

HORIBA LABORATORY.

(The Laboratory of Physical Chemistry.)

(Director: Prof. Dr. Shinkichi Horiba.)

The chief aim of the Laboratory is to do scientific research in the field of physical chemistry including colloid chemistry and electrochemistry. In cases when the results are applicable to technical problems, we pursue the course of their industrial application. Therefore, the laboratory consists of the following three departments: (I) Scientific Research, (II) Research for Application, (III) Works.

I. Department of Scientific Research.

The department investigates various kinds of physico-chemical problems, keeping up a close connection with the Department of Physical Chemistry of the Kyoto Imperial University (which is also directed by Prof. S. Horiba). The leading subjects which have already been taken up are as follows:

- (1) Some problems concerning the relation between light and colloid.
- (2) Formation of Organosol.
- (3) Chemical Kinetics of Contact Catalysis.
- (4) Thermal Analysis of Chemical Reaction Velocity.
- (5) Some Other Studies on Chemical Kinetics.
- (6) Studies on Surface Properties of Some Catalysts.
- (7) Becquerel Effect, etc.

Of the studies on those problems made under Prof. Horiba's guidance, some of the chief results obtained during the past ten years since the establishment of the Institute will be summarized below.

(1) Light and Colloid.

(A) The Change of the Osmotic Pressures of Some Colloidal Solutions by the Action of Light. (by H. Baba¹⁾)

It was found that when some colloidal solutions absorb light their osmotic pressures increase in exposure to light, while they decrease to their original values on shutting off light, and the experiments on carbon sol, gold sol, silver sol, and solutions of

Prussian blue and Congo red were carried out in visible light and also those on gelatine in ultra violet ray. As for such a colloid acting on light as arsenic trisulphide, the osmotic pressure increases, but it does not recover after shutting off light.

(B) The Change of the Brownian Motion by the Action of Light. (by R. Kiyama²⁾)

The increase in the Brownian motion by the action of light was experimentally verified by means of an ultramicroscope with silver hydrosol.

(C) Formation of Colloid by Light. (by L. Chen³⁾ and S. Ishii⁴⁾)

The formation of silver sol by the reduction of silver nitrate by light was investigated and it was found that this photochemical reaction can be caused by the catalytic action of halogen ion, especially Cl', and also that in that case many organic substances, such as aniline and oxalic acid, act as promoters. Through this photochemical reaction the possibility of the estimation of such a minute quantity of Cl' as that in distilled water was established. It was stated that copper sol is formed from both cuprous chloride and cuprous bromide by the action of light, which enabled us to make copper positive photography. (Patented in Japan)

(D) Studies on the Weigert Effect. (by T. Kondo⁵⁾ and T. Yoshida⁶⁾)

In 1919, Weigert of Leipzig investigated the action of polarized light on photohalide, which is called the Weigert Effect. This effect was examined in colloidal systems of Cu, Ag, Hg, and their compounds, and moreover, the examination of 2000 colouring matters showed that the effect was produced on about 500 colouring matters. Then, the relation between the natures of those colouring matters and the effect was discussed.

(2) Formation of Organosol. (by M. Odagiri)

Any organosol which had hitherto been made was too dilute and unstable. In our laboratory a new method for preparing concentrated and stable organosols of gold, silver, mercury, copper, iron and other metals, and their salts in oil and fat was invented, and various natures of the organosols thus made were investigated. This method holds more than ten patent rights of Japan.

(3) Studies on Chemical Kinetics of Contact Catalysis.

The reaction velocity of the decomposition of CO by reduced nickel

was measured, being taken up as one of the simplest examples of the contact catalysis, and it was found that the reaction proceeds successively as the retardation type, first order, zero order and fractional order. This phenomenon was attributed to the existence of active centres with different activities on the surface of the catalyst, and the reaction mechanism was discussed in detail from the standpoint of kinetics (by T. Ri⁷⁾). In the investigations of the decomposition of methane by a heated platinum wire (by M. Kubokawa⁸⁾ and of the hydrogenation of ethylene by reduced nickel (by O. Toyama⁹⁾), the reaction velocity formulae were determined and the reaction mechanisms were discussed.

