the real thermoanalytical curve from which the kinetic parameter can be obtained directly has been established in this paper. The theoretical equation for calorimeter, in which the delay of sensing has been considered, and the thermo-kinetic research method for faster reactions, namely the modifier method of distorted thermoanalytical curve, have been suggested. The thermo-kinetics of a few faster reaction systems has been studied with this method and the validity of the theory and method has been verified by the experimental results.

Keywords: Thermo-kinetics; Thermo-kinetic research method; Delay of sensing; Modifier method of distorted thermoanalytical curve; Faster reaction

1. Introduction

The conduction calorimeter is an important tool for the thermo-kinetic investigation and has been applied widely to study reactions involving thermal change processes in many fields. However, owing to thermal inertia, the thermal delay of calorimetric elements, especially the delay between the temperature sensor and the reaction system, which is called the delay of sensing, the measured thermoanalytical curve is delayed and distorted [1], and hence the recorded curve is unable to represent the real thermal change process correctly. Therefore, it is an important step to correct or modify the distortion in order to obtain the kinetic information using calorimetric measurement.

So far, several corrected methods have been proposed. Of these, the correction procedures of the measured curve of the methods based on the convolution theory [2,3] were much more complex and the assumption of zero initial condition in some case made the thermo-kinetic reconstruction difficult or impossible. In the method based on the multi-body theory [4], the physical sense of many parameters of calorimetric system are not defined clearly and the determination of these parameter are also difficult. Additionally, all these methods reconstruct the output thermoanalytical curve into the input heat power curve, which is not convenient to obtain the kinetic parameter, and so they are not of good applicability in

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the studies of thermo-kinetics of faster chemical reactions.

In our previous article [5], the method to reconstruct the conduction thermoanalytical curve into the adiabatic curve was suggested on the basis of the double-parameter theoretical model of the conduction calorimeter. But the reconstruction procedure was complex and there existed the lower degree of precision in the mathematical model to calculate the kinetic parameters. In order to enrich and perfect the thermo-kinetic research method for faster reactions, based on thermal balance equation of calorimetric system, the theoretical equation of the conduction calorimeter, in which the delay of sensing has been considered, is suggested in this paper, and the method to modify the distorted curve into the ideal real thermoanalytical curve which can be suitable for treatment, by Tian equation [6], is established, and a thermo-kinetic research method for faster reactions, namely the modifier method of distorted thermoanalytical curve, with which the kinetic parameter can be obtained directly from the modified thermoanalytical curve, is proposed. The validation of the theory and method is verified by the experimental results.

2. Theory and method

2.1. Theoretical equation of the conduction calorimeter considered the delay of sensing

When a thermal change course takes place in the conduction calorimeter, according to the heat balance equation and Fourier equation of heat conduction, it can be proved that

$$\frac{\Phi}{\epsilon_1} = C_1\theta_R + \frac{d\theta_R}{dt}, \tag{1}$$

where Φ is the rate of heat generation, ϵ_1 the effective heat capacity, C_1 the cooling constant of calorimetric system, and θ_R represents the temperature rise of reaction system at time t.

We define that θ_{S0} is the response temperature rise of the sensor at time t under the ideal condition in which the delay of sensing can be neglected, and then

$$\theta_R = \theta_{S0}. \tag{2}$$

Supposing

$$\Delta_0 = g\theta_{S0}, \tag{3}$$

where Δ_0 is the voltage signal produced by the sensor, i.e. the peak height of thermoanalytical curve at time t under the ideal condition and g is the proportional constant.

Therefore,

$$\theta_R = \frac{\Delta_0}{g}. \tag{4}$$

From Eqs. (1) and (4), it can be proved that

$$\frac{\Phi}{\Lambda} = C_1\Delta_0 + \frac{d\Delta_0}{dt}, \tag{5}$$

where $\Lambda = \epsilon_1/g$, and is called the heat capacity constant of the calorimetric system. Eq. (5) is called Tian equation, which describes the dynamic properties of the calorimetric system under the ideal condition.

