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TIME-VARIABLE METHOD FOR STUDYING REACTION RATES IN A CALORIMETER

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Abstract

A novel method for the determination of rate constants of reactions, the time-variable method, is proposed in this paper. The method needs only three time points (t), peak heights (Δ) and pre-peak areas (α), obtained from the measured thermoanalytical curve. It does not require the thermokinetic reaction to be completed. It utilizes data-processing on a computer to give the rate constants. Four reaction systems, including a first-order reaction, second-order reactions (with equal concentrations and with unequal concentrations) and a third-order reaction, were studied with this method. The method was validated and its theoretical basis was verified by the experimental results.

Keywords: calorimetry, thermokinetics, time variable method

Introduction

The calorimetric study of chemical kinetics is a very interesting and significant technique. On the basis of the fundamental theory of thermokinetics, several thermokinetic research methods have been proposed to determine rate constants of chemical reactions in a conduction calorimeter, including the dimensionless parameter method [1–3], the reduced-extent method [4], and the analog thermoanalytical curve method [5]. These methods all need a completed thermoanalytical curve for the acquisition of data for analysis. In the present paper, a novel thermokinetic research method, derived from basic equations of thermokinetics and involving a data-processing method on a computer, is proposed. The method does not require the thermokinetic reaction to be completed. It needs only three time points and the corresponding peak heights and pre-peak areas to calculate the rate constants of the studied reactions. This method is considered suitable for thermokinetic studies of chemical and biochemical reactions.

Theory and method

From fundamental theories of thermokinetics [1], the thermokinetic equation for an irreversible reaction can be expressed as

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$$\frac{G\alpha^* - C\Delta}{GA} = F(t) \tag{1}$$

where $\alpha*$ is the peak area after time t, Δ is the peak height at time t, A is the total peak area under the thermoanalytical curve, G and C are the coefficient of heat losses and the effective capacity of the calorimetric system, and $F(t)$ is a function with respect to time t. For reactions of different orders, $F(t)$ has different expressions (as shown in Table 1).

Table 1 $F(t)$ expressions for reactions of different orders

Reaction type	$F(t)$*
First-order reaction	$e^{-k_1 t}$
Second-order reaction with equal concentrations	$\frac{1}{1+K_2 t}$
Second-order reaction with unequal concentrations	$\frac{r-1}{re^{K_2' t}-1}$
n^{th}-order reaction with equal concentrations	$\frac{1}{[1+(n-1)K_n t]^{1/(n-1)}}$

*$K_2=k_2C_o$, $K_2'=k_2(A_o-B_o)$, $r=A_o/B_o$, $K_n=k_nC_o^{n-1}$, $n\neq1$. A_o, B_o and C_o are the initial concentrations of the reactants

We define $\beta=G/C$, which is called the cooling constant of the calorimetric system, and $\alpha=A-\alpha*$, generally called the pre-peak area.

From Eq. (1), we can obtain

$$\frac{A-\alpha}{A} - \frac{\Delta}{\beta A} = F(t) \tag{2}$$

$$\beta A\left(\frac{1}{F(t)} - 1\right) - \frac{\beta\alpha}{F(t)} - \frac{\Delta}{F(t)} = 0 \tag{3}$$

On defining $x=1/F(t)$ and inserting into Eq. (3), we obtain

$$\beta A(x-1) - \beta\alpha x - \Delta x = 0 \tag{4}$$

If we suppose that α_1, α_2, and α_3 and $F(t_1)$, $F(t_2)$ and $F(t_3)$ are the values of the pre-peak area and $F(t)$ at times t_1, t_2 and t_3 respectively, then from Eq. (4) we can obtain the following equation set for β and A:

$$\begin{cases} \beta A(x_1-1) - \beta\alpha_1 x_1 - \Delta_1 x_1 = 0 \\ \beta A(x_2-1) - \beta\alpha_2 x_2 - \Delta_2 x_2 = 0 \\ \beta A(x_3-1) - \beta\alpha_3 x_3 - \Delta_3 x_3 = 0 \end{cases} \tag{5}$$