(4) Thermal Analysis of Chemical Reaction Velocity.

A new method of measuring reaction velocities has been developed in our laboratory. It is made by the analysis of the amount of heat brought about by reactions. It has a strong point in the measurement of extremely rapid reaction velocities, especially in the measurement of the initial phenomena in reactions. Being satisfactorily applicable for various kinds of reactions, such as photochemical reactions, reactions in solutions, explosive reactions, and enzyme reactions, it produces results worthy of special mention in discussions of reaction mechanisms. A more detailed report of the investigations made by means of this method is inserted after the list of the literature concerning our research.

(5) Some Other Studies on Chemical Kinetics.

As to the first order reaction, the decompositions both at high pressures and in the melted state of N_2O_5 were investigated, and proved to be of the first order (by W. Jono¹⁰⁾). As to the second order reaction, the reaction between ammonia and hydrogen chloride was examined and it was found that the action of H_2O takes part in the reaction as a complex, $NH_3 \cdot H_2O$ or $ClH \cdot OH_2$ (by Y. Okayama¹¹⁾). Next, the reaction between CO_2 and NH_3 is also influenced by the presence of H_2O and the reaction below $0^\circ C.$ is of the second order, having a negative temperature coefficient, and its reaction mechanism was explained by the assumption that the complex $NH_3 \cdot H_2O$ takes part in the reaction (by T. Yoshida¹²⁾). As to the third order reaction, the reaction between nitrogen oxide and oxygen, famous for its negative temperature coefficient, was investigated at low temperatures and its mechanism discussed (by R. Goto¹³⁾).

(6) Studies on Surface Properties of Catalysts.

The adsorption of H_2 for reduced copper (by T. Kitagawa¹⁴⁾) and

that of H_2 for reduced nickel (by T. Iishima¹⁵¹) were studied. It was also discovered that CO_2 is chemisorbed by reduced iron and its reaction mechanism was proposed (by K. Kawakita¹⁶¹). Electrolytic potential, electron emission, photoelectric effect, electron impact and others are now in research from the standpoint of catalytic action.

(7) Studies on the Becquerel Effect.

The photovoltaic potential effect of copper oxide in alkali solution, or the Becquerel effect, was investigated. In our experiments, only when CuO electrode in alkali solution reached an equilibrium, $2 CuO \rightleftharpoons Cu_2O + \frac{1}{2} O_2$, did it have a constant potential. The action of light is attributed to the reaction, $2 CuO \xrightleftharpoons[\text{dark}]{\text{light}} Cu_2O + \frac{1}{2} O_2$, and the reaction velocity was measured through the photovoltaic potential and its reaction mechanism was proposed (by N. Hayami¹⁷¹).

II. Department of Research for Application.

Of the above mentioned researches and others, studies which are regarded as adaptive to industrial purposes are expanded further in this department.

(1) Studies on Colloidal Medicine (by M. Odagiri, M. Ogino, and K. Kirita).

The object is to prepare various kinds of organosols of metals and their salts, and to examine their medical effects. For instance, it was observed that the organosol of gold produces a curable effect in the treatment of leprosy and tubercular skin diseases. Its medical and clinical effect is now being examined in Prof. Matsumoto's laboratory.

(2) Preparation of Ship's Bottom Paint (by H. Baba, T. Maekita, B. Hitotsuyanagi, O. Hirabayashi, and S. Shimomoto).

From the standpoint of colloidal chemistry, poisons and vehicles for ships' bottom paints were studied and a new paint has been prepared, which proves to be of an excellent quality after thorough practical test.

(3) Hydrogenation of Oils (by H. Baba and Y. Endo).

This is a method for continuously hydrogenizing fish oil at ordinary pressures by means of a catalyst and an improved apparatus.

(4) Preparing method of Tetralin and Dekalin. (by H. Baba and Y. Endo).

This is also a method of hydrogenating naphthalene continuously at

ordinary pressuers.

(5) Studies on Lyophile Colloids, such as Agar-agar, Gelation and Others. (by S. Nishimura and E. Koze).

(6) Improvement of the Ammonia Soda Process.

The Solvay process was re-examined from the standpoint of the Phase Rule and the process was improved. (by R. Kiyama).

(7) Making of Reflection Reprica Grating. (by T. Kondo).

By the application of a photochemical reaction a reflecting reprica grating was made and distributed for the purpose of optical study.

(8) Making of 'Sperrschrift' Photo-Cell. (by T. Itakura).

Note. (7) and (8) are now in suspension for lack of demand.

III. Works.

(1) Works of Medical Colloid.

The manufacture of products has already been transferred to private enterprise, but "Neo Silbersol" and "Orsol Gold" (or gold organosol) is now being prepared and sold.

(2) Electrochemical Works. (by S. Koizumi).

The preparation of sodium perborate had been carried out, but it is now under private management.

Literature.

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T. Kondo: Ueber der photoanisotropen Effekt (Weigert Effekt) an Farbstoffen. Zeit. wiss. Phot, **31**, 152, 185 (1932).

6) T. Yoshida: The Weigert Effect of Mercury Iodide. Rev. Phys. Chem. Japan, **4**, 133 (1930).

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S. Horiba and T. Ri: Taylor Theory of Active Centers and the Kinetics of Heterogeneous Gaseous Reactions. *Rec. Trav.*, **51**, 691 (1931).
- 8) K. Kubokawa: The Decomposition of Methane on the Surface of Platinum. *Rev. Phys. Chem. Japan*, **6**, 81, (1932); **8**, 18, 33 (1934); **11**, 180 (1937).
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- 10) W. Jono: The Decomposition of Nitrogen Pentoxide at High Pressure. *Rev. Phys. Chem. Japan*, **5**, 1 (1930).
- 11) Y. Okayama: The Reaction between Hydrogen Chloride and Ammonia. I-III. *Rev. Phys. Chem. Japan*, **7**, 85, 106, 124 (1933).
- 12) T. Yoshida: The Reaction between Ammonia and Carbon Dioxide. *Proc. Imp. Acad. Tokyo*, **12**, 191 (1936); *Rev. Phys. Chem. Japan*, **10**, 189 (1936).
- 13) R. Goto: The Reaction between Nitrogen Oxide and Oxygen at Low Temperature. *Rev. Phys. Chem. Japan*, **5**, 152, (1930).
- 14) T. Kitagawa: The Sorption of Hydrogen by Reduced Copper. *Rev. Phys. Chem. Japan*, **6**, 106 (1932).
- 15) T. Iishima: The Adsorption of Hydrogen by Reduced Nickel, I-III. *Rev. Phys. Chem. Japan*, **7**, 3, 24, 36 (1933).
- 16) K. Kawakita: On the Chemisorption of Carbon Dioxide by Reduced Iron. *Rev. Phys. Chem. Japan*, **8**, 89 (1934); **10**, 200 (1936); **11**, 25 (1937); *Proc. Imp. Acad. Tokyo*, **12**, 61 (1936).
- 17) S. Horiba and N. Hayami: On the Becquerel Effect of Copper Oxide Electrode in Alkali Solution. *Rev. Phys. Chem. Japan*, **4**, 55 (1930); **9**, 37 (1935).

Thermal analysis of chemical reaction velocity will be fully reported in the following paper.

Thermal Analysis of Chemical Reaction Velocity,*

By Shinkichi Horiba.

The measurement of the velocity of a chemical reaction has hitherto been made either by means of chemical analysis or through the change in the physical nature of the reaction system. Several years ago, on the study of photochemical union of hydrogen and chlorine¹⁾, 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 :

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

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; then $\frac{dT}{dt} - \frac{dT'}{dt}$ 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 previously 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 acquired 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 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

* 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. Y. Osaka) 73 (1927).

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 I 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.

(by M. Tamura¹⁾)

The research of this theme was first carried out by Horiba and Ichikawa²⁾, 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). Fig. 1 is the results thus obtained.

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 light intensity I and the reaction velocity in its stationary state is represented by

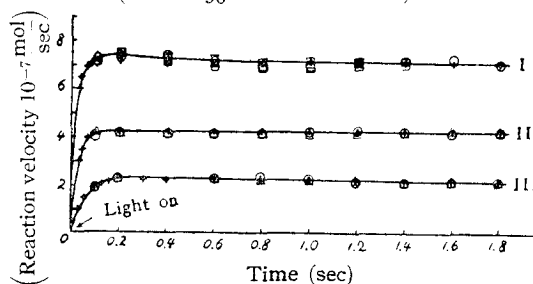


Fig. 1. Reaction velocity during the exposure.

$[\text{Cl}_2]=258$ mm. $[\text{H}_2]=100$ mm. $[\text{HCl}]=7$ mm. 21°C .
Light source: a 1000 C. P. Pointolite lamp, operating from a battery supply.

The light was passed through a 78 mm. of a solution $\left(\frac{\text{CuSO}_4 + 1080 \text{ NH}_3}{90}\right)$ (normal).

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

1) M. Tamura: Rev. Phys. Chem. Japan, **11**, 1 (1934).

2) S. Horiba and T. Ichikawa: *loc. cit.*; Ichikawa: Ztschr. Physik. Chem. (B) **10**, 299 (1930).

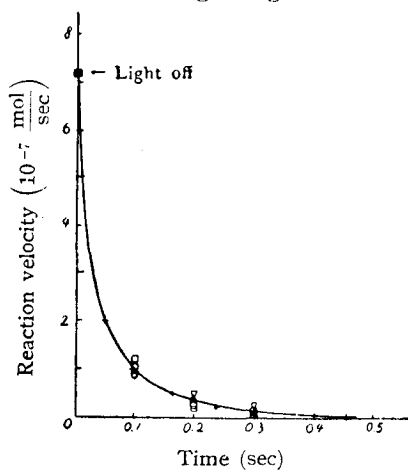
This relation and the quantum yield are given in Table 1.

Table 1.

| 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 |

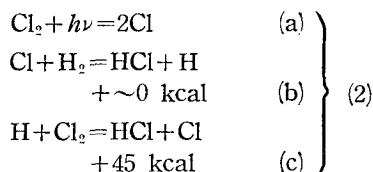
The reaction velocity after shutting off light is graphically shown in Fig. 2.

Fig. 2. Reaction velocity after shutting off light.

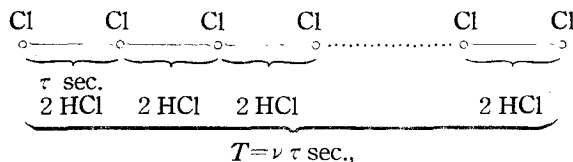


From the results obtained by the above mentioned thermal analysis the following discussion may be made for the mechanism of this reaction.

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



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



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 , 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 in exposure since the chain after shutting off light becomes

longer, and so we get $\nu'_m=950$ by our experimental calculation¹⁾ and then we have $\tau = \frac{T'_m}{\nu'_m} = \frac{1}{20} \times \frac{1}{950} = \frac{1}{19000}$ sec.

When equations (2) are 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 attributed 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 2.

| | 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", $\text{Cl} + \text{Cl} + \text{M} = \text{Cl}_2 + \text{M}$, 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 $\text{Cl}_3 + \text{Cl}_3 = 3\text{Cl}_2$. 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.

(B) Photochemical Formation of Phosgene.

(by M. Tamura²⁾)

In the thermal analysis of the photochemical reaction, $\text{CO} + \text{Cl}_2 = \text{COCl}_2$, it is necessary for the calculation of $\frac{dx}{dt}$ from the change of $\angle p$ 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 3.

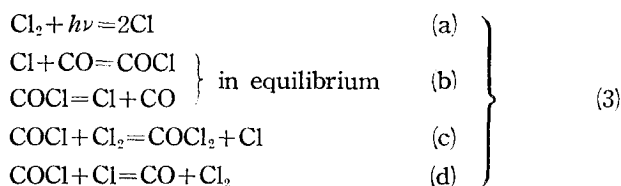
1) M. Tamura: Rev. Phys. Chem. Japan, (Japanese Edition) 7, 49 (1933).

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

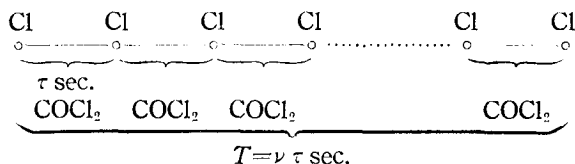
Table 3.

| | J_0 | $[\text{Cl}_2]$ mm. | $[\text{CO}]$ mm. | $\frac{dx}{dt} \cdot 10^8$ mol sec. | $k'' \cdot 10^{11}$ | 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 :



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

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

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 3 the following results are obtained.

Table 4.

| | |
|-----|--|
| I | $T_m = \frac{1}{6450} \cdot 0.97 \cdot 10^3 \cdot \frac{1}{2} = \frac{1}{13} \text{ sec.}$ |
| II | $T = \frac{1}{6450} \cdot 1.6 \cdot 10^3 \cdot \frac{1}{2} = \frac{1}{8.1} \text{ sec.}$ |
| III | $T_m = \frac{1}{6450} \cdot 2.6 \cdot 10^3 \cdot \frac{1}{2} = \frac{1}{5.0} \text{ sec.}$ |

This brings us to the calculation of the concentration of chain carriers, or

1) k'' denotes the velocity constant according to Bodenstein's equation $-\frac{d[\text{COCl}_2]}{dt} = k'' \sqrt{J_0} [\text{Cl}_2]^{\frac{3}{2}} [\text{CO}]^{\frac{1}{2}}$.

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.**

(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 stand-point 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 in exposure the reaction velocity was proportional to the 0.64th power of the light intensity, it is supposed that, some of 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: $\text{COCl} + \text{O}_2 = \text{CO}_2 + \text{ClO}$, and he assumes that this reaction is more efficient than the reaction of the formation of phosgene, $\text{COCl} + \text{Cl}_2 = \text{COCl}_2 + \text{Cl}$. Contrary to this assumption, according to Tamura's experimental results, the velocity of oxidation of CO in the present reaction in its earlier stage is lower than that of the formation of phosgene. It is not admitted, therefore, that the very reaction takes place simply according to the equation: $\text{COCl} + \text{O}_2 = \text{CO}_2 + \text{ClO}$.

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

**(D) Explosive Reaction of the Mixture of Hydrogen
and Oxygen.**

(by W. Jono¹⁾)

The purpose of this research is to investigate the mechanism of explosive reaction by studying the reaction in the 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 all of a sudden mixed up and

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

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.

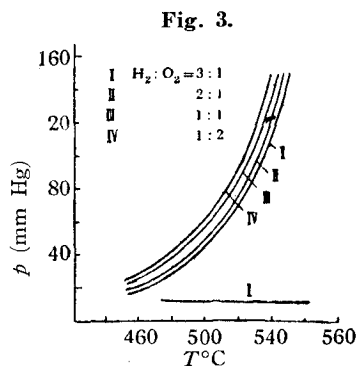
It is well known that in an explosive reaction there exist two kinds of critical pressures — upper and lower — as shown in Fig. 3.

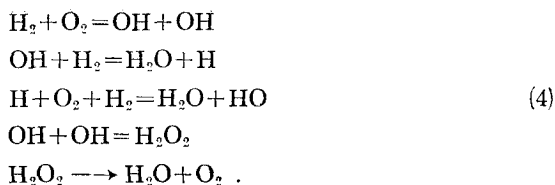
At what we call lower critical pressures the reaction velocity changes smoothly and continuously as the pressure increases, and at last the reaction becomes explosive. In this transition region from the non-explosive to the explosive the reaction velocity is measurably small, and the heating of the system 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 at upper critical pressures. Generally speaking, above the upper critical pressures the reaction velocity is accelerated first from a small value up to a certain maximum and then down to 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 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 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 great in order that the reaction may become explosive. Nevertheless, in the case that 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.

From these considerations the reaction scheme may be as follows:





III. Reactions in Liquid Systems.

(A) Photochemical Decomposition of Hydrogen Peroxide.

(by H. Baba¹⁾)

This study was made only for the comparison of two methods—thermal analysis and chemical one—in the measurement of reaction velocity, and the results of the experiments 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 Sató²⁾.

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

(by Y. Nakanishi)

Dahr and his co-workers studied the reaction velocities of the reduction of chromic acid first by oxalic acid³⁾ and later by tartaric acid⁴⁾ 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 light⁵⁾, 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 velocity of the reaction between chromic acid and oxalic acid: this reaction is 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.

- 1) S. Horiba and H. Baba: Rev. Phys. Chem. Japan, (Japanese Edition) **6**, 47 (1932).
- 2) S. Horiba and K. Sató: Rev. Phys. Chem. Japan, (Japanese Edition) **6**, 16 (1932).
- 3) N. R. Dahr: Journ. Chem. Soc. London, **111**, 707 (1917); **123**, 1856 (1923).
- 4) A. N. Day and N. R. Dahr: Ztschr. Elektrochem., **32**, 586 (1926).
- 5) A. K. Battacharya and N. R. Dahr: Ztschr. anorgan. allgem. Chem., **176**, 377 (1928).

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 written as follows :

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

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

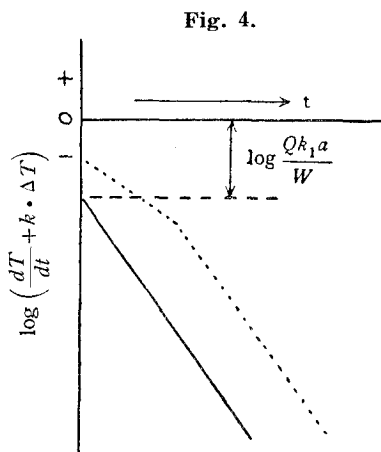
$$(a-x) = ae^{-k_1t}.$$

Putting these in (1'), we have

$$\frac{dT}{dt} + k\Delta T = \frac{Q}{W} k_1 a e^{-k_1t}, \quad (5)$$

and taking the logarithm,

$$\ln\left(\frac{dT}{dt} + k\Delta T\right) = \ln\frac{Qk_1a}{W} - k_1t. \quad (6)$$



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.

(by T. Kósaki¹⁾)

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 sufficient to explain the deviation.

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

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

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 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 :

$$\frac{dx}{dt} = k_1 \sqrt{a+x}, \quad (7)$$

where k_1 and a , are constants.

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

$$\frac{dx}{dt} = b_1 \frac{a-x}{1+c(a-x)}, \quad (8)$$

where b_1 and c are constants; a is 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, we considered it as due to the contact-catalytic action of the colloidal system of saccharase; we derived a reaction velocity formula from the following mechanism as a heterogeneous system. And this derivation could be attained thus: the surface of

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

enzyme is a kind of homogeneous adsorption surface 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 we derived the following formulae:

$$\frac{dx}{dt} = k \cdot S \sqrt{\frac{b_{H_2O} C_{H_2O}}{b_s}} \sqrt{\left\{ \left(\frac{1}{b_s} - a \right) + x \right\}} \quad (9)$$

for the earlier stage, and

$$\frac{dx}{dt} = k' \cdot S \cdot b_s \frac{(a-x)}{1 + b_s (a-x)} \quad (10)$$

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; C_{H_2O} the concentration of water.

These theoretical formulae (9) and (10) coincide with the empirical ones (7) and (8) respectively, and the relation between the value of 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 we conclude that our study of the action of saccharose as contact-catalytic has opened a new field in the research of enzymes.

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

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