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THERMAL ANALYSIS OF CHEMICAL REACTION VELOCITY.*

By SHINKICHI HORIBA.

The measurement of the velocity of a chemical reaction has hitherto been made either by chemical analysis or through the change of the physical nature of the reaction system. Several years ago, on the study of photochemical union of hydrogen and chlorine[1], the author and Ichikawa succeeded in deducing very rapid reaction velocities from the observation of the change of heat evolved in the course of reaction. Since then, this method has been applied to various studies of reaction kinetics in the author's laboratory and has been proved to give very satisfactory results. Some of them will be here summarized as "thermal analysis of chemical reaction velocity".

I. The Principle of Thermal Analysis.

The principle of this method can be represented by a simple equation as this:

$$\frac{dT}{dt}-\frac{dT'}{dt}=\frac{Q}{W}\frac{dx}{dt}=K\frac{dx}{dt}, \qquad (1)$$

where $\frac{dT}{dt}$ denotes the observed value of the temperature change in a reaction system, $\frac{dT'}{dt}$ the cooling velocity due to the temperature difference between a reaction system and its surroundings, $\frac{dT}{dt}-\frac{dT'}{dt}$ the adiabatic heating velocity, Q the reaction heat, W the heat capacity of the system, and $\frac{dx}{dt}$ the reaction velocity.

If we measure preliminarily the cooling velocity $\frac{dT'}{dt}$, particular to any reaction vessel to be used, the value of reaction velocity $\frac{dx}{dt}$ can be easily obtained through the observation of $\frac{dT}{dt}$. Nevertheless, in a reaction in gaseous systems it is hard to make the observation of $\frac{dT}{dt}$ directly. Under the assumption that the Ideal Gas Law should be applicable to such a case, $\frac{dT}{dt}$ may be easily calculated from the observation of $\frac{dp}{dt}$. This enables us to make a considerably profound

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* The main part of this paper is the reprint from the Honda Anniversary Volume of the Science Reports of the Tôhoku Imperial University, 1st Ser., 430 (1936).

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

research, such as the observation of velocities in the primary stages of some gaseous reactions before they reach their stationary states as well as the velocity of photochemical after-effect, that is, residual velocity after shutting off light in some photochemical reactions. Thus the method offers interesting materials for the study of reaction mechanism. In a reaction in liquid systems the direct measurement of $\frac{dT}{dt}$ is possible, but we find it very difficult to measure such a high reaction velocity as that obtainable from $\frac{dp}{dt}$ in gaseous reactions. In some cases, however, our method is more advantageous to the study of the earlier period of a reaction than any other ordinary methods.

Here the author will give some typical examples of this method successfully applied to the reactions in gaseous and liquid systems.

II. Reactions in Gaseous Systems.

(A) Photochemical Union of Chlorine and Hydrogen.

(Worked by M. TAMURA[2].)

The research of this theme was first carried out by Horiba and Ichikawa[3], and further made by Tamura very comprehensively. The experimental method was thus: a mixture of pure chlorine and hydrogen was illuminated and the change of pressure increment Δp in the reaction system with time was observed. In this case Δp is of course the change of pressure brought about by the reaction heat, and $\frac{d\Delta p}{dt}$ corresponds to $\frac{dT}{dt}$ in Formula (1). The measurement of Δp after shutting off light enables us to calculate the values of $\frac{dT'}{dt}$, particular to each system, through $\frac{d\Delta p}{dt}$ in the stage where the after-effect of reaction has disappeared. Accordingly the change of $\frac{dx}{dt}$ either in the course of exposure or after shutting off light can be obtained by equation (1). The results obtained are shown in Fig. 1.

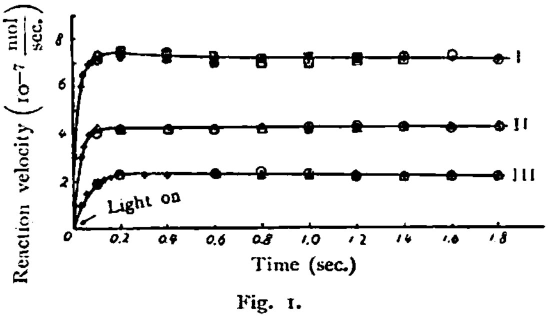

Fig. 1.

Reaction velocity during the exposure.

