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DIMENSIONLESS PARAMETER METHOD IN THERMOKINETICS *

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ABSTRACT

A data processing method for the thermokinetics of reactions in the liquid phase is proposed in this paper. With this method the rate constants of a reaction can be calculated from the thermogram data without using the apparatus constants of the calorimeter. To test the validity of the method, the saponification of ethyl benzoate in aqueous ethanol solvent has been studied. The rate constants calculated with this method are in agreement with those in the literature and therefore the theoretical basis of the method is believed to be correct.

INTRODUCTION

It is very interesting to study the chemical kinetics of a reaction in the liquid phase with a calorimeter. Such studies have been undertaken by Calvet and Prat [1], Bell and Clunie [2], Borchard and Daniels [3] and Zielenkiewicz [4]. The calculation of rate constants from thermogram data without using the apparatus constants of the calorimeter is an unresolved problem. The dimensionless parameter method, in which the calibration of the calorimeter is unnecessary, is proposed to solve this problem. The principles of the method and its applications to first-order and second-order reactions are reported in this paper.

THEORY AND METHOD

Theoretical model of calorimeter

When a chemical reaction is taking place in a conduction calorimeter, a thermogram like that shown in Fig. 1 is recorded.

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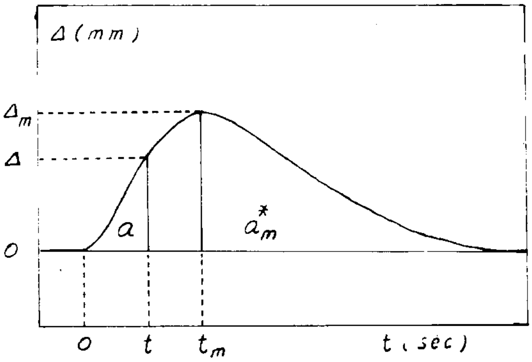

Fig. 1. Thermogram of a chemical reaction.

According to Calvet and Prat [1], the rate of heat production, Ω, can be calculated using Tian's equation:

$$\Omega = K\Delta + \Lambda\dot{\Delta} \tag{1}$$

where Δ is the peak height at time t and K and Λ are the apparatus constants of the calorimeter. On integration, the following equation is obtained:

$$Q = Ka + \Lambda\Delta \tag{2}$$

$$Q_\infty = KA \tag{3}$$

and

$$\frac{Q_\infty - Q}{Q_\infty} = \frac{Ka^* - \Lambda\Delta}{KA} \tag{4}$$

where Q is the heat produced before time t, Q_∞ is the total heat effect, 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.

These quantities (Δ, a, a^*, A) in the above equations are called the thermogram data at time t. The quantities (Δ_m, a_m, a^*_m, A) at the time when $t = t_\mathrm{m}$ are called the characteristic data of a thermogram and are very important in the dimensionless parameter method.

We can define the cooling constant k of the calorimeter as $k = K/\Lambda$. Then, multiplying both sides of Tian's equation by a factor e^{kt} and integrating between the limits 0 and t, we obtain

$$K\Delta\, \mathrm{e}^{kt} = \int_0^t \Omega\, \mathrm{e}^{kt}\, \mathrm{d}(kt) \tag{5}$$

This is called the thermogram equation.

Extent of reaction

Let us consider a homogeneous closed system within a volume V in which there is a chemical reaction taking place among the components $A_1, A_2, \ldots, A_c$ and suppose that the reaction can be written concisely as

$$0 = \sum_{i=1}^{c} \nu_i \, A_i \tag{6}$$

where ν_i is the stoichiometric number of component A_i which is taken as positive for a product and negative for a reactant.

The extent of reaction may be defined by the amount or the concentration of A_i as

$$\xi = \frac{n_i - n_{i,0}}{\nu_i} \tag{7}$$

$$\chi = \frac{C_i - C_{i,0}}{\nu_i} \tag{8}$$

where $n_{i,0}$ and $C_{i,0}$ are the amount and the concentration of A_i respectively at $t = 0$.

It is clear that

$$\xi = V\chi \tag{9}$$

For a reacting system in the liquid phase, the volume V can be assumed to be constant during the reaction. Differentiating eqn. (9) with respect to time gives

$$\dot{\xi} = V\dot{\chi} \tag{10}$$

The derivative of the extent of reaction with respect to time is defined as the rate of reaction.