This equation set must satisfy the full and necessary condition

$$\begin{vmatrix} x_1 - 1 & -\alpha_1 x_1 & -\Delta_1 x_1 \\ x_2 - 1 & -\alpha_2 x_2 & -\Delta_2 x_2 \\ x_3 - 1 & -\alpha_3 x_3 & -\Delta_3 x_3 \end{vmatrix} = 0 \tag{6}$$

Equation (6) can be simplified as

$$A_o x_1 x_2 x_3 + A_1 x_2 x_3 + A_2 x_1 x_3 + A_3 x_1 x_2 = 0 \tag{7}$$

where $A_1=\alpha_3\Delta_2-\alpha_2\Delta_3$, $A_2=\alpha_1\Delta_3-\alpha_3\Delta_1$, $A_3=\alpha_2\Delta_1-\alpha_1\Delta_2$ and $A_o=-A_1-A_2-A_3$.

On dividing Eq. (7) by $x_1x_2x_3$, we obtain

$$\frac{A_1}{x_1} + \frac{A_2}{x_2} + \frac{A_3}{x_3} + A_o = 0 \tag{8}$$

and we therefore have

$$A_1 F(t_1) + A_2 F(t_2) + A_3 F(t_3) + A_o = 0 \tag{9}$$

Equation (9) is the mathematical model of the time-variable parameter. The values of A_1, A_2, A_3 and A_o are calculated from the corresponding thermoanalytical data, and hence for a reaction of known order K_n is the only unknown parameter in Eq. (9). Through the use of a data-processing method on a computer, the root can be calculated for this equation. Thus, the kinetic parameter K_n can be obtained.

Experimental

Reaction systems

In order to test the validity of the time-variable method, we have studied the following reaction systems:

- A pseudo-first-order reaction: the saponification of ethyl acetate in the presence of a large excess of ester or alkali. In this case, the reaction can be treated as a pseudo-first-order reaction, with, $k_1^*=k_2[\mathrm{OH}^-]$ (alkali in excess) or $k_1^*=k_2[\mathrm{ester}]$ (ester in excess).
- A second-order reaction with equal concentrations: the saponification of ethyl acetate in aqueous solution at 30°C.
- A second-order reaction with unequal concentrations: the saponification of ethyl butyrate in 85% (v:v) ethanol-water solution at 30°C.
- A third-order reaction: the ring-opening reaction of epichlorohydrin with hydrobromic acid in aqueous solution at 20°C.

Reagents

Epichlorohydrin, 40% hydrobromic acid aqueous solution, ethyl acetate, ethyl butyrate, ethanol and potassium hydroxide were all analytically pure reagents.

Deionized distilled water was used in all solutions. The concentration of potassium hydroxide in solution was standardized with potassium hydrogen phthalate.

Apparatus

A batch conduction calorimeter, whose basic construction was similar to that of the Calvet calorimeter [6], was applied to measure the thermoanalytical curves of the studied reaction system. The effects of mixing, dilution, stirring and evaporation in the working 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 calculated results and examples of thermoanalytical curve analysis of the above-mentioned reaction systems with use of the time-variable method are listed in Tables 2–9. It can be seen from these Tables that the results calculated via the time-variable method are in good agreement with those to be found in the literature. The results show that the calculated rate constants are quite reproducible and self-consistent. Thus, the time-variable method is verified as being a correct method.

The time-variable method does not need the thermokinetic reaction to be completed. Therefore, it can be extremely useful for two kinds of reactions: reactions with very low rates (the long reaction times of such reactions result in drift of the baseline of the thermoanalytical curve, which causes error in the calculated results), and reactions involving side-reactions in the final stage of the reaction. The heat effects produced in the side-reactions influence the calculated results of the studied reaction. Additionally, this method is suitable for studying relatively fast reactions. As an example, the saponification of ethyl acetate is a relatively fast reaction (Tables 2–5).

