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An interfacial model of a conduction calorimeter and its analog thermo-analytical curve equation

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Abstract

In order to describe how a conduction calorimeter works, a novel model, namely the interfacial model of a conduction calorimeter, has been proposed in this paper. Based on the model, a corresponding analog thermo-analytical curve equation has also been established. For verification of its validity, thermo-analytical curves of alkaline hydrolysis of ethyl propionate and ethyl acetate have been measured at 25°C, respectively. The data calculated by this model are in reasonable agreement with those read from the thermo-analytical curves. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Interfacial model; Interface of heat transfer; Irreversible process; Steady state; Analog thermo-analytical curve equation; Dimensionless time

1. Introduction

Deng [1,2] was the first to establish the thermo-kinetic research method, namely the dimensionless parameter method. Most studies since this early investigation have focused on kinetic measurements using the related thermo-kinetic method. Some real progress has been made towards the establishment of various kinds of thermo-kinetic research methods for an analysis of thermo-kinetic curves involved [3–10]. In contrast, only scant work has been done on modeling how a conduction calorimeter works. However, as the conduction calorimeter has been widely used to investigate thermo-kinetics of reactions with any orders [3–10], the apparatus itself should be studied in detail. The present work attempts to use a so-called interfacial model in the correct interpretation of a conduction calorimeter. Based on this novel model, a named analog thermo-analytical curve equation has been suggested in this paper. Whereas, its validity has been verified by comparison with relevant experimental results. In addition, it is easily found that the analog thermo-analytical curve equation has same formalism as that proposed in literature [9]. Therefore, such a model established in this paper provides a theoretical basis for the thermo-kinetic research methods suggested in the previous article [9]. It fits the experimental data well.

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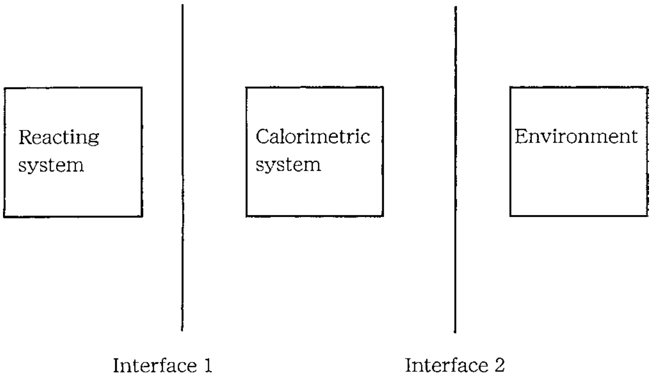

Fig. 1. Schematic representation of interface modelling of conduction type calorimeter.

2. Theory

2.1. The interfacial model of a conduction calorimeter

A conduction calorimeter can be divided into two parts: reactive system and calorimetric system. There are two interfaces of heat transfer between reactive system and calorimetric system, as well as between calorimetric system and environment, respectively (see Fig. 1).

The whole part of calorimeter can be looked as a closed system for reactants and products. However, the system is especially open to a rise in temperature resulting from the reactive heat release. Thus, the temperature rise, regarded as a reactive intermediate, can be exchanged between the interfaces. In the reactive system, chemical reaction is an irreversible process without a steady state. The cases on the interfaces 1 and 2 (see Fig. 1) act much differently. Under a perfect operation of conduction calorimeter, heat conduction on the interface 1 should be an irreversible process having a steady state:

$$\mathrm{d}Q/\mathrm{d}t = 0 \tag{1}$$

where $\mathrm{d}Q/\mathrm{d}t$ denotes change of heat effect Q in respect of time t. Thus, it can be assured that the heat released by a chemical reaction occurring in the reactive system cannot be accumulated on the interface 1 between the reactive system and calorimetric system. This not only keeps the reactive system at a controlled constant temperature, but also avoids tracking error for measurement of temperature resulted from hysteresis of heat transfer.

On the interface 2, the rate of change of heat with time, measured by temperature-sensors in the calorimetric system, equals to the difference between the rate of change of reactive heat transferred by the interface 1, and the rate of conductive heat from the calorimetric system to environment. Due to at constant heat capacity, heat is in direct proportion to peak height of the thermo-analytical curve. Hence, the above relationship can be expressed as follows by the rate of peak height Δ of thermo-analytical curve with time:

$$\frac{\mathrm{d}\Delta}{\mathrm{d}t} = \left(\frac{\mathrm{d}\Delta}{\mathrm{d}t}\right)_{\mathrm{react}} - \left(\frac{\mathrm{d}\Delta}{\mathrm{d}t}\right)_{\mathrm{condu}}$$

where the subscripts ‘react’ and ‘condu’ designate terms of the reactive heat and term of thermal conduction, respectively. In fact, such relationship can be reduced to the Tian equation:

$$\Omega = \kappa\Delta + \Lambda\dot{\Delta} \tag{2}$$

where Ω is the rate of heat production, κ and Λ are the apparatus constants, denoting the heat constant and heat capacity constant of the calorimetric system, respectively.

As analyzed above, heat conduction on the interface 2 is an irreversible process without steady state. Consequently, a normal operation of a conduction calorimeter should be attributed to the irreversible process with steady state on the interface 1. In such conditions, the irreversible process without steady state in which transfer of mass occurs in the reactive system can be contrasted with the irreversible process without steady state in which heat conduction occurs in the calorimetric system. Thus, a so-called thermo-kinetic transformation equation can be obtained [1]. In the establishment of a series of thermo-kinetic research methods [3–9], the above basic relationship reflects the synchronous relationship between the changes in energy and in extent of the reactive system at constant temperature and pressure. Such a relationship is the basis of the thermo-kinetic method of dimensionless parameters [1,2].

2.2. The analog thermo-analytical curve equation

In a conduction calorimeter, the Newtonian cooling law can be used. It indicates that the cooling rate of a system is in direct proportion to the difference of temperature between the reactive system and the environment. Its kinetic expression is similar to the kinetic equation of the first-order reaction:

$$\left(\frac{\mathrm{d}\theta}{\mathrm{d}t}\right)_{\mathrm{condu}} = -k\theta \tag{3}$$

where $k = \bar{\kappa}/\Lambda$, k is defined as the cooling constant of the reactive system; $\bar{\kappa}$ and Λ the heat constant of the reactive system, respectively; θ the temperature rise as a result of reactive heat release. If it is assumed that for both the reactive system and calorimetric system the corresponding constants satisfy the following linear relationships with a proportional coefficient ∂:

$$\kappa = \partial\bar{\kappa} \quad \text{and} \quad \Lambda = \partial\Lambda$$

then the cooling constant in the both systems is equal to each other.

In fact, this means that the process of heat conduction on the interface 1 can be simulated as a consecutive reaction:

$$\mathrm{R} \xrightarrow{k_1} \theta \xrightarrow{k} \mathrm{S}$$

where R denotes reactants, S the temperature-sensors. Such consecutive reaction consists of two processes. In process 1 heat released by the reaction is conducted to the interface 1 $(\mathrm{A} \xrightarrow{k_1} \theta)$; and in the process 2 the heat accumulated on the interface 1 is conducted to the temperature-sensors of the calorimetric system $(\theta \xrightarrow{k} \mathrm{S})$. Its kinetic equation can be expressed as

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{\Omega}{C_\nu} - k\theta \tag{4}$$

where C_ν is the heat capacity at constant volume.

Let $\theta = \theta_0$ at $t = 0$,integration of Eq. (3) reaches to:

$$\theta = \theta_0 \exp(-kt) \tag{5}$$

Inserting of Eq. (5) into Eq. (4), we get

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{\Omega}{C_\nu} - k\theta_0 \exp(-kt) \tag{5}$$

When it reaches to steady state, from Eq. (1), we have $\mathrm{d}\theta/\mathrm{d}t = 0$, then

$$\Omega = C_\nu k\theta_0 \exp(-kt)$$

Transformation of the above equation leads to

$$\Omega\exp(kt) = C_\nu k\theta_0 = \text{const.}$$

Differentiating the two sides of the above equation with respect to time t, we have

$$[\Omega\exp(kt)]' = 0. \tag{6}$$

On the other hand, Tian equation can be used to describe heat conduction on the interface 2. Hence, integration of Eq. (2) yields:

$$Q_\infty = \kappa A, \tag{7}$$

where Q_∞ is the total reactive heat, A is the total area under thermo-analytical curve. Eq. (2) divided by Eq. (7) gives:

$$\Psi_Q = \frac{k\Delta + \Lambda\dot{\Delta}}{\kappa A} \tag{8}$$

where Ψ_Q is the reduced variation in heat at time t, and the above impression can also be re-written as:

$$\Psi_Q = \frac{k\Delta + \dot{\Delta}}{kA}$$

Multiplying it by $\exp(kt)$ and then differentiating it with respect to time t, we get:

$$[\exp(kt)\Psi_Q]' = [\Delta\exp(kt)/kA]'' \tag{9}$$

However, as described in this model of the conduction calorimeter, we see clearly that the relationship (6) should be a boundary condition for an analysis of the rate of heat conduction on the interface 2 with respect to time t. From Eq. (6) we readily have

$[\exp(kt)\Psi_Q]' = 0$, thus from Eq. (9), we can get:

$$[\Delta\exp(kt)/kA]'' = 0$$

and $\ddot{\Delta} + 2k\dot{\Delta} + k^2\Delta = 0$.