According to Prigogine and Defay [5], any function of state of a reacting system can be expressed as a function of T, P and ξ. For example, the enthalpy H can be written as $H = H(T, P, \xi)$. Therefore at constant temperature and pressure, the rate of heat production may be derived as

$$\Omega = -\left(\frac{\partial H}{\partial \xi}\right)_{T,P} \dot{\xi} = -\left(\frac{\partial H}{\partial \xi}\right)_{T,P} V\dot{\chi} \tag{11}$$

On integration, we obtain

$$Q = -\left(\frac{\partial H}{\partial \xi}\right)_{T,P} \xi = -\left(\frac{\partial H}{\partial \xi}\right)_{T,P} V\chi \tag{12}$$

$$Q_\infty = -\left(\frac{\partial H}{\partial \xi}\right)_{T,P} \xi_\infty = -\left(\frac{\partial H}{\partial \xi}\right)_{T,P} V\chi_\infty \tag{13}$$

Thus, it is clear that

$$Q/Q_\infty = \xi/\xi_\infty = \chi/\chi_\infty \tag{14}$$

and

$$\Omega/Q_\infty = \dot{\xi}/\xi_\infty = \dot{\chi}/\chi_\infty \tag{15}$$

These are the relations between the change in energy and the change in concentration of a reacting system. It means that these changes must be proceeding synchronously in a reacting system at constant temperature and pressure.

Thermokinetic equations

According to chemical kinetics, the rate equations of a first-order reaction are

$$\frac{\chi_\infty - \chi}{\chi_\infty} = \frac{C_0 - \chi}{C_0} = e^{-k_1 t} \tag{16}$$

$$\frac{\dot{\chi}}{\chi_\infty} = \frac{\dot{\chi}}{C_0} = k, e^{-k_1 t} \tag{17}$$

where C_0 is the initial concentration of the reactant and k_1 is the rate constant. Combining them with eqns. (4), (14) and (15), we obtain

$$\frac{Ka^* - \Lambda\Delta}{KA} = e^{-k_1 t} \tag{18}$$

$$\frac{K\Delta + \Lambda\dot{\Delta}}{KA} = k_1\, e^{-k_1 t} \tag{19}$$

These are called the thermokinetic equations of a first-order reaction. Therefore, the rate of heat production in a first-order reaction is an exponential function of time t:

$$\Omega = KAk,\, e^{-k_1 t} \tag{20}$$

which is called the input function of the calorimeter. Inserting it into eqn. (5) and performing the integration, we obtain the thermogram equation of a first-order reaction:

$$\Delta = A\left(\frac{k_1 k}{k - k_1}\right)(e^{-k_1 t} - e^{-kt}) \tag{21}$$

Thus, the thermogram of a first-order reaction is also an exponential function of time t, which is called the output function of the calorimeter.

For other reactions, the thermokinetic equations can be derived in the same way.

Since the rate equations of the second-order reaction can be shown to be

$$\frac{\chi_\infty - \chi}{\chi_\infty} = \frac{C_0 - \chi}{C_0} = \frac{1}{1 + K_2 t} \tag{22}$$

$$\frac{\dot{\chi}}{\chi_\infty} = \frac{\dot{\chi}}{C_0} = \frac{K_2}{(1 + K_2 t)^2} \tag{23}$$

where $K_2 = k_2 C_0$, with C_0 the initial concentration of reactants and k_2 the rate constant, the thermokinetic equations of a second-order reaction can be obtained as

$$\frac{Ka^* - \Lambda\Delta}{KA} = \frac{1}{1 + K_2 t} \tag{24}$$

$$\frac{K\Delta + \Lambda\dot{\Delta}}{KA} = \frac{K_2}{(1 + K_2 t)^2} \tag{25}$$

Thus, the rate of heat production in a second-order reaction is

$$\Omega = \frac{KAK_2}{(1 + K_2 t)^2} \tag{26}$$

and its thermogram equation will be

$$\Delta = A\,\mathrm{e}^{-kt} \int_0^t \frac{K_2\,\mathrm{e}^{kt}\,\mathrm{d}(kt)}{(1 + K_2 t)^2} \tag{27}$$

Therefore the thermogram of a second-order reaction is an exponential integral function of time t.

Dimensionless parameter method

For a first-order reaction whose rate constant is k_1, we can define R as $R = k/k_1$, which is called the dimensionless parameter of a first-order reaction. Then, from eqns. (18), (19) and (21), it can be proved that

$$k_1 = \frac{\Delta_\mathrm{m}}{a_\mathrm{m}^*} \frac{(1 + R)}{R} = \frac{\Delta_\mathrm{m}}{a_\mathrm{m}^*} \mathrm{f}(R) \tag{28}$$

TABLE 1

Correspondence of f(R) to F(R)

R	F(R)	f(R)
5.57	0.81	1.18
6.41	0.82	1.16
7.37	0.83	1.14
8.48	0.84	1.12
9.76	0.85	1.10
11.27	0.86	1.09
13.06	0.87	1.08
15.22	0.88	1.07
17.86	0.89	1.06
21.12	0.90	1.05
25.25	0.91	1.04
30.62	0.92	1.03

TABLE 2

Correspondence of f(S, Σ) to F(S, Σ)

S	Σ	F(S, Σ)	f(S, Σ)
4.691	6.316	0.86	1.56
5.879	7.642	0.87	1.47
7.508	9.430	0.88	1.39
9.301	11.338	0.89	1.33
11.436	13.649	0.90	1.28
14.837	17.242	0.91	1.23
18.975	21.569	0.92	1.19
23.712	26.483	0.93	1.16

and

$$a_{\mathrm{m}}^{*}/A=(1+R)R^{R/(1-R)}=\mathrm{F}(R) \tag{29}$$

Because f(R) and F(R) are functions of a common variable R, the value of f(R) can be obtained from the ratio of the thermogram data (a_{m}^{*}/A) without using the cooling constant k of the calorimeter. This is shown explicitly in Table 1.

