

## THERMAL ANALYSIS OF THE CATALYTIC ACTION OF COLLOIDS. (III).

### The Effect of Acid and Base upon the Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum.

By Eiji Suito.

Generally, a solid substance in an electrolytic solution adsorbs an electrolyte selectively on its surface and an electric double layer is built up by the adsorbed ion at the solid-liquid interface. This phenomenon is remarkably recognized on colloidal particles and the surface charge due to the double layer keeps the stability of a sol. In colloidal catalysis, therefore, it seems probable that there should hold a close relation between such a surface state of the colloidal catalyst and its catalytic activity.

By the method of thermal analysis of reaction velocity, the author has investigated kinetically the catalytic decomposition of hydrogen peroxide by platinum sol as one of the most common and fundamental cases of colloidal catalysis.<sup>1)</sup> The constitution of platinum sol has already been made considerably clear by many researchers.<sup>2-4)</sup> The object of the present experiments is to investigate the decomposition of hydrogen peroxide by the platinum sol, to which an acid or a base has been added, for the purpose of elucidating the relation between the surface state of the colloidal particles and the reaction.

### Experimental.

The *platinum sol* used was prepared by Bredig's electric dispersion method (40 volts, 6 amp., D. C.) as in the previous research<sup>1)</sup>, and its concentrations at the time of the reaction were  $8 \times 10^{-6}$  g.-atom/litre in Series A and  $10-20 \times 10^{-6}$  g.-atom/litre in Series B. The

- 1) E. Suito, *This Journal*, 13, 74 (1939); 15, 1 (1941).
- 2) S. W. Pennycook, *J. Chem. Soc.*, 2600 (1927), 551, 2108 (1928), 618, 623 (1929), 1447 (1930); *Koll. Z.*, 49, 407 (1929), 54, 21 (1930); *J. Am. Chem. Soc.*, 52, 4621 (1930), 61, 2234 (1939).
- 3) W. Pauli u. T. Schild, *Koll. Z.*, 72, 165 (1935);  
W. Pauli u. A. Baczewski, *Monatsh. Chem.*, 69, 204 (1936);  
W. Pauli, W. Hoff and F. Lichtenstern, *J. Am. Chem. Soc.*, 61, 2295 (1939).
- 4) N. Bach u. N. Balaschowa, *Acta Physicochim. U. R. S. S.* 3, 79 (1935);  
N. Bach and A. Rakow, *ibid.*, 7, 85 (1937);  
N. Balashowa and N. Bach, *ibid.*, 7, 899 (1937);  
A. Zimin and N. Bach, *ibid.*, 11, 1 (1939).

hydrogen peroxide solution used was made by diluting Mërck's "perhydrol", and its initial concentration was 0.029 mol/litre. For the acid and base, sulphuric acid and potassium hydroxide were used at concentrations varying over the range of  $10^{-5}$  to  $10^{-1}$  mol/litre. They were preliminarily added to the hydrogen peroxide solution in Series A and to the platinum sol in Series B. The temperatures of the experiments in Series A and B were 25°C and 30°C respectively.

The apparatus and the procedure of the thermal analysis were similar to that in the previous report<sup>1)</sup>. Namely, 50 c.c. of hydrogen peroxide solution and 50 c.c. of platinum sol, to either of which a given amount of the acid or the base was added, were mixed together in a glass calorimeter (a Dewar vessel) dipped in a thermostat. The temperature rise,  $\Delta T$ , in the reaction system by the heat generated was measured with time,  $t$ , by means of Beckmann's thermometer. From the  $\Delta T-t$  curve thus obtained, shown in Fig. I (Curve I) as an instance, the reaction velocity,  $\frac{dx}{dt}$  is obtained according to the theoretical equation of thermal analysis:

$$\frac{dT}{dt} + K(\Delta T - \tau) = \frac{Q}{W} \cdot \frac{dx}{dt} \quad (1)$$

where  $\frac{dT}{dt}$  is the temperature change in the reaction system, obtained from the slope of the curve.  $K$  is the cooling constant,  $\tau$  is the correction term,  $W$  is the water equivalent of the reaction system: these values have been previously obtained by the electrical heating method.  $Q$  is the reaction heat, i.e., the heat of the decomposition of  $H_2O_2$ , whose values were reported in the first paper of this series<sup>1)</sup>. The values used in the present experiment are as follows:

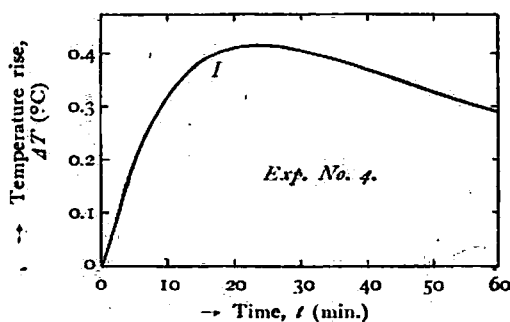
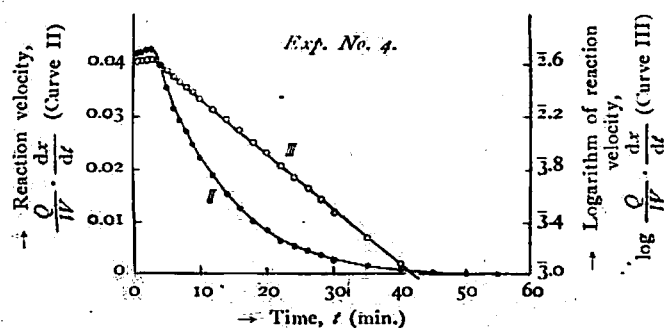


Fig. 1.

An example of the reaction.



Curve I:  $\Delta T-t$  relation.

Curve II:  $\frac{Q}{W} \cdot \frac{dx}{dt} - t$  relation.