$[Cl_2]=258$ mm. $[H_2]=100$ mm. $[HCl]=7$ mm. 21°C. Light source: a 1000 C. P. Pointolite lamp, operating from a battery supply.

The light was passed through a 78 mm. layer of a solution $\left(\frac{CuSO_4+1080\,NH_3}{90}\text{(normal)}\right)$.

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[2] M. Tamura, *Rev. Phys. Chem. Japan*, 11, 1 (1937).

[3] S. Horiba and T. Ichikawa, *loc. cit.*; Ichikawa, *Z. Phys. Chem.*, (B), 10, 299 (1930).

Curves I, II, and III in Fig. 1 show the experimental results made with various intensities of light. As seen from these, the reaction reaches its stationary state within 0.2 sec. after the instant of the exposure. The relation between the light intensity I and the reaction velocity in its stationary state is represented by

$$\frac{dx}{dt}=kI^{0.6}.$$

This relation and the quantum yield are given in Table I.

Table I.

No.	Light intensity in arbitrary unit	Reaction velocity in stationary state	k	Quantum Yield
I	1.00	7.14	7.1	1760
II	0.42	4.29	7.2	2490
III	0.13	2.19	7.5	4130

The reaction velocity after shutting off light is graphically shown in Fig. 2.

From the results obtained by the above mentioned thermal analysis the following discussion may be made for the mechanism of this reaction.

As the effect of water vapour upon this reaction is doubtful, the Nernst chain will be adopted for simplicity as follows:

$$\left.\begin{array}{ll}Cl_2+h\nu=2Cl & \text{(a)}\\ Cl+H_2=HCl+H+\sim 0\text{ kcal} & \text{(b)}\\ H+Cl_2=HCl+Cl+45\text{ kcal} & \text{(c)}\end{array}\right\}(2)$$

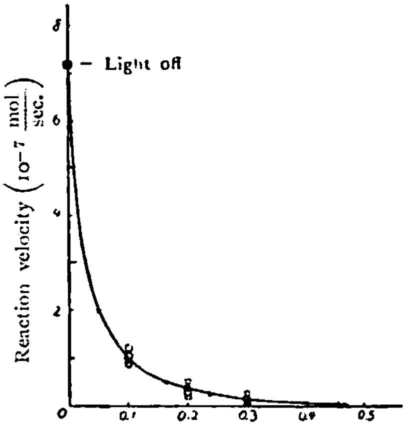

Fig. 2.
Reaction velocity after shutting off light.

When light is not so intense, the reaction chain is not considered to branch. Consequently the chain is schematically represented as follows:

$$\underbrace{\underbrace{\overset{Cl}{O}\text{———}\overset{Cl}{O}}_{\substack{\tau\text{ sec.}\\ 2\,HCl}}\underbrace{\text{———}\overset{Cl}{O}}_{2\,HCl}\underbrace{\text{———}\overset{Cl}{O}}_{2\,HCl}\cdots\cdots\cdots\overset{Cl}{O}\underbrace{\text{———}\overset{Cl}{O}}_{2\,HCl}}_{T=\nu\tau\text{ sec.,}}$$

where τ denotes the time taken by a chain link, which must be a constant, T the time taken by a chain, ν the number of chain links contained in a chain. From the said reaction mechanism it is clear that the mean value of ν and ν_m is a quarter of the quantum yield. Therefore, if the mean life of a chain T_m is calculated, τ is easily obtained from the equation $\tau=\frac{T_m}{\nu_m}$. T_m in a stationary state, however, can not be directly calculated. Now from the reaction velocity after shutting off light shown in Fig. 2, we have $T'_m=\frac{1}{20}$ sec. This T'_m differs from that during the exposure since the chain after shutting off light becomes longer, and so we get $\nu'_m=950$ by our experimental calculation[4] and then we have $\tau=\frac{T'_m}{\nu'_m}=\frac{1}{20}\times\frac{1}{950}=\frac{1}{19000}$ sec.

When equation (2) is regarded as the chain mechanism, τ is the time taken by the partial reactions (*b*) and (*c*). Nevertheless, as the time taken by the reaction (*c*) can be neglected in comparison with that of the reaction (*b*), τ is to be due to the reaction (*b*). Accordingly the collision yield of the reaction (*b*) is 1.4×10^{-5} by calculation.