For a second-order reaction whose rate constant is k_2 and the initial concentrations are equal to C_0, we define

$$K_2=k_2C_0 \qquad S=k/K_2 \qquad \Sigma=S+kt_{\mathrm{m}}$$

where S and Σ are called dimensionless parameters of a second-order reaction. Then, from eqns. (24), (25) and (27), it can be proved that

$$K_2=\frac{\Delta_{\mathrm{m}}}{a_{\mathrm{m}}^{*}}\frac{(1+\Sigma)}{S}=\frac{\Delta_{\mathrm{m}}}{a_{\mathrm{m}}^{*}}\,\mathrm{f}(S,\,\Sigma) \tag{30}$$

$$\frac{a_{\mathrm{m}}^{*}}{A}=\frac{S(1+\Sigma)}{\Sigma^{2}}=\mathrm{F}(S,\,\Sigma) \tag{31}$$

and

$$\int_{S}^{\Sigma}\frac{\mathrm{e}^{y}}{y^{2}}\,\mathrm{d}y=\frac{\mathrm{e}^{\Sigma}}{\Sigma^{2}} \tag{32}$$

According to eqn. (32), it is clear that only one of these two dimensionless parameters is independent. Therefore the value of f(S, Σ) can be obtained from the ratio of the thermogram data (a_{m}^{*}/A) without using the cooling constant k of the calorimeter. The correspondence of f(S, Σ) to F(S, Σ) is shown in Table 2.

EXPERIMENTAL

Reagents

The saponification of ethyl benzoate was studied to test the validity of this dimensionless parameter method. Chemically pure ethyl benzoate was purified by distillation three times under reduced pressure. The mixed solvent was prepared from analytically pure ethanol and deionized water. The sodium hydroxide used was of guaranteed grade and its concentration in solution was standardised with potassium hydrogen phthalate.

Apparatus

The experiments were carried out in a conduction calorimeter whose constructional details have been reported previously [6]. The heat effects of mixing, dilution, stirring and evaporation had to be completely compensated with the same heat effects produced in the reference calorimeter.

RESULTS AND DISCUSSIONS

If the initial concentrations of reactants are unequal and C_0(ester) $\gg$ C_0(NaOH), the saponification may be treated as a pseudo-first-order reaction. The thermogram data and the rate constants calculated by the dimensionless parameter method are listed in Table 3.

If C_0(ester) = C_0(NaOH), the saponification is a second-order reaction. The experimental results are listed in Table 4.

TABLE 3

Saponification of ethyl benzoate (solvent, 50 vol.%CH_3CH_2OH–50 vol.%H_2O; $t = 25.0\,°C$; C_0(NOH) = 0.046 mol dm^{-3}; $k_1^* = k_2 C_0$(ester))

C_0(ester) (mol dm^{-3})	Δ_m (mm)	$a_m^* \times 10^{-4}$ (mm s)	$A \times 10^{-4}$ (mm s)	F(R)	f(R)	$k_1^* \times 10^4$ (s^{-1})
0.331	20.0	4.77	5.28	0.90	1.05	4.40
0.331	18.6	4.44	4.98	0.89	1.06	4.44
0.397	25.8	5.55	6.36	0.87	1.08	5.02
0.397	26.0	5.52	6.45	0.86	1.09	5.13

TABLE 4

Saponification of ethyl benzoate (solvent, 50 vol.%CH_3CH_2OH–50 vol.%H_2O; $t = 25.0\,°C$; C_0(ester) = C_0(NaOH) = 0.300 mol dm^{-3})

Δ_m (mm)	$a_m^* \times 10^{-5}$ (mm s)	$A \times 10^{-5}$ (mm s)	F(S, Σ)	f(S, Σ)	$k_2 \times 10^3$ (dm^3 mol^{-1} s^{-1})
61.0	2.03	2.30	0.885	1.36	1.36
58.3	2.01	2.28	0.880	1.39	1.34
62.8	2.03	2.29	0.890	1.33	1.37

From these tables, it can be seen that the rate constants calculated by the dimensionless parameter method in this paper are in fair agreement with those in the literature [7], and therefore the principles of this method are believed to be correct.

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