Its generation solution of the above differential equation is

$$\Delta = (c_1 + c_2t)\exp(-kt) \tag{10}$$

where c_1 and c_2 are constants with values to be determined by features of the real thermo-analytical curve.

When $t = 0, \Delta = 0$, from Eq. (10) we have $c_1 = 0$ and

$$\Delta = c_2t\exp(-kt). \tag{11}$$

When $t = t_m$ (m means the time interval when the maximum peak height appears), $\dot{\Delta} = 0$ and $\Delta = \Delta_m$. Rearrangement and combination with Eq. (11) gives:

$$k = 1/t_m \quad \text{and} \quad c_2 = (\Delta_m e)/t_m$$

Hence,

$$\Delta = (t/t_m)\Delta_m\exp(1-t/t_m)$$

where Δ_m is the maximum peak height of thermo-analytical curve at time t_m. Define dimensionless time as $r = t/t_m$, we can obtain the characteristic expression of the analog thermo-analytical curve of a conduction calorimeter:

$$\Delta = \Delta_m r\exp(1-r) \tag{12}$$

Consequently, the above-deduced analog thermo-analytical curve equation is similar to that proposed in literature [9].

3. Experimental

3.1. Reactive systems

In order to test the validity of application of the interfacial model of a conduction calorimeter and the correctness of its analog thermo-analytical curve equation, the thermo-analytical curves of the two reactions, as shown below, have been studied:

- Saponification of ethyl propionate at 25°C.
- Saponification of ethyl acetate at 25°C.

3.2. Apparatus

The apparatus for measuring the thermo-analytical curves of the saponification is a twin heat conduction calorimeter, which was described in detail in a previous paper [11]. The typical thermo-analytical curve of a chemical reaction has been schematically given in the article [9].

4. Results and discussion

At 25°C, the thermo-analytical curves of saponification of ethyl propionate and ethyl acetate, were respectively measured for the validity of this method. The peak heights of thermo-analytical curve were theoretically calculated by Eq. (12) (see Tables 1 and 2). From these tables, it can be readily found that

Table 1
Thermo-analytical data of saponification of ethyl propionate ($T = 25$°C, g: graphic data, c: calculated data, *d*: relative error)

r	t (s)	Sample 1[a]			Sample 2[b]			Sample 3[c]		
		Δ_g (mm)	Δ_c (mm)	*d*	Δ_g (mm)	Δ_c (mm)	*d*	Δ_g(mm)	Δ_c (mm)	*d*
0	0	0	0	0	0	0	0	0	0	0
0.5	$0.5t_m$	52.5	53.0	0.95%	28.0	28.0	0	19.0	19.8	4.2%
1	t_m	65.0	65.0	0	34	34	0	24.0	24.0	0
1.5	$1.5t_m$	60.0	59.1	1.5%	31.0	30.9	0.32%	21.5	21.8	1.4%
2	$2t_m$	50.0	47.8	4.4%	25.0	25.0	0	17.2	17.6	2.3%
3	$3t_m$							10.0	9.7	3.0%
3.5	$3.5t_m$							7.0	6.9	1.4%
4	$4t_m$							5.0	4.8	4.0%
∞	∞							0	0	0

[a] [NaOH] = 0.0499 mol l^{-1}, [ester] = 0.0495 mol l^{-1}.
[b] [NaOH] = 0.0349 mol l^{-1}, [ester] = 0.0344 mol l^{-1}.
[c] [NaOH] = 0.0250 mol l^{-1}, [ester] = 0.0250 mol l^{-1}.

Table 2
Thermo-analytical data of saponification of ethyl acetate ($T = 25°C$, [NaOH] = 0.0299 mol l^{-1}, [ester] = 0.0291 mol l^{-1}, g: graphic data, c: calculated data, *d*: relative error)

r	*t*(s)	Δ_g (mm)	Δ_c (mm)	*d*
0	0	0	0	0
0.5	$0.5t_m$	25.0	25.0	0
1	t_m	31.0	31.0	0
1.5	$1.5t_m$	29.0	28.2	2.7%
2	$2t_m$	23.0	22.8	0.87%

the calculated data of the peak height of thermo-analytical curve by this method is in good agreement with the corresponding graphic data. Its maximum relative error is within 4.4%. Therefore, the interfacial model of a conduction calorimeter and its corresponding analog thermo-analytical curve equation established in this paper, clearly portray the evolution of the real thermo-analytical curve in such kind of calorimeter.

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