Next we will proceed to the consideration of the chain carrier. When the number of chlorine atoms to be formed by light in 1 c.c. per second is represented by n_0, the number of chain carriers in 1 c.c. will be $N=n_0\ T_m$ as given in the following table.

Table II.

	n_0	T_m (sec.)	N	Partial Press. of Chain Carriers (mm. Hg)	Number of "Dreierstoss"
I	2.8×10^{12}	$\frac{1}{42}$	6.6×10^{10}	1.8×10^{-6}	0.0003
II	1.2×10^{12}	$\frac{1}{30}$	4.0×10^{10}	1.1×10^{-6}	0.0002
III	0.36×10^{12}	$\frac{1}{19}$	1.9×10^{10}	0.53×10^{-6}	0.0002

It may be supposed that the chain breaking reaction is brought about by a mutual collision of chain carriers. As seen from the above table, the number of the "Dreierstoss", $Cl+Cl+M=Cl_2+M$, is too small to be taken as a chain breaking reaction, so it is probable that the chain breaking is due to such a reaction as $Cl_3+Cl_3=3Cl_2$ If this assumption is right, Cl in the Nernst chain must be replaced by Cl_3.

The theoretical $\frac{dx}{dt}-t$ curve deduced from the reaction mechanism above assumed coincided well with that experimentally obtained.

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[4] ν'_m is calculated by extrapolation of the relation between the reaction velocity and the quantum yield. See Tamura's paper, *loc. cit.*

(B) Photochemical Formation of Phosgene.

(Worked by M. TAMURA[5].)

In the thermal analysis of the photochemical reaction, $CO+Cl_2=COCl_2$, it is necessary for the calculation of $\frac{dx}{dt}$ from the change of Δp with time that the decrease of molecules in number due to the reaction should be taken into consideration. Except this correction the method of calculation is similar to the preceding (A). The experimental results are given in Table III.

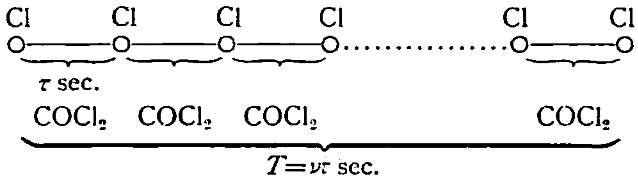
Table III.

	I_0	$[Cl_2]$ mm.	$[CO]$ mm.	$\frac{dx}{dt}\cdot 10^8 \frac{\text{mol}}{\text{sec.}}$	$k''\cdot 10^4$ [6]	Quantum Yield
I	1	306	96	132	25.1	0.97×10^3
II	0.42	304	94	88.2	26.5	1.6×10^3
III	0.13	304	94	47.6	25.7	2.6×10^3
By Calculation	1	380	380	373	25.8	2.2×10^3

According to Bodenstein, the mechanism of this reaction is as follows:

$$\left.\begin{array}{lll} Cl_2+h\nu=2Cl & & (a) \\ \left.\begin{array}{l} Cl+CO=COCl \\ COCl=Cl+CO \end{array}\right\} & \text{in equilibrium} & (b) \\ COCl+Cl_2=COCl_2+Cl & & (c) \\ COCl+Cl=CO+Cl_2 & & (d) \end{array}\right\} \qquad (3)$$

Many other investigators have proposed different mechanisms, but all of them regarded COCl as an intermediate product, assuming no branching of the chain, thus;



As in the preceding experiment, getting $T'_m=0.214$ sec., and $\nu'_m=1380$ from the reaction velocity after shutting off light we have

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[5] M. Tamura, *Rev. Phys. Chem. Japan* (Japanese Edition), 7, 49 (1933).

[6] k'' denotes the velocity constant according to Bodenstein's equation $\frac{d[COCl_2]}{dt}=k''\sqrt{I_0}\,[Cl_2]^{\frac{3}{2}}[CO]^{\frac{1}{2}}$.

$$\tau=\frac{T'_m}{\nu'_m}=\frac{1}{6450}\text{ sec.,}$$

where τ may be taken, according to the Bodenstein mechanism, as the time taken by the partial reaction (*c*) in (3). In a stationary state ν is half of the quantum yield. Accordingly, from Table III the following results are obtained

Table IV.