In fact, owing to thermal delay of calorimeter, the response temperature rise of sensor at time t is delayed relatively to the temperature rise of reaction system, and then there exists a temperature difference $(\theta_R - \theta_S)$ between the reaction system and the sensor. In this case, we have

$$\frac{d\theta_S}{dt} = C_2(\theta_R - \theta_S), \tag{6}$$

where C_2 is the cooling constant of the sensor.

Rearranging Eq. (6), we get

$$\theta_R = \theta_S + \frac{d\theta_S/dt}{C_2}. \tag{7}$$

Eq. (7) denotes the relationship between the temperature rise of the reaction system and the response temperature rise of the sensor when the delay of sensing is considered.

Supposing

$$\Delta = g\theta_S, \tag{8}$$

where Δ is the voltage signal produced by the sensor, i.e, the peak height of measured thermoanalytical curve at time t.

From Eqs. (7) and (8), we have

$$\theta_R = \frac{\Delta}{g} + \frac{(d\Delta/dt)}{(C_2 g)}. \tag{9}$$

Therefore, from Eqs. (1) and (9), it can be obtained that

$$\frac{\Phi}{\Lambda} = C_1\Delta + \frac{(1 + C_1/C_2)\mathrm{d}\Delta}{\mathrm{d}t} + \frac{(1/C_2)\mathrm{d}^2\Delta}{\mathrm{d}t^2}. \tag{10}$$

Eq. (10) is the theoretical equation of the conduction calorimeter in which the delay of sensing has been considered.

2.2. Modification of the distorted thermoanalytical curve

From Eq. (9), it can be seen that the peak height at time *t* on the measured thermoanalytical curve ($\Delta \sim t$) could not represent the real temperature rise of reaction system because of the thermal delay between the sensor and the reaction system.

Comparison Eq. (4) with Eq. (9), we can get

$$\Delta_0 = \Delta + \frac{(\mathrm{d}\Delta/\mathrm{d}t)}{C_2}. \tag{11}$$

The second term of right side of Eq. (11) represents the influence of the delay of sensing. Therefore, according to Eq. (11), the distorted curve ($\Delta \sim t$) can be modified directly into the ideal real thermoanalytical curve ($\Delta_0 \sim t$) which can be suitable for treatment with Tian equation (Eq. (5)).

2.3. Mathematical model of thermo-kinetic research method for faster reaction

According to Eq. (5), the thermo-kinetic transformation equation [7] and the principle of chemical kinetics, it can be proved that the thermo-kinetic equations of simple order reactions can be described as

$$\frac{\alpha_0^*}{A_0} - \frac{\Delta_0}{(C_1A_0)} = F(t), \tag{12}$$

$$\frac{\Delta_0}{A_0} + \frac{(\mathrm{d}\Delta_0/\mathrm{d}t)}{(C_1A_0)} = K_nF(t)^n, \tag{13}$$

where α_0^* and Δ_0 are the peak area after time *t* and the peak height at time *t* of the modified real thermoanalytical curve ($\Delta_0 \sim t$), respectively, and A_0 is the total area under this curve. $F(t)$ is the function with respect to time. For different order reactions, $F(t)$ has different expressions $K_n = k_nC_0^{n-1}$, k_n is the rate constant of *n*th order reaction, and C_0 is the initial concentration of reactant.

$t_{0\mathrm{m}}$ is the time corresponding to maximum peak height $\Delta_{0\mathrm{m}}$ of the modified thermoanalytical curve, when $t=t_{0\mathrm{m}}$, then $\Delta_0=\Delta_{0\mathrm{m}}$, $\alpha_0^* = \alpha_{0\mathrm{m}}^*$, $\mathrm{d}\Delta_0/\mathrm{d}t=0$. From Eqs. (12) and (13), it can be obtained that

$$K_n = \frac{(\Delta_{0\mathrm{m}}/A_0)}{[\alpha_{0\mathrm{m}}^*/A_0 - \Delta_{0\mathrm{m}}/(C_1A_0)]^n}. \tag{14}$$

Eq. (14) is the mathematical model of thermo-kinetic research method for faster reactions.