Table 2 Saponification of ethyl acetate at 25°C

C_{KOH}/ mol l^{-1}	C_{es}/ mol l^{-1}	k_1^*/ s^{-1}	k_2/ l mol^{-1} s^{-1}
$5.727\cdot10^{-3}$	0.1000	0.0107	0.107
$7.158\cdot10^{-3}$	0.1000	0.0105	0.105
$1.002\cdot10^{-2}$	0.1000	0.0111	0.111
$1.253\cdot10^{-2}$	0.1000	0.0113	0.113
0.1000	$8.000\cdot10^{-3}$	0.0106	0.106
0.1000	$9.000\cdot10^{-3}$	0.0110	0.110
0.1000	$1.000\cdot10^{-2}$	0.0120	0.120
0.1000	$1.250\cdot10^{-2}$	0.0119	0.119
		Average:	0.111±0.004
		Literature value:	0.118 [7]

Table 3 Example of data analysis*

t/ s	Δ/ mm	α/ mm^2	k_1^*/ s^{-1}	k_2/ l mol^{-1} s^{-1}
360	39.6	624		
900	14.9	1399	0.0121	0.121
1440	5.6	1682		
396	37.7	702.5		
936	14.2	1427	0.0123	0.123
1476	5.4	1693		
432	35.5	777		
972	13.4	1454	0.0118	0.118
1512	5.1	1704		
468	33.4	847		
1008	12.6	1479	0.0125	0.125
1548	4.8	1714		
504	31.2	912		
1044	11.9	1502	0.0118	0.118
1584	4.6	1724		
540	29.1	973		
1080	11.2	1525	0.0112	0.112
1620	4.4	1733		
		Average:	0.0120	0.120

*C_{KOH}=0.1000 mol l^{-1}, C_{es}=1.000·10^{-2} mol l^{-1}

Table 4 Saponification of ethyl acetate at 30°C*

C_o/ mol l^{-1}	K_2/ s^{-1}	k_2/ l mol^{-1} s^{-1}
0.020	2.91·10^{-3}	0.146
0.025	3.72·10^{-3}	0.149
0.030	4.63·10^{-3}	0.154
0.045	6.78·10^{-3}	0.151
0.050	7.23·10^{-3}	0.145
	Average:	0.149±0.004
	Literature value:	0.145 [7]**

*$C_o=C_{es}=C_{KOH}$, $K_2=k_2C_o$

**Calculated from data at 25°C and activation energy

Table 5 Example of data analysis*

t/ s	Δ/ mm	α/ mm^2	K_2/ s^{-1}	k_2/ $l\ mol^{-1}\ s^{-1}$
360	79.2	1067		
900	45.6	2995	$6.71\cdot10^{-3}$	0.149
1440	23.1	4008		
396	78.0	1225		
936	43.7	3086	$7.00\cdot10^{-3}$	0.156
1476	22.0	4054		
432	76.5	1380		
972	42.0	3173	$6.90\cdot10^{-3}$	0.153
1512	21.0	4098		
468	74.5	1532		
1008	40.4	3256	$6.56\cdot10^{-3}$	0.146
1548	20.2	4140		
504	72.4	1681		
1044	38.8	3256	$7.19\cdot10^{-3}$	0.160
1584	19.5	4180.5		
640	70.2	1825		
1080	37.1	3410.5	$6.30\cdot10^{-3}$	0.140
1620	18.3	4219.5		
		Average:	$6.78\cdot10^{-3}$	0.151

* $C_o=C_{es}=C_{KOH}=0.045$ mol l^{-1}

Table 6 Saponification of ethyl butyrate in 85% ethanol-water (v:v) solution at 30°C

C_{es}/ mol l^{-1}	C_{KOH}/ mol l^{-1}	r	K_2^*/ s^{-1}	k_2/ $l\ mol^{-1}\ s^{-1}$
0.3005	0.04706	6.385	$6.71\cdot10^{-3}$	$2.65\cdot10^{-3}$
0.5650	0.06275	9.004	$1.37\cdot10^{-3}$	$2.72\cdot10^{-3}$
0.3333	0.06275	5.312	$7.81\cdot10^{-4}$	$2.89\cdot10^{-3}$
0.2651	0.06667	3.976	$5.35\cdot10^{-4}$	$2.70\cdot10^{-3}$
0.333	0.333	1	$9.12\cdot10^{-4}$	$2.74\cdot10^{-3}$
			Average:	$(2.74\pm0.08)\cdot10^{-3}$
			Literature value:	$2.79\cdot10^{-3}$ [8]