I	$T'_m=\frac{1}{6450}\cdot 0.97\cdot 10^3\cdot\frac{1}{2}=\frac{1}{13}$ sec.
II	$T_m=\frac{1}{6450}\cdot 1.6\cdot 10^3\cdot\frac{1}{2}=\frac{1}{8.1}$ sec.
III	$T_m=\frac{1}{6450}\cdot 2.6\cdot 10^3\cdot\frac{1}{2}=\frac{1}{5.0}$ sec.

This brings us to the calculation of the concentration of chain carriers, or of the collision yield of partial reactions. Furthermore, the theoretical deduction of the $\frac{dx}{dt}-t$ curve and comparison of the curve thus deduced with the experimental have been well done.

(C) Photochemical Oxidation of the Carbon Monoxide sensitized by Chlorine.

(Worked by M. TAMURA.)

The photochemical formation of phosgene is retarded by a small quantity of oxygen. When oxygen increases in quantity and chlorine decreases, the oxidation of CO mainly takes place and the formation of $COCl_2$ is greatly reduced. Thus Tamura investigated the photochemical oxidation of CO sensitized by chlorine from the standpoint of thermal analysis.

There is no established theory for the mechanism of this reaction, and any theory proposed is so complex and never agrees with the results obtained by our thermal analysis.

As for Tamura's experimental results it is very interesting to mention that the chain terminated in different ways—in exposure to light and after shutting off it: the chain after shutting off light had a constant probability in spreading and it seemed to terminate owing to the union of the chain carriers with impurities, while as during the exposure the reaction velocity was proportional to the 0.64th power of the light intensity, it is supposed that some of the chains terminated due to the union of the chain carriers between themselves.

Rollefson maintains that CO_2 is formed in a stage of the reaction mechanism: $COCl+O_2=CO_2+ClO$, and he assumes that this reaction is more efficient than the reaction of the formation of phosgene, $COCl+Cl_2=COCl_2+Cl$. Contrary to this assumption, according to Tamura's experimental results, the velocity of oxidation of CO in the present reaction is smaller in its earlier stage than that of the formation of phosgene. It is not admitted, therefore, that the very reaction takes place simply according to the equation, $COCl + O_2 = CO_2 + ClO$.

As for the mechanism of this reaction we must rely on further research of it.

(D) Explosive Reaction of a Mixture of Hydrogen and Oxygen.

(Worked by W. JONO[7].)

The purpose of this research is to investigate the mechanism of explosive reaction by studying the reaction in a mixture of hydrogen and oxygen from the standpoint of thermal analysis. The method was as follows: the two gases separately heated to a certain temperature were suddenly mixed and the progress of the reaction was read by the change of pressure, which caused some displacement of a metallic membrane forming an electric condenser with another fixed plate, and the change of capacity thus caused was brought to the change of the intensity of electric current, which was recorded on films by an oscillograph.

It is well known that in an explosive reaction there exist two kinds of critical pressures—upper and lower—as shown in Fig. 3.

At what we call lower critical pressures the reaction velocity changes smoothly and continuously as the pressure increases, and at last the reaction becomes explosive. In this transition region from the non-explosive to the explosive the reaction velocity is measurably small, and the heating of the system seldom occurs and yet luminescence appears. Jono succeeded in observing OH band by photographing the spectrum of luminescence after more than 16,000 explosions in the above mentioned region. Thermal analysis can be dispensed with in the study of a reaction at lower critical pressures, while it is indispensable for the study of a reaction of upper critical pressures. Generally speaking, above upper critical pressures the reaction velocity is accelerated first from a small value up to a certain maximum and then down to a stationary one. With the decrease of pressure, the nearer it comes to the critical limit, the higher the maximum velocity is, but with the increase of pressure

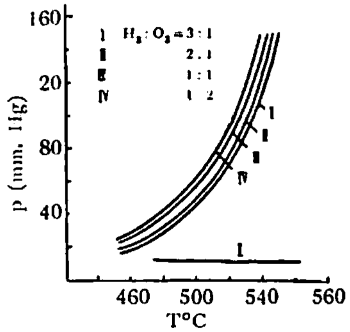

Fig. 3.

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[7] W. Jono, *Rev. Phys. Chem. Japan* (Japanese Edition), 9, 1 (1935).

it gets low and the reaction no longer tends to explosion. In this case, however, the primary reaction velocity simply corresponds to the pressure increase. These indicate that the reaction is a chain reaction and that there exists a continuity of reaction between the non-explosive region and the explosive one.