Curve III:  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  relation.

$$K=0.0133 \text{ at } 25^{\circ}\text{C.}$$

$$0.0140 \text{ at } 30^{\circ}\text{C.}$$

$$W=119.5 \text{ cal.}$$

$$\tau=0.020 \text{ at } 25^{\circ}\text{C.}$$

$$0.018 \text{ at } 30^{\circ}\text{C.}$$

$$Q=23.9 \text{ Kcal per g.-mol.}$$

The reaction velocity curve  $\left(\frac{Q}{W} \cdot \frac{dx}{dt} - t, \text{ as } Q \text{ and } W \text{ are constants}^b\right)$  is shown as curve II and the relation of the logarithm of the reaction velocity for the time  $\left(\log \frac{Q}{W} \cdot \frac{dx}{dt} - t\right)$  is shown as curve III in Fig. 1. If the latter relation is expressed by a straight line, the reaction is of the first order, and the velocity constant of the first order,  $k_1$ , is obtained from its slope.

## Experimental Results.

### (1) The Effect of Acid on the Reaction.

*Series A. The reaction between the acidified solution of hydrogen peroxide and the platinum sol.*

The hydrogen peroxide solution acidified by various amounts of sulphuric acid were decomposed by the platinum sol. The concentrations of the acid were 0.00001, 0.0001, 0.001, 0.01, 0.02 and 0.1 mol/litre at the time of the reaction. The results obtained are shown in Fig. 2 and Table 1.

As is seen in the curves of Exp. Nos. 2—6 shown in Fig. 2, the reaction type is not changed by the addition of the acid. Namely, it is similar to the standard reaction with no addition (Exp. No. 1) and shows a characteristic form: the main part of the reaction, excepting the *initial* stage in which it is retarded, is of the first order and we will call it

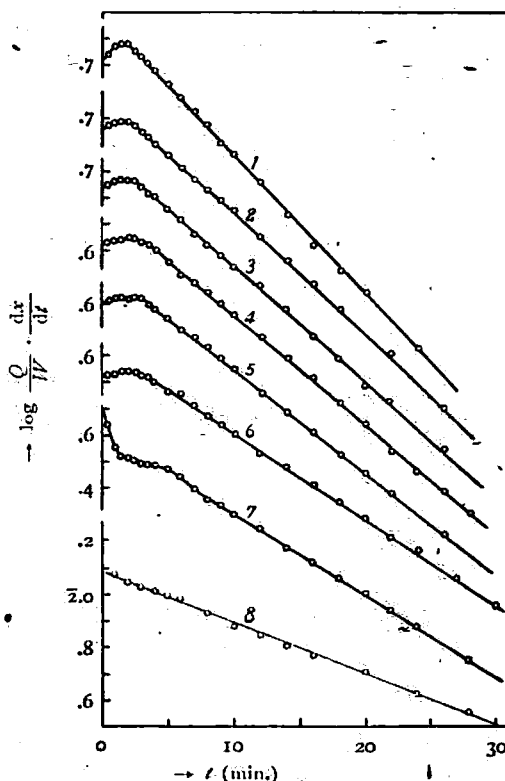


Fig. 2. The reactions between the acidified solution of hydrogen peroxide and the platinum sol.

(Though the abscissa is displaced for each curve, its scale is the same for all curves.)

$$5) \frac{Q}{W} = \frac{23900}{119.5} = 200 \therefore \frac{Q}{W} \cdot \frac{dx}{dt} = 200 \frac{dx}{dt} \text{ (mol/min.) and } \log \frac{Q}{W} \cdot \frac{dx}{dt} = 2.301 + \log \frac{dx}{dt}.$$

Table I.

Initial conc. of  $\text{H}_2\text{O}_2$ : 0.029 mol/litre.Conc. of Pt-sol (No. 6):  $8 \times 10^{-6}$  g.-atom/litre.Temperature:  $30^\circ\text{C}$ .

Exp. No.	Conc. of $\text{H}_2\text{SO}_4$ (mol/litre)	$\alpha$ (min.)	$\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{\text{int.}}$	$k_1$ (min. <sup>-1</sup> )	Coagulation.
1	0	2	0.0549	0.119	no coag.
2	0.00001	2	0.0498	0.111	no coag.
3	0.0001	2	0.0444	0.098	coag.
4	0.001	2	0.0418	0.094	coag.
5	0.01	2.5	0.0404	0.091	coag.
6	0.02	3	0.0330	0.074	coag.
7	0.1	4	(0.0315)	0.069	coag.
(8)	0.001	0	0.0119	0.035	coag.
9	0	2	0.0550	0.119	no coag.

(Note) Exp. No. 1 and 9 were carried out first and last respectively in this series as the standard reaction. There was found no change of activity of the sol by ageing. In Exp. No. 8, the acid was preliminarily added not to the hydrogen peroxide solution but to the sol as in Series B. The value of  $\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{\text{int.}}$  in Exp. No. 7 is obtained neglecting a sudden temperature rise at the beginning of the reaction caused by the heat of dilution.

'the acid type'. In the curve of Exp. No. 7, a sudden temperature rise at the beginning of the reaction is ascribed to the heat of dilution of  $\text{H}_2\text{SO}_4$ , for its concentration is as large as 0.1 mol/litre and has no influence on the reaction type. The duration of the initial stage,  $\alpha$ , which is 2—4 minutes, is scarcely increased with increasing concentration of the acid. The initial reaction velocity,  $\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{\text{int.}}$ , and also the first order velocity constant,  $k_1$ , in the later stage decrease slightly with increasing concentration of the acid, as shown in the fourth and fifth columns of Table I respectively.

Examining the solution after the reaction, it was known that the sol was not coagulated when the concentration of the acid was 0.00001 mol/litre, but coagulated when it was more than 0.0001 mol/litre.

