87. Thermal Analysis of the Second Order Reaction.

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Prof. S. Horiba's thermal analysis of chemical reaction velocity¹⁾—a method of measuring a chemical reaction velocity from the change in heat evolution in the course of the reaction—has been applied by several investigators to various kinds of the reactions in gaseous and liquid systems and made much contribution to studies on the initial part or the mechanism of a reaction.²⁾ By this method the same reaction system can be examined continuously without any removal of the samples from it, and both the velocity constant and the reaction heat can be easily calculated. It is believed, therefore, that the method is advantageous to the research of kinetics of the reaction in homogeneous liquid systems.³⁾ This method has not yet been applied to any reaction of the second order. Now, the present study has proved that the method can be applied to the said reaction as well as to the cases of the first order, as will be mentioned below.

Formulae of thermal analysis for the second order reaction.

The fundamental formula of the thermal analysis is this:

$$\frac{d\theta}{dt} = \frac{dT}{dt} - \frac{dT'}{dt} = \frac{dT}{dt} + K\Delta T = \frac{Q}{W} \frac{dx}{dt}, \quad (1)$$

where $\frac{dT}{dt}$ is the observed value of the temperature change of the reaction system, $\frac{dT'}{dt}$ the cooling velocity, K the cooling constant, ΔT the temperature difference between the reaction system and its surroundings, $\frac{d\theta}{dt}$ the temperature change of the system corrected for cooling, Q the reaction heat, W the heat capacity of the system, and $\frac{dx}{dt}$ the reaction velocity.

1. If a reaction is of the second order and the concentrations of its two reacting substances are same,

$$\frac{dx}{dt} = k_2(a-x)^2$$

and

$$k_2 = \frac{1}{t} \frac{x}{a(a-x)}.$$

1) Horiba, S. and Ichikawa, T.: The Sexagint (Collection of Papers dedicated to Prof. Osaka) (1927) p. 73.

2) Horiba, S., Rev. Phys. Chem., **6**, 16 (1932); **11**, 189 (1937). (Summary).

3) Horiba, S. and Kosaki, T., Proc. **11** (1935), 232; Suito, E., Ibid, **12** (1936), 229.

From these equations,

$$\frac{dx}{dt} = k_2 \left(\frac{a}{k_2 a t + 1} \right)^2.$$

Transforming this expression and substituting it in equation (1), we have

$$\frac{1}{\sqrt{\frac{d\theta}{dt}}} = \sqrt{\frac{W}{Qk_2}} \cdot k_2 t + \frac{1}{a} \sqrt{\frac{W}{Qk_2}}, \quad (2)$$

hence

$$\sqrt{k_2} \cdot \sqrt{\frac{W}{Q}} = \frac{1}{t_2 - t_1} \left\{ \frac{1}{\sqrt{\left(\frac{d\theta}{dt}\right)_{t_2}}} - \frac{1}{\sqrt{\left(\frac{d\theta}{dt}\right)_{t_1}}} \right\}. \quad (3)$$

Accordingly, in equation (2) the relation between $\frac{1}{\sqrt{\frac{d\theta}{dt}}}$ and t is linear.

The slope of the line is given by $\sqrt{\frac{Wk_2}{Q}}$ and the length of the ordinate at $t=0$ is by $\frac{1}{a} \sqrt{\frac{W}{Qk_2}}$. Let S and I represent the former and the latter respectively, then we have

$$k_2 = \frac{S}{I \times a} = \frac{S^2 \times Q}{W} = \frac{W}{I^2 \times Q \times a^2} \quad (4)$$

and

$$Q = \frac{W}{S \times I \times a}. \quad (5)$$

2. When the concentrations of the two reacting substances are not same, such a simple relation as above mentioned will not be obtained. In this case, calculating k_2 from equation (4) and Q from the integrated form of equation (1) or from equation (5) or from the values obtained from thermochemical data, we may verify the observed curve of $\frac{d\theta}{dt} \sim t$ for the whole course of the reaction with the following theoretical equation:

$$\frac{d\theta}{dt} = \frac{Q}{W} \cdot k_2 a b (a-b)^2 \cdot \frac{e^{k_2 t(a-b)}}{\{a e^{k_2 t(a-b)} - b\}^2} \quad (6)$$

which has been deduced from the equation: $\frac{dx}{dt} = k_2(a-x)(b-x)$.

Experimental.