In the chain reaction the course of the reaction is taken according to the combination of the following three reactions: (1) Primary reaction (Starting of the chain), (2) Reaction of the Chain, (3) Chain breaking reaction. The velocity of Reaction (1) should be considerably large that the reaction may become explosive. Nevertheless, in the case when Reaction (3) is of a higher order than Reaction (2) with regard to the intermediate product, it may be assumed that when the velocity of Reaction (1) is too great, the chain may be so short and the reaction velocity will become not great but small. This justifies the existence of the upper critical pressure of explosion.

The chain breaking at lower pressures may occur due to the collision of intermediate products against the wall, while that at higher pressures is considered to be due to the mutual destruction of intermediate products in the gaseous phase.

III. Reactions in Liquid Systems.

(A) Photochemical Decomposition of Hydrogen Peroxide.

(Worked by H. BABA[8].)

This study was made only for the comparison of two methods—thermal analysis and chemical one—in the measurement of reaction velocity, and the experimental results obtained quite well coincided each other, showing that the photochemical decomposition of hydrogen peroxide proceeded as the reaction of the first order. In our method of thermal analysis, however, we could obtain the heat of reaction at the same time: $Q=20.4-20.7$ kcal.

The experiments of this thermal analysis were carried out in a simple glass calorimeter, whose properties were extensively studied by Horiba and Satô[9].

(B) Reduction of Chromic Acid by Some Organic Acids.

(Worked by Y. NAKANISHI.)

Dahr and his co-workers studied the reaction velocities of the reduction of

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[8] S. Horiba and H. Baba, *Rev. Phys. Chem. Japan* (Japanese Edition), 6, 47 (1932).

[9] S. Horiba and K. Sato, *Rev. Phys. Chem. Japan* (Japanese Edition), 6, 16 (1932).

chromic acid first by oxalic acid[10] and later by tartaric acid[11] and they have shown that, when the concentrations of those organic acids are in excess, the reaction proceeds as the first order in the former case, while in the latter as the zero order. The velocities of the reduction in both cases became larger by exposure to light[12], but the order of each reaction remained unchanged.

The results of Nakanishi's experiments obtained by thermal analysis coincided as a whole with those of Dahr, but Nakanishi detected a peculiarity in the rate of the reaction between chromic acid and oxalic acid: this reaction was throughout of the first order type, but it proceeds in two stages, having different values of velocity constant. The observation of this earlier stage of the reaction is impossible for any ordinary chemical method and the velocity constant of the later stage obtained by thermal analysis agrees well with that of chemical. In the case of the reaction between chromic acid and tartaric acid it proceeded as the zero order from the beginning. These results were quite the same both in the dark and in the light, only showing somewhat higher values of velocity constants in the latter case.

The heat of reaction between chromic acid and oxalic acid, which was obtained by thermal analysis, was 297 kcal, and that of the reaction between chromic acid and tartaric acid was 208 kcal. These values agreed well with those calculated from thermochemical data.

Here, as an example of our method of analysis, the method of calculation of the first order reaction will be explained, to show how easily velocity constant and at the same time heat of reaction can be obtained by thermal analysis and how possible it is to find, if any, some peculiarity in the earlier stage of the reaction, which would otherwise be missed.

Our fundamental equation (1) will be writen as follows:

$$\frac{dT}{dt} + k\Delta T = \frac{Q}{W}\frac{dx}{dt}, \qquad (1')$$

where k is the cooling constant, when the Newton law of cooling is applicable. If the reaction is of the first order type,

$$\frac{dx}{dt} = k_1(a-x),$$

or

$$(a-x) = ae^{-k_1 t}.$$

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[10] N. R. Dahr, *J. Chem. Soc.*, 111, 707 (1917); 123, 1856 (1923).

[11] A. N. Day and N. R. Dahr, *Z. Elek. Chem.*, 32, 586 (1926).

[12] A. K. Bhattacharya and N. R. Dahr, *Z. anorg. Chem.*, 176, 377 (1928).