2.4. Determination of cooling constants C_1 and C_2

C_1 and C_2 are important parameters in our method. Their values can be determined by electric calibration.

When a constant heat power Φ_0 is generated by a heater in the calorimeter vessel, according to Eq. (10), we obtain that

$$\frac{\Phi_0}{\Lambda} = \frac{C_1\Delta + (1 + C_1/C_2)\mathrm{d}\Delta}{\mathrm{d}t} + \frac{(1/C_2)\mathrm{d}^2\Delta}{\mathrm{d}t^2}. \tag{15}$$

When heating is stopped, $\Phi_0=0$, we have

$$\frac{\mathrm{d}^2\Delta}{\mathrm{d}t^2} + \frac{(C_1 + C_2)\mathrm{d}\Delta}{\mathrm{d}t} + C_1C_2\Delta = 0. \tag{16}$$

The general solution of Eq. (16) is

$$\Delta = A_1\mathrm{e}^{-C_1t} + A_2\mathrm{e}^{-C_2t}, \tag{17}$$

where A_1 and A_2 are integral constants. Eq. (17) is called the cooling curve equation. If four data Δ_1, Δ_2, Δ_3, Δ_4 are taken from the cooling curve at fixed time interval Δt, according to Eq. (17), it can be got that

$$C_1 = (1/\Delta t)\ln(M - \sqrt{M^2 - N}), \tag{18}$$

$$C_2 = (1/\Delta t)\ln(M + \sqrt{M^2 - N}), \tag{19}$$

where

$$M = \frac{(\Delta_1\Delta_4 - \Delta_2\Delta_3)}{[2(\Delta_2\Delta_4 - \Delta_3^2)]}, \tag{20}$$

$$N = \frac{(\Delta_1\Delta_3 - \Delta_2^2)}{(\Delta_2\Delta_4 - \Delta_3^2)}. \tag{21}$$

3. Experimental

3.1. Reaction systems and reactants

In order to test the validity of the theory and method proposed in this paper, we have studied the thermokinetics of saponifications of ethyl acetate, methyl acetate and ethyl formate in aqueous solution at different temperature, respectively.

Chemical pure methyl acetate and ethyl formate were purified further by distillation under reduced pressure. Ethyl acetate and potassium hydroxide were analytically pure. The concentration of potassium hydroxide was standardized with potassium hydrogen phthalate.

3.2. Measurement and modification of thermoanalytical curves

A twin conduction calorimeter, whose construction details have been reported previously [8], was applied to study the above-mentioned reaction systems. The cooling constants were determined by using electrical calibration. The data of thermoanalytical curves were sampling and modified directly on the basis of Eq. (11) by a computer and the modified real thermoanalytical curves were printed.

4. Results and discussion

4.1. Verification of the theory and method

The electrical calibration results of the cooling constants C_1 and C_2 are listed in Table 1. From Table 1, it is found that the value of the cooling constant C_1 varies with the different reaction systems and temperatures, but the cooling constant C_2 of the sensor keep a constant value basically. The ratio of C_2 to C_1 of studied reaction systems is in agreement with the literature [9,10]. Therefore, the method to determine the cooling constants C_1 and C_2 is believable and reasonable.

The kinetic parameters of studied faster reactions calculated from the modified thermoanalytical curve and the distorted curve are presented in Table 2. It can be seen that the rate constants calculated from the modified curve are in agreement with those in literatures, but those from the distorted curve are deviated from the literature value. Therefore, the modifier method of distorted thermoanalytical curve for faster reactions is believed to be correct.

Comparing the distorted curve with the modified curve, it can be seen that the modified curve shifted along the time axis and the peak shape was changed, and then, $\Delta_m<\Delta_{0m}$, $\alpha_m^* < \alpha_{0m}^*$, but $t_m>t_{0m}$. The modified curve and distorted curve has the same total peak area, which indicate that the total heat effect of the chemical reaction is not changeable with the modification of measured thermoanalytical curve. This conformed to reality.