According to A. Skrabal and A. Zahorka,¹⁾ in the reaction between sulphurous acid and iodic acid in aqueous solution, when the latter is

1) Z. Elektrochem., **33**, 42 (1927).

not in excess compared with the former and the *pH* value of the solution is 4 ~ 5, the following velocity equation is established :

$$\frac{-d[\text{IO}_3^-]}{dt} = \kappa [\text{HSO}_3^-] [\text{IO}_3^-] [\text{H}^+],$$

where κ is a constant. Accordingly, when hydrogen ion concentration $[\text{H}^+]$ is fixed with acetic-acetate buffer solution, the following irreversible reaction is regarded as of the second order with respect to sulphurous acid and iodic acid :

Now, the formula of the thermal analysis has been applied to the case. Calculating the change of the reaction heat with time from the measurement on a glass calorimeter with a Beckmann thermometer in order to find the relation between $\frac{1}{\sqrt{\frac{d\theta}{dt}}}$ and t , it was found

that the relation was linear as in the case of the first order reaction, as shown in Fig. 1. Constancy of the values of the velocity constant

Fig. 1. Linear relationship between $1/\sqrt{\frac{d\theta}{dt}}$ and t .

(Expt. 4 in Table 2.)

k_2 obtained from equation (3) was also satisfactory as seen in Table 1. Some of the experimental results obtained at 25° C. are given in

TABLE 1.
(Expt. 4. in Table 2.)

$t_2 - t_1$ (min.)	$\frac{d\theta}{dt}$ (deg./min.)	$\sqrt{k_2} \cdot \sqrt{\frac{W}{Q}}$	k_2
—	0.0750	—	—
0.5	541	(1.30)	(239)
1	367	1.57	348
1.5	281	1.54	335
2	218	1.54	335
2.5	177	1.54	335
3	149	1.51	322
4	106	1.52	327
5	81	1.49	314
6	63	1.50	318
7	46	1.59	357

mean : 332

Table 2. In this table the values of Q and k_2 of Expt. 7 have been calculated from the formula of the thermal analysis for the first order reaction, taking the reaction as a pseudo-unimolecular reaction with respect to iodic acid.

TABLE 2.

Expt. No.	conc. of reacting substances (mol/litre)				$Q^\dagger$ (Cals)		k_2 (litres/mol-min.)		
	NaHSO ₃	KIO ₃	HAc	NaAc	from eq. (1)*	$\frac{W}{S \cdot I \cdot a}$	$\frac{S}{I \cdot a}$	$\frac{S^2 \cdot Q^*}{W}$	$\frac{W}{I^2 \cdot Q \cdot a^2}^*$
1	0.006	0.002	0.06	0.12	156.3	157.5	83	82	83
2	0.006	0.002	0.12	0.12	159.8	165.6	185	178	191
3	0.006	0.002	0.18	0.12	160.1	156.1	247	254	241
4	0.006	0.002	0.24	0.12	156.2	163.1	349	334	364
5	0.012	0.004	0.12	0.12	163.8	163.0	199	200	198
6	0.003	0.001	0.03	0.03	129.2	124.2	53	55	51
7	0.03	0.001	0.03	0.03	234.0	227.8	65		

† From thermochemical data, $Q=159.6$ (Cals).

* By graphical integration from the $\Delta T \sim t$ curve.

* The value of Q 'from eq. (1)' was used.

As seen from Table 2, the values of Q and k_2 in each experiment obtained thermoanalytically by various methods of calculation are in good agreement with each other. It may be easily seen from Expt. 1, 2, 3 and 4 that the reaction is proportional to the first power of the hydrogen ion concentration. If the 'salt effect' is taken into consideration, it may be admitted that the value of k_2 of Expt. 2 agrees with that of Expt. 5 and that the value of Expt. 6 with

that of Expt. 7. In carrying out a similar experiment as Expt. 6 by titration analysis, Skrabal and Zahorka¹⁾ have found the constant as 29. Its difference from the author's result is tolerably great, but such deviation may be possible from the difference in the experimental conditions.

For the application of equation (6), Expt. 7 was taken up. If $\frac{d\theta}{dt}$ is plotted for t by this equation putting $k=65$ and $Q=234.0$, which have been calculated from the formula of the first order reaction, the curve obtained coincides quite well with the observed curve in the main part of the earlier period, as is shown in Fig 2.

As seen from the above results, it may be concluded that the formula of the thermal analysis newly proposed to the second order reaction is capable of successful application.

In certain cases some peculiarities have been found at the initial part of the reaction. The consideration about its mechanism will be given in another press.²⁾

Fig. 2. $\frac{d\theta}{dt} \sim t$ curve of Expt. 7.
(pseudo-unimolecular)

1) Loc. cit.

2) The detailed report on the reaction will be given in Rev. Phys. Chem. Japan.