Putting them in (1′), we have

$$\frac{dT}{dt} + k\Delta T = \frac{Q}{W} k_1 a e^{-k_1 t}, \tag{4}$$

and taking the logarithm,

$$\ln\left(\frac{dT}{dt} + k\Delta T\right) = \ln\frac{Qk_1 a}{W} - k_1 t. \tag{5}$$

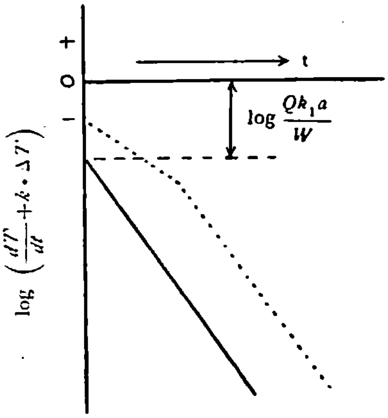

Fig. 4.

Then if we plot the values $\ln\left(\frac{dT}{dt} + k\Delta T\right)$ obtained directly from the experiments against the time t, we must have a straight line as shown in Fig. 4. Now the velocity constant k will be calculated from the inclination of this straight line, and the heat of reaction Q from the length of the ordinate at $t=0$. In ordinary experiments, if the maximum rise of temperature in calorimetric experiments is less than 1°C., the correction of k_1 for temperature is negligible, but, if necessary, the correction is possible.

In Nakanishi's experiments on the reaction between chromic acid and oxalic acid, the straight line thus obtained, as shown in Fig. 4 with a dotted line, had always a 'Knick' after about three minutes from the beginning of the reaction.

(C) The Action of Saccharase.

(Worked by T. Kosaki[13].)

The action of saccharase has long been a subject of research, and many valuable results have been attained. All of them, however, are what have been obtained by the observation of reduction power or degree of rotation. Accordingly, the reaction in its earlier stage is not fully explained yet. As for the reaction in its later stage it has been regarded as a first order reaction, and has been supposed to be one of homogeneous reactions. The experimental results, however, deviate a little; this has given rise to various empirical formulae, none of which are satisfactory to explain the deviation.

First calculating the inversion heat of saccharose by integrating (1), we got

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13) S. Horiba and T. Kosaki, *Proc. Imp. Acad.*, 11, 232 (1935); T. Kosaki, *Rev. Phys. Chem. Japan* (Japanese Edition), 9, 151 (1935).

4.1 kcal as an average of well agreeing value. Then we observed the relation between $\frac{dx}{dt}$ and t through the relation between $\frac{dT}{dt}$ and t. From these relations, putting k_m thus:

$$k_m = \frac{\log\left\{\left(\frac{dx}{dt}\right)_{t_1} \Big/ \left(\frac{dx}{dt}\right)_{t_2}\right\}}{0.4343\,(t_2 - t_1)},$$

we have obtained the relation between k_m and $\frac{dx}{dt}$. Our analytical results prove that the inversion of saccharose by saccharase consists of the following two stages, which is not yet noticed in all the experimental researches hitherto made.

(1) The earlier stage: here the $\frac{dx}{dt}-t$ curve becomes linear. The empirical formula of reaction velocity is as follows:

$$\frac{dx}{dt} = k_1 \sqrt{a_1 + x}\,, \tag{6}$$

where k_1 and a_1 are constants.

(2) The later stage: here the $\frac{dx}{dt}-k_m$ curve becomes linear, and the empirical formula is as follows:

$$\frac{dx}{dt} = b_1 \frac{a - x}{1 + c\,(a - x)}\,, \tag{7}$$

where b_1 and c are constants, and a the initial concentration of saccharose.

Various explanations could be made for such an experimental result. Dejecting the ordinary idea that it is a homogeneous reaction, it was considered as due to the contact-catalytic action of the colloidal system of saccharase; a reaction velocity formula was derived from the following mechanism as a heterogeneous system. And this derivation could be attained thus: the surface of enzyme is a kind of homogeneous adsorption surfaces as Langmuir proposed; the adsorption coefficient of saccharose is far greater than that of water; so in the earlier stage of the reaction the surface area adsorbed by saccharose is large. Accordingly, the reaction velocity relates principally to the adsorbed water. Here it is assumed that the adsorbed water dissociates into ions. As the reaction proceeds, however, the area adsorbed by saccharose becomes smaller, and the reaction velocity should depend on that adsorbed surface area. From these assumptions the following formulae were derived:

$$\frac{dx}{dt} = k \cdot S \sqrt{\frac{b_{H_2O}\, C_{H_2O}}{b_s}}\ \sqrt{\left\{\left(\frac{1}{b_s} - a\right) + x\right\}} \tag{8}$$

for the earlier stage, and

$$\frac{dx}{dt}=k'\cdot S\cdot b_s\frac{(a-x)}{1+b_s(a-x)} \qquad (9)$$

for the later stage, where k and k' are velocity constants, b_{H_2O} and b_s adsorption coefficients of water and saccharose respectively, S the whole surface of enzyme, and C_{H_2O} the concentration of water.