4.2. About thermo-kinetic research method for faster reactions

In the thermo-kinetic investigation of chemical reaction, on the basis of Tian equation, many thermo-kinetic research methods [11–14] for slower reactions have been developed, in which the kinetic parameters can be calculated directly from the measured thermoanalytical curve within the experimental error. But for the faster reaction, especially the rate of

Table 1
Calculated results of the cooling constants C_1 and C_2

Reaction system	T (°C)	$C_1\times10^3$ (s^{-1})	$C_2\times10^2$ (s^{-1})
Saponification of ethyl acetate in aqueous solution	25	2.412	1.450
	35	2.568	1.461
Saponification of methyl acetate in aqueous solution	25	2.379	1.442
	35	2.503	1.448
Saponification of ethyl formate in aqueous solution	15	2.255	1.455
	20	2.360	1.459

Table 2
The rate constants calculated from the modified curve and the distorted curve of studied faster reaction[d]

Reaction system	T (°C)	k_2 (experimental) (L mol^{-1} s^{-1})		k_2 (literature) (L mol^{-1} s^{-1})
Saponification of ethyl acetate in aqueous solution	25	0.114[a]	0.0457[b]	0.111 [15]
	35	0.194	0.0605	0.199 [16][c]
Saponification of methyl acetate in aqueous solution	25	0.157	0.0667	0.152 [17]
	35	0.272	0.0874	0.263 [16][c]
Saponification of ethyl formate in aqueous solution	15	1.24	0.136	1.25 [16][c]
	20	1.87	0.142	1.89 [16][c]

[a] Calculated value from the modified curve.
[b] Calculated value from the distorted curve.
[c] Calculated value according to the activation energy value from [16].
[d] Average value of five times experiments under the same experimental condition.

heat generation is significantly greater than the rate of heat transfer, the distortion degree of measured thermoanalytical curve owing to the delay of sensing will increase obviously, and hence the kinetic parameter cannot be obtained directly from the distorted curve. In this case, it is necessary for evaluating the kinetic parameter to reconstruct the distorted curve into the real thermo-kinetic curve based on Eq. (10), which describes the dynamic properties of calorimeter. However, in the thermo-kinetic investigation of chemical reactions, using Eq. (10) is not convenient. If the distorted curve has been modified by using our method into the real thermoanalytical curve, we can use Tian equation, which can be easily treated in mathematics, and set up the research method to calculate the kinetic parameter conveniently.

4.3. About the modifier method for distorted thermoanalytical curves

Among the delays of calorimetric elements, the thermal delay between the reaction system and the sensor, which is called the delay of sensing, is most remarkable. According to Eq. (11), the distorted curve can be modified into the real thermoanalytical curve from which the kinetic parameter of studied reaction system can be obtained easily by using this method. The experimental results show that this modifier method for distorted thermoanalytical curves eliminates greatly the influence of the delay of sensing on determination of kinetic parameters.

At present, the most corrected methods in literatures are mainly confined to the research work in theory, and their theoretical equations are much more complex than Tian equation, and the thermo-kinetic research method to calculate the rate constant of faster chemical reactions cannot be established. Comparison with these corrected methods, our novel method has simple principle and concise mathematical model to calculate the kinetic parameter, and hence the corrected procedure only need a little computing effort and works.

The cooling constants C_1 and C_2 are important parameters in our method, which must be determined in advance by using electric calibration. Same as the other methods, it is assumed that during calibration, as well as during the calorimetric measurement, we are dealing with the same dynamic system in our method. However, this assumption is not always true; and may sometimes introduce error in the modification. This is an inevitable system error in our method. If we determine the C_1 and C_2 using an known similar faster reaction, this error can be deduced.

The theoretical basis of our method is the heat balance equation of the calorimeter, in which the delay of sensing has been considered. It has universality in the thermo-kinetic investigation of chemical reaction taking place in the calorimeter. But owing to the limitation of the sensitivity and measurable range of the calorimeter, this method can be used to determine the faster reaction whose half time could be greater than 2 s.

As stated above, the modifier method for distorted curve, in which the physical significance of parameters are very definite and the correcting procedure is simple, can be applied extensively to the thermokinetic studies of faster reactions.

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