Table 7 Example of data analysis*

t/ s	Δ/ mm	α/ mm^2	K_2^*/ s^{-1}	k_2/ $l\ mol^{-1}\ s^{-1}$
720	42.0	1229.5		
1620	28.0	3013.5	$6.50\cdot10^{-4}$	$2.57\cdot10^{-3}$
2520	15.0	4066.5		
630	42.0	1019.5		
1530	29.5	2868.5	$6.42\cdot10^{-4}$	$2.53\cdot10^{-3}$
2430	16.1	3987.5		
810	41.3	1438.5		
1710	26.5	3149.5	$6.72\cdot10^{-4}$	$2.65\cdot10^{-3}$
2610	14.1	4139.5		
900	40.0	1642.5		
1800	25.1	3278.5	$7.05\cdot10^{-4}$	$2.78\cdot10^{-3}$
2700	13.2	4208.5		
990	39.0	1840.5		
1890	23.6	3399.5	$6.86\cdot10^{-4}$	$2.71\cdot10^{-3}$
2790	12.5	4273.5		
		Average:	$6.71\cdot10^{-4}$	$2.65\cdot10^{-3}$

* C_{es}=0.3005 mol l^{-1}, C_{KOH}=0.04706 mol l^{-1}, r=6.385

Table 8 Ring-opening reaction of epichlorohydrin with HBr at 20°C*

C_o/ mol l^{-1}	K_3/ s–1	k_3/ $L^2\ mol^{-2}\ s^{-1}$
0.120	$3.05\cdot10^{-4}$	$2.12\cdot10^{-2}$
0.140	$3.75\cdot10^{-4}$	$1.91\cdot10^{-2}$
0.150	$4.34\cdot10^{-4}$	$1.93\cdot10^{-2}$
0.161	$4.81\cdot10^{-4}$	$1.86\cdot100^{-2}$
0.178	$6.33\cdot10^{-4}$	$2.00\cdot10^{-2}$
	Average:	$(1.96\pm0.09)\cdot10^{-2}$
	Literature value:	$2.17\cdot10^{-2}$ [9]

*$K_3=k_3C_o^2$

The time-variable method can also be suitable for investigating the kinetics of an unknown reaction. For an unknown reaction, the kinetic parameter and reaction order can be determined by means of a heuristic method. The rate constant of the studied reaction may be calculated with a presumed reaction order by using this method. If the rate constants are in agreement with each other for different initial concentra-

Table 9 Example of data analysis*

t/ s	Δ/ mm	α/ mm^2	K_3/ s^{-1}	k_3/ L^2 mol^{-2} s^{-1}
600	98.0	1627		
1800	48.0	4197.5	$4.75\cdot10^{-4}$	$1.83\cdot10^{-2}$
3000	21.1	5524.3		
900	80.6	2558		
2400	37.3	4957	$4.55\cdot10^{-4}$	$1.76\cdot10^{-2}$
3600	18.3	5977		
900	80.6	2558		
1800	48.0	4197.5	$4.92\cdot10^{-4}$	$1.90\cdot10^{-2}$
2700	23.1	5228		
1200	64.2	3240		
2400	37.3	4957	$4.85\cdot10^{-4}$	$1.87\cdot10^{-2}$
3600	18.3	5977		
750	91.4	2066		
1950	40.8	4411	$4.97\cdot10^{-4}$	$1.92\cdot10^{-2}$
3150	23.2	5577		
		Average:	$4.81\cdot10^{-4}$	$1.86\cdot10^{-2}$

* C_o=0.161 mol l^{-1}

tions of the reactants, then the presumed reaction order is the order of the unknown reaction.

The method is simple considering the data-processing with a computer. The choice of three time points is random. However, since subtraction is involved in A_1, A_2, A_3 and A_0, it is best to choose three points where the Δ values are quite different from each other, in order to make the error smallest. For the same reason, it is best to choose the time points at equal intervals ($\Delta=t_3-t_2=t_2-t_1$).

Overall, as a novel method for the determination of rate constants, time-variable method can be widely used to study chemical and biochemical reactions.

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