These theoretical formulae (8) and (9) coincide with the empirical ones (6) and (7) respectively, and the relation between the constants—k_1, a_1, b_1, and c—and the experimental conditions, such as the concentration of saccharose, the quantity of enzyme, the concentration of hydrogen ion satisfies the relation required by the theoretical formulae quite well.

Thus it is concluded that a study of the action of saccharose as contact-catalytic has opened a new field in the research of enzymes.

(D) The Action of Inorganic Ferment.

(Worked by E. SUITO[14].)

Since Bredig and his co-workers studied in detail the catalytic decomposition of hydrogen peroxide by colloidal metal, numerous researches have been made. But all the measurements of them have been done by means of chemical analysis, such as titration and the measurement of evolving oxygen, which might be inadequate for the examination of the initial part of the reaction. Therefore, the said reaction was studied from the standpoint of thermal analysis for the elucidation of its mechanism.

In a glass calorimeter (a Dewar vessel) dipped in a thermostat (30± 0.005°C.) the platinum sol 50 c.c. (5~15 × 10^{-6} g. atom) prepared by Bredig's method is quickly mixed with 50 c.c. of hydrogen peroxide solution (ca 0.003 g. mol). Soon after this, the change of temperature

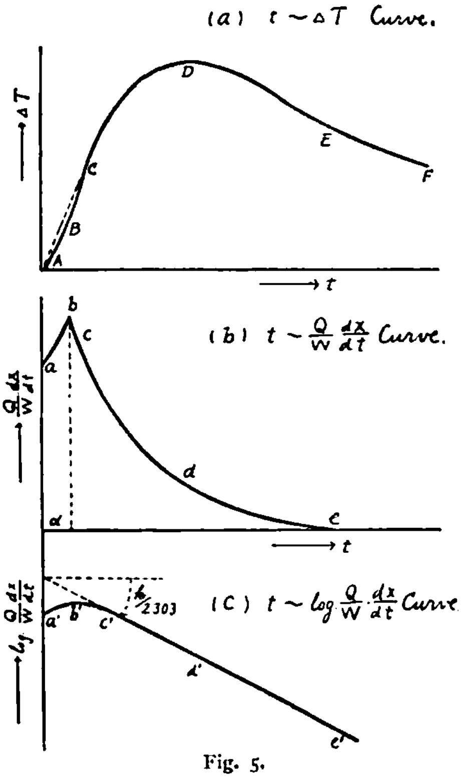

Fig. 5.

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[14] E. Suito, *Proc. Imp. Acad.*, 12, 231 (1936); *Rev. Phys. Chem. Japan* (Japanese Edition), 10, 5 (1936).

in the reaction system was observed by means of Beckmann's thermometer. The $t-\Delta T$ curve was obtained from this observation, and hence the reaction velocity $\frac{dx}{dt}$ and the reaction heat Q were calculated from formula (1). Further, the velocity constant of the first order reaction k_1 was gained from the $t-\log\frac{Q}{W}\frac{dx}{dt}$ relation. The experiments were carried out over a considerable range of the amounts of the colloid and hydrogen peroxide, and the results obtained by this analysis are as follows.

The reaction proceeded consecutively in two stages—earlier and later.

1) The Earlier Stage (*ab* in Fig. 5). The reaction type in this stage could not be determined, but it was found that the mean reaction velocity was generally proportional to the second power of the amount of the colloid and to the first power of the amount of hydrogen peroxide. The duration of this stage (1–4 min.) was seldom affected by the amount of hydrogen peroxide, while the larger the amount of the colloid, the shorter it became. It should be added that this stage was found for the first time by this thermal analysis.

2) The Later Stage (*cde* in Fig. 5). This stage, which was the main part of the reaction, was exactly of the first order, and its velocity constant was proportional to the second power of the amount of the colloid.

The heat of the decomposition of hydrogen peroxide was 23.9±0.5 kcal as mean value. Moreover, it is interesting to mention that the colloid increases its activity when left alone.

Further researches of reaction kinetics by 'thermal analysis' are in progress.

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