**Series B.** *The reaction between the hydrogen peroxide solution and the acidified platinum sol.*

In this series was investigated the decomposition of the hydrogen peroxide solution by the platinum sols, to which various amounts of sulphuric acid had been added and the ionic state of the colloidal surface had been changed before the reaction. The concentrations of the acid were 0.00001, 0.0001, 0.001 and 0.01 mol/litre at the time of reaction. The results are shown in Fig. 3 and Table II.

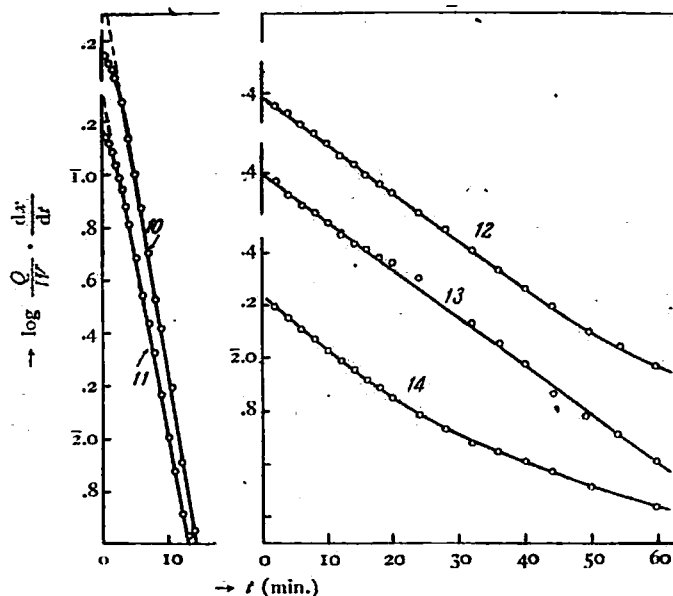


Fig. 3. The reactions between the hydrogen peroxide solution and the acidified platinum sol.

Table II.

Initial conc. of  $\text{H}_2\text{O}_2$ : 0.029 mol/litre.

Temperature: 25°C.

(a) Conc. of Pt-sol (No. 7):  $20 \times 10^{-6}$  g.-atom/litre.

Exp. No.	Conc. of $\text{H}_2\text{SO}_4$ (mol/litre)	$\alpha$ (min.)	$\left(\frac{Q}{V} \cdot \frac{dx}{dr}\right)_{\text{int.}}$	$k_1$ (min. <sup>-1</sup> )	Coagulation
10	0	3	0.140	0.340	no coag.
11	0.00001	3	0.138	0.325	no coag.
12	0.0001	0	0.0216	0.042	coag.
13	0.001	0	0.0230	0.041	coag.
14	0.01	0	0.0153	0.05—0.02	coag.

(b) Conc. of Pt-sol (No. 7):  $15 \times 10^{-6}$  g.-atom/litre.

15	0	2	0.0941	0.207	no coag.
16	0.00001	3	0.0920	0.203	no coag.
17	0.0001	0	0.0256	0.042	coag.
18	0.001	0	0.0292	0.046	coag.
19	0.01	0	0.0123	0.04—0.02	coag.

When the sol is not coagulated by low concentration of the acid (0.00001 mol/litre), the reaction velocity is almost equal to that of the standard reaction without addition of the acid, and the reaction type is also the same. (Exp. No. 11 and 16). But in the case of the coagulated sol, in which more than 0.0001 mol/

litre of the acid has been added, the reaction velocity is reduced to  $\frac{1}{4} - \frac{1}{5}$  of the standard and the retardation in the initial stage of the reaction is not recognized. This fact is verified by comparing both reactions of Series A and B each other, which were studied with the *same* sol; *vis.*, the reaction velocity of Exp. No. 8, which was carried out on the same conditions as Exp. No. 4 excepting the difference of adding process of the acid, is clearly smaller than that of the latter, and the retardation in the initial stage does not appear (*see* Fig. 2 and Table I). Thus, it is interesting that the reaction velocities of Series A and B are very different when the sol is coagulated.

## (2) The Effect of Base on the Reaction.

**Series A.** *The reaction between the basic solution of hydrogen peroxide and the platinum sol.*

The catalytic decomposition of the basic solution of hydrogen peroxide by the platinum sol was examined. The concentrations of potassium hydroxide were 0.00001, 0.0001, 0.0002, 0.0005, 0.001, 0.005 and 0.01 mol/litre at the time of reaction. The results are shown in Fig. 4 and Table III.

When the concentration of the base is small (0.00001 mol/litre), the reaction is the same as the standard one without the base (Exp. No. 20), *i.e.*, it is still of

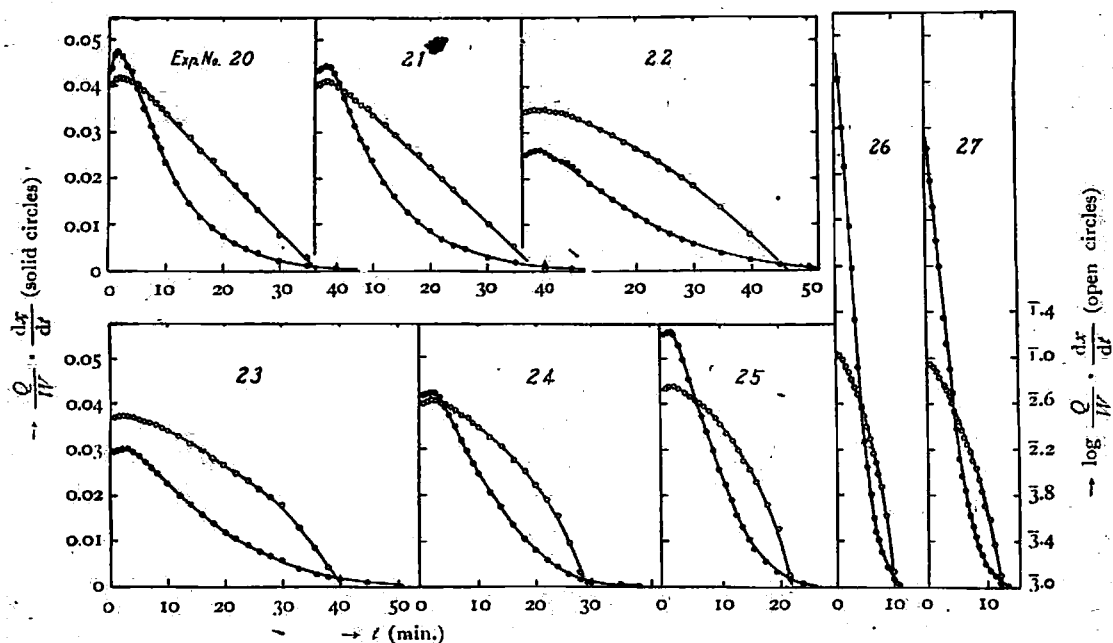


Fig. 4. The reactions between the basic solution of hydrogen peroxide and the platinum sol.

Table III.

Conc. of Pt-sol (No. 6):  $8 \times 10^{-6}$  g.-atom/litre.Temperature:  $30^\circ\text{C}$ .

Exp. No.	Conc. of KOH (mol/litre)	$\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{\text{int.}}$	$k_1$ (min. <sup>-1</sup> )	$t_{1/2}$ (min.)	Coagulation	Initial Conc. of $\text{H}_2\text{O}_2$ (mol/litre)
20	0	0.0474	0.117	10	no coag.	0.029
21	0.00001	0.0436	0.115	10.5	no coag.	0.029
22	0.0001	0.0255		19	no coag.	0.028
23	0.0002	0.0290		16	no coag.	0.027
24	0.0005	0.0415		12	no coag.	0.027
25	0.001	0.0552		9.5	partial coag.	0.026
26	0.005	0.1110		3.5	coag.	0.021
27	0.01	0.0960		4	coag.	0.021
(28)*	0.01	(0.0370)		(10.5)	coag.	0.029

\* In this reaction, the base was preliminarily added to the sol as in Series B.

'the acid type', as shown in Exp. No. 21. However, when the concentration of the base is increased above 0.0001 mol/litre, the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curve is not a straight line even in the later stage of the reaction. Namely, the reaction is not of the first order and we will now call it 'the base type'.

In the latter case, there is no distinction between the initial stage and the later stage in the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curves, and as for the  $\frac{Q}{W} \cdot \frac{dx}{dt} - t$  curves, the transition stage from the initial to the later stage is extended. Consequently, the deviation of the reaction in this type from the first order may be ascribed to the strong retardation which appears at the initial stage. (It may be also supposed as one of the reasons why, as hydrogen peroxide is unstable and is decomposed in a basic solution, such a *homogeneous* decomposition takes place in parallel with the *catalytic* decomposition by platinum. However, the former can be neglected, because it only amounts to 5 or 6% of the latter even in such a high concentration of KOH as 0.01 mol/litre, as will be stated below.)

As the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curve is not a straight line, the first order reaction velocity constant,  $k_1$ , can not be obtained; and so the time, ( $t_{1/2}$ ), taken for the reaction velocity to become half of the initial velocity, will be used instead of  $k_1$ . The value obtained increases at first and then decreases with increasing concentration of the base, as shown in the fifth column of Table III.

The sol was not coagulated after the reaction when the concentration of the base was less than 0.0005 mol/litre; it was partially coagulated when 0.001 mol/litre and completely coagulated when greater than 0.005 mol/litre.

It is known that hydrogen peroxide is stable in an acidic solution, but it is unstable in a basic solution and is fairly decomposed. In every experiment, before the start of the reaction it took about two hours after the base was added to hydrogen peroxide solution, for introducing the solution into the calorimeter and then leaving it in the thermostat so that the thermal equilibrium of the reaction system might be obtained. During this time, hydrogen peroxide was partly decomposed and the initial concentration decreased. Its values<sup>6)</sup> decreased with increasing concentration of the base, as shown in the last column of Table III. In the case of 0.01 mol/litre of KOH (Exp. No. 27), for instance, the homogeneous decomposition by the base before the reaction was about 28%  $\left( \frac{0.029 - 0.021}{0.029} \right)$  for 2 hours, and the remaining 72% was decomposed catalytically within 12 minutes in the reaction. As compared with the catalytic decomposition by the sol, therefore, the homogeneous decomposition by the base was very slow even in the case of the highest concentration of the base.

**Series B.** *The reaction between the hydrogen peroxide solution and the basic platinum sol*

In this series, hydrogen peroxide was decomposed by the platinum sols, to which various amounts of potassium hydroxide had been added in order to make the ionic exchange on the colloidal surface. The concentrations of the base were the same as in Series A. The results obtained are shown in Fig. 5 and Table IV.

The reaction types are almost the same as in Series A with the same concentration of the base. Namely, they are of 'the acid type' in low concentration of the base and 'the basic type' in high concentration. However, in the coagulated sol, to which 0.005 and 0.01 mol/litre of the base has been added, the reaction velocity is remarkably small as compared with that in Series A. The temperature rises at the beginning of the reaction in the curve of Exp. No. 36 is ascribed to the heat of dilution of KOH<sup>7)</sup>, as in Exp. No. 7 in the case of H<sub>2</sub>SO<sub>4</sub>.

6) The total heat generated by the reaction can be obtained by graphical integration of the  $\Delta T$  curve, and from its value the initial concentration of hydrogen peroxide is calculated. The values obtained by this method agreed well with those obtained by titrating the same samples with the standard solution of KMnO<sub>4</sub>.

7) Neglecting this temperature rise, the values of  $\left( \frac{Q}{V} \cdot \frac{dx}{dt} \right)_{\text{int.}}$  and  $t_{1/2}$  were obtained in both Exp. No. 36 and Exp. No. 28. This rise could not be observed in the curve of Exp. No. 27, because the reaction was very fast.



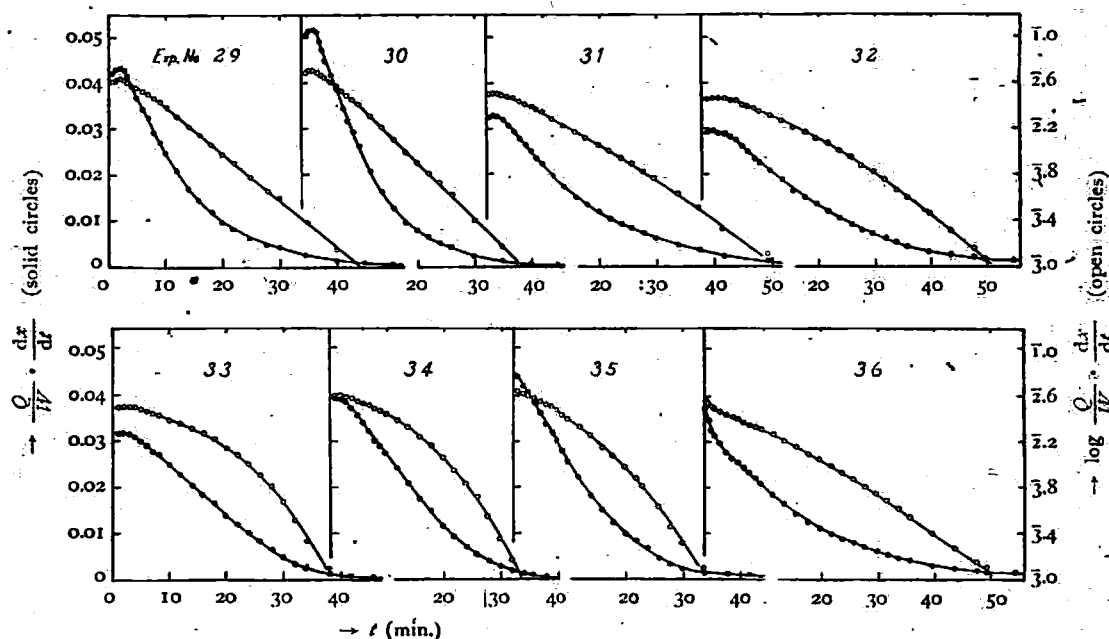


Fig. 5. The reactions between the hydrogen peroxide solution and the basic platinum sol.

Table IV.

Initial conc. of  $\text{H}_2\text{O}_2$ : 0.029 mol/litre.  
 Conc. of Pt-sol (No. 7):  $10 \times 10^{-6}$  g.-atom/litre.  
 Temperature:  $25^\circ\text{C}$ .

Exp. No.	Conc. of KOH (mol/litre)	$\left(\frac{Q}{W} \cdot \frac{d.r.}{d.t.}\right)_{\text{int.}}$	$k_1$ (min. <sup>-1</sup> )	$t_{1/2}$ (min.)	Coagulation
29	0	0.0424	0.091	12	no coag.
30	0.00001	0.0513	0.112	10	no coag.
31	0.0001	0.0324	0.069	14.5	no coag.
32	0.0002	0.0291		17.5	no coag.
33	0.0005	0.0321		18	no coag.
34	0.001	0.0396		14.5	coag.
35	0.005	0.0443		11.5	coag.
36	0.01	(0.0300)		(15)	coag.

To confirm the difference of the reaction velocity between Series A and B in the coagulated case, Exp. No. 28 was made on the same experimental condition with the same sol as Exp. No. 27. As it has been expected, its reaction velocity is much smaller than that of Exp. No. 27 (see Table III), and almost a similar curve to Exp. No. 36 is obtained.

## Discussion.

## (1) The Relation between the pH-value of the Solution and the Reaction Velocity, the Activity of Sols.

The relative reaction velocities or the activities of the sols in each series are obtained by taking as unit the velocity of the standard reaction, in which neither the acid nor the base is added, and they are tabulated in the second and third columns of Table V. The pH values of the reacting solutions are given in the fourth column; the relation between the relative reaction velocities and the pH values are shown in Fig. 6.

Table V.

Conc. of Acid or Base (mol/litre)	Relative reaction velocity*		pH**	Coagulation	Reaction type
	Series-A	Series-B			
H <sub>2</sub> SO <sub>4</sub>	0.1	0.58	(1.2)	coag.	acid
	0.02	0.62	1.5	coag.	acid
	0.01	0.74	1.8	coag.	acid
	0.001	0.78	3.0	coag.	acid
	0.0001	0.82	4.6	coag.	acid
	0.00001	0.93	5.3	no coag.	acid
	0	1.00	5.4	no coag.	acid
KOH	0.00001	0.98	5.6	no coag.	acid
	0.0001	0.60	5.9	no coag.	base
	0.0002	0.65	6.4	no coag.	base
	0.0005	0.85	7.5	(no) coag.	base
	0.001	1.10	8.7	coag.	base
	0.005	2.8	9.8	coag.	base
	0.01	2.4	(11.0)	coag.	base

\* In the series of H<sub>2</sub>SO<sub>4</sub>, these values obtained from  $\left(\frac{Q}{V} \cdot \frac{dx}{dt}\right)_{\text{int.}}$  agree well with those from  $k_1$ . In the series of KOH, in which  $k_1$  is unobtainable, the values in the table are the means of the two values obtained from  $\left(\frac{Q}{V} \cdot \frac{dx}{dt}\right)_{\text{int.}}$  and  $k_2$ .

\*\* The pH values were obtained by the colorimetry of the indicator with the solutions after the reaction.

As is seen, the activity of sol is slightly decreased by increasing the concentration of the acid, while in the case of the base there is a minimum at pH 6–6.5 and a maximum at pH ca 10. As to the maximum, its existence has already been reported with platinum sol<sup>8)</sup> and also with other metallic sol (gold<sup>9)</sup>, palladium<sup>10)</sup>)

8) G. Bredig and R. M. von Beérneck, *Z. physik. Chem.*, **31**, 259 (1899).

9) G. Bredig and W. Reinders, *ibid.*, **37**, 323 (1901).

10) G. Bredig and M. Fortner, *Ber.*, **37**, 798 (1904).

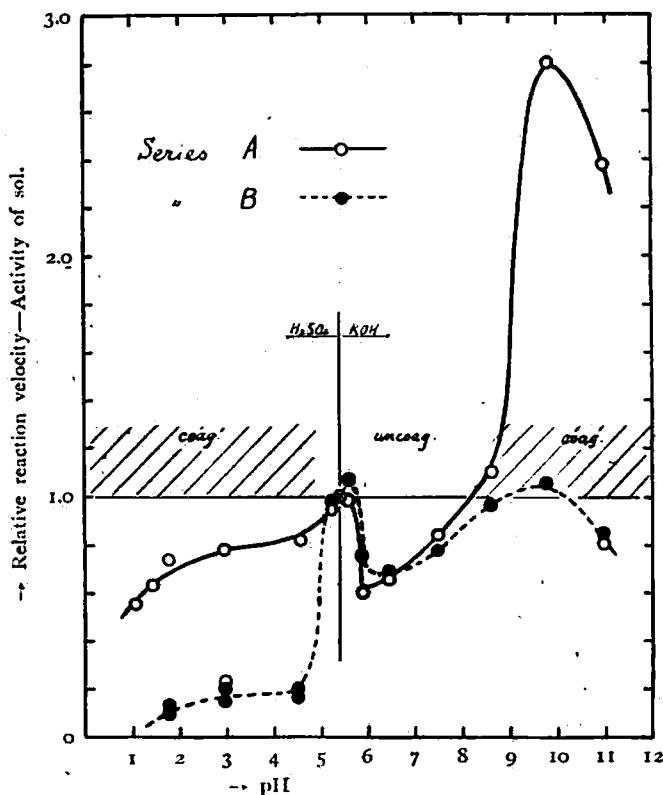


Fig. 6. Relation between the pH-value and the activity of sols.

for the decomposition of hydrogen peroxide; and it was explained by J. Weiss<sup>11)</sup> from the theory of catalysis on free electron in metal. As the concentration of the base is very high, the change of the molecular structure and dissociation degree of  $\text{H}_2\text{O}_2$  should also be considered.<sup>12)</sup> In any event, the reason for this maximum is supposed to depend upon the concentration of the base in the intermicellar liquid. On the other hand, the minimum at low concentration of the base, which was found first in this experiment, seems to depend upon the base adsorbed on the colloidal surface. This will be stated below in detail (Section (3)).

## (2) The Effect of Coagulation on the Reaction Velocity.

As the Bredig platinum sol is a sort of acidoid sol<sup>13)</sup>, the present sol in itself is also acidic and its pH value is 5.4. It is so unstable for the acid as it is

11) J. Weiss, *Trans. Farad. Soc.*, **31**, 1547 (1935).

12) A. Simon and F. Fehér (*Z. Electrochem.*, **41**, 290 (1935)) have studied the effect of a change in hydrogen ion concentration on the Raman spectrum of  $\text{H}_2\text{O}_2$ . They conclude that not only is there a loosening of the O-O bond on neutralization with NaOH but a dissociation to an  $\text{H}^+[\text{HO}_2]^-$  configuration.

coagulated by adding only 0.0001 mol of the acid per litre, *i.e.*, by making the pH of the sol 5, while it is fairly stable for the base as it is coagulated by adding more than 0.001 mol of the base per litre, *i.e.*, by making the pH 8.5. Namely, on the addition of the base, the acidoid sol is first neutralized and then gradually made basic. Generally, the coagulation of sol is caused when  $\zeta$ -potential of colloidal particles becomes less than a critical value. Taking into account of the change of  $\zeta$ -potential, that is, the change of the surface state of the platinum colloid on the addition of the acid or the base as will be mentioned below (Section (4)), it can be readily explained that the sol is stable in the pH range between 5 and 8.5 and their middle nearly corresponds to the neutralization point.

Now, the reaction velocities, or the activities, of both Series A (the case of adding preliminarily to hydrogen peroxide solution) and Series B (that of adding to platinum sol) are nearly equal in the *uncoagulated* zone (pH 5—8.5). But in the *coagulated* zone both in the acidic (pH < 5) and basic side (pH > 8.5), Series B shows  $\frac{1}{3} - \frac{1}{4}$  of the activity for Series A because of the decay in the dispersity of the sol, namely, the coagulation effect.

This fact also shows that the coagulation velocity is markedly slow as compared with the reaction velocity. And this is also confirmed by the fact that the reaction with the acid was of first order in Series A even when the sol was coagulated. Taking into consideration the fact that the reaction types of Series A and B are the same for the equal concentration of the acid or the base, the following conclusion is drawn: The ionic exchange on the surface of colloidal particles, which is the primary cause of the coagulation as well as the reason for the two distinct types of the reaction as will be stated below (Section (4)), starts instantly after the mixing of hydrogen peroxide solution with the sol; but, the velocity of coagulation caused by the collision of the colloidal particles is remarkably smaller than the reaction velocity.

### (3) The Relation between the $\zeta$ -potential (Cataphoretic Velocity) of Colloidal Particles and their Catalytic Activity.

The  $\zeta$ -C curve, which shows the influence of the concentration of the positive ion on the  $\zeta$ -potential of such negatively charged particles as platinum sol, takes a particular type according to the valency of the ion.<sup>13)</sup> For the univalent cation, the  $\zeta$ -potential gradually decreases to a minimum, and then it increases, approach-

13) Cf. A. von Buzáph, "Kolloidik", T. Steinkoff, Dresden u. Leipzig (1935) p. 223; R. J. Hartman, "Colloid Chemistry", Houghton Mifflin Co., U. S. A. (1939) p. 234; etc.

ing to zero. In fact, S. W. Pennycuik<sup>14)</sup> has reported that  $\zeta = -65$  millivolt (cataphoretic velocity  $u = -35 \times 10^{-5}$  cm/sec/volt/cm) when  $C=0$  and that  $\zeta$  is at a minimum ( $-125$  millivolt) ( $u = -63 \times 10^{-5}$  cm/sec/volt/cm) when  $C=0.00015$  mol/litre in the case of the univalent base, NaOH, added to the Bredig platinum sol. Also, N. Bach and his collaborators<sup>15)</sup> have reported that the similar  $\zeta$ -C curve is obtained in the case of KOH and NaOH added to the Bredig hydrogen-platinum sol and that its minimum corresponded almost to the neutralisation point.

Therefore, the minimum activity seen at pH 6-6.5 ( $C=0.0001-0.0002$  mol/litre) in Fig. 6 may be regarded as due to the minimum  $\zeta$ -potential.

Such a parallel relation between the  $\zeta$ -potential (the cataphoretic velocity) of colloidal particles and their catalytic activity has been found in other cases of micro-heterogeneous catalysis.<sup>16)</sup> And the fact that the  $\zeta$ -potential exerts an influence on the electrode reaction which is the cause of overvoltage has been theoretically<sup>17)</sup> and experimentally<sup>18)</sup> ascertained regarding the hydrogen-platinum electrode. Thus, it is note-worthy that the  $\zeta$ -potential plays an important rôle in surface reactions at the solid-liquid interface.

#### (4) The Relation between the Reaction and the Constitution of Colloidal Surface.

Now, we will discuss in detail the change of  $\zeta$ -potential by the addition of the acid or the base from the stand-point of the ionic exchange on the colloidal surface<sup>19)</sup> and derive the relation between its constitution and the reaction.

Generally, the constitution of a hydrophobic sol is considered as follows: The surface of colloidal particles adsorbs ions,—ion common to the substance of the colloid, *i.e.*, the "potential determining ion", or another ion. These ions attach ions of opposite sign in the intermicellar solution near the surface. The former is called "surface ionogen" and the latter "counter ion", and both of them constitute the electrical double layer. The counter ions are divided, furthermore, into a mono-

14) S. W. Pennycuik, *J. Chem. Soc.*, 1447 (1930).

15) A. Balashova and N. Bach; A. Zimin and N. Bach, *loc. cit.*

16) R. J. Kepfer and J. H. Walton, *J. Phys. Chem.*, **35**, 557 (1931);

M. A. Heath and J. H. Walton, *ibid*, **37**, 979 (1933);

E. C. Larson and J. H. Walton, *ibid*, **44**, 70 (1940).

17) A. Frumkin, *Z. physik. Chem.*, **A 164**, 121 (1933).

18) A. Frumkin, A. Slygin, B. Ershler, etc., *Acta Physicochim. U. R. S. S.*, **3**, 791 (1935), **4**, 910, **5**, 819 (1936), **6**, 195, **7**, 326 (1937), **8**, 564 (1938), **11**, 45 (1939), **13**, 747 (1946).

19) Cf. H. R. Kruyt, *Bull. Soc. chim. Belg.*, **43**, 559 (1934);

E. J. W. Verwey, *Koll. Z.*, **72**, 189 (1935), *Chem. Rev.*, **16**, 363 (1935);

H. B. Weiser, "Inorganic Colloid Chemistry" Vol. 1, J. Wiley and Sons, N. Y. (1939) p. 184.

molecular inner layer<sup>20)</sup> (Stern layer), which moves together with the surface, and a diffused outer layer (Gouy layer), and the potential at the interface of both layers gives  $\zeta$ -potential. S. W. Pennycuik<sup>21)</sup> and W. Pauli<sup>22)</sup> have investigated in detail the Bredig platinum sol, and have mentioned as adsorbing electrolytes the platinum acid, hexahydroxyplatinic acid ( $\text{H}_2\text{Pt}^{\text{IV}}(\text{OH})_6$ ) and platin-hydroxo acid ( $\text{H}_2\text{Pt}^{\text{IV}}(\text{OH})_4$ ), which are formed in the preparation of sol.

Thus, the present author considers the existence of the diffuse double layer on the colloidal surface,  $\text{Pt-R}=\cdots\text{H}^+$ , possessing the acid radical as the surface ionogen and hydrogen ion as the counter ion, as schematically shown in Fig. 7, to be probable.

If a surface-inactive acid, such as a common inorganic acid, e.g.  $\text{H}_2\text{SO}_4$ , is added to such a sol, the concentration of  $\text{H}^+$ -ions not only in the intermicellar solution but also of those absorbed on the colloidal surface increases. As theoretically explained by L. W. Janssen<sup>21)</sup> and E. J. W. Verwey<sup>22)</sup>, such increase of the concentration of counter ions compresses the thickness of the double layer and decreases  $\zeta$ -potential. (Cf. Fig. 7 b). As the result, the surface charge is reduced to less than the critical value of agglomeration and the sol is coagulated.

On the other hand, on the addition of KOH, the  $\text{H}^+$ -ions present in the intermicellar solution are first reduced by neutralisation and, consequently, the  $\text{H}^+$ -ions in the double layer are transferred into the intermicellar solution and, in place of them, some of the  $\text{K}^+$ -ions move to the outer part of the double layer; namely, the

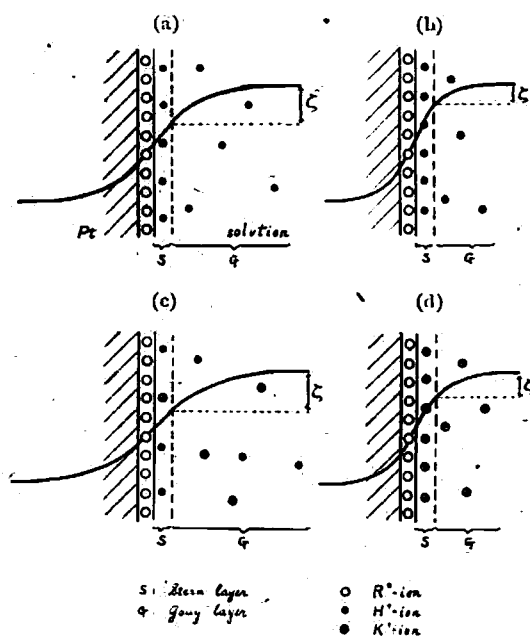


Fig. 7. Diagrammatic representation of the constitution of the colloidal platinum micelle.

- (a) before the addition of acid or base.
- (b) after the addition of acid.
- (c) after the addition of base (below the neutralization point).
- (d) after the addition of base (above the neutralization point).

<sup>20)</sup> Recently, W. G. Eversole and P. H. Lahr (*J. Chem. Phys.*, 9, 530 (1941)) maintain the multilayer.

<sup>21)</sup> L. W. Janssen, *Phys. Z. Sov.*, 4, 322 (1933).

<sup>22)</sup> E. J. W. Verwey, "Hydrophobic Colloids" D. B. Centen's Uitg., Amsterdam (1938) p. 73-78.

"exchange adsorption" of the  $K^+$ -ions occurs, as  $mPt \cdot nR = \dots nH^+ + K^+ \longrightarrow mPt \cdot nR = \dots \left\{ \frac{(n-x)}{x} K^+ \right\} H^+$  (Fig. 7 c) After the exchange, the ratio of  $K^+$ -ions and  $H^+$ -ions in the Gouy-layer will agree with that in the intermicellar liquid, but that in the Stern-layer will be determined also by specific forces between the surface and the adhering ion. Namely, a new distribution of ions in both layers is made and the  $\zeta$ -potential may increase or decrease, depending on chemical properties of the ions added. As  $K^+$ -ion is an exchanging ion weaker than  $H^+$ -ion, the  $\zeta$ -potential increases in the present exchange.<sup>23)</sup> When the pH value becomes larger than the neutralisation point on further addition of KOH, only  $K^+$ -ions remain as counter ions and the  $\zeta$ -potential decreases according to the concentration effect, as already stated in the case of  $H_2SO_4$ . (Fig. 7 d)

Thus, the coagulation of the sol (stated in Section (2)) and the change of the  $\zeta$ -potential (stated in Section (3)) can be sufficiently explained by the change of surface constitution of the colloid on the addition of  $H_2SO_4$  or KOH.

In short, on the addition of  $H_2SO_4$ , the surface constitution of the colloid is hardly different from that in the case of no addition, as expressed by  $Pt \cdot R = \dots H^+$ , but on the addition of KOH, the surface salt  $Pt \cdot R = \dots K^+$  is formed above the neutralisation point. In the present experiment, it was found that the reaction was of the acid type when  $H_2SO_4$  was added, as was the case when nothing was added; while in the case of KOH being added it was of the base type above the neutralisation point (see Table V.). It follows, therefore, that the difference between both types is caused by that of the surface constitution of the catalyst, namely, by that of the adsorbed electrolytes on the surface, especially the counter ions.

The base type may be ascribed to strong retardation, which appears only weakly at the initial stage in the case of the acid type, as above mentioned. Then, it may be maintained that the retardation is influenced by the adsorbed ions. This fact has already been ascertained in the second paper of this series<sup>9)</sup>. Since the present reaction is the catalysis in the liquid phase and the concentration of the reacting substance,  $H_2O_2$ , is small, it seems probable that it takes considerably long time before its adsorption equilibrium on the surface of the catalyst is established. And this may appear as the retardation of the initial stage. It is, therefore, appropriate to conclude that the retardation is influenced by the adsorbed ions of the double layers through which the reactant passes.

### Summary.

- (1) By the thermal analysis of reaction velocity, the influence of an acid

and a base upon the catalytic decomposition of hydrogen peroxide by the Bredig platinum sol has been examined. As the acid and base,  $\text{H}_2\text{SO}_4$  and  $\text{KOH}$  were used, whose concentration ranges were from  $10^{-5}$  to  $10^{-1}$  mol/litre.

(2) The reaction type is not changed by adding the acid, but it deviates from the first order reaction type when the base is added.

(3) The reaction velocity decreases slightly by increasing the concentration of the acid, but, in the case of the base, there is a minimum at about pH 6 and a maximum at pH 10.

(4) The relation between the  $\zeta$ -potential of colloidal particles and their catalytic activity has been discussed, and the minimum activity has been explained from the minimum of the  $\zeta$ -potential.

(5) According to the ionic adsorption theory, the difference of the reaction types between the acidic and the basic solutions has been discussed from the standpoint of the surface constitution of the colloid, and it is concluded that the ions adsorbed on the solid surface exert a close influence on the reaction.

In conclusion, the author has great pleasure in expressing his sincere thanks to Professor S. Horiba for his valuable guidance during the course of this research.

This paper is presented to the Committee of Catalysis of the Japan Society for the Promotion of Scientific Research.

*The Laboratory of Physical Chemistry,  
Kyoto Imperial University.*

(Received June 1, 1941)

## ERRATA.

*Second paper of this series by EIJI SUIITO, Vol. XV, p. 1 (1941).*

Page 5, line 2 from top: for  $\ln \frac{k_1}{k_2} = ER \frac{T_2 - T_1}{T_1 T_2}$  read  $\ln \frac{k_2}{k_1} = E/R \cdot \frac{T_2 - T_1}{T_1 T_2}$

Page 6, line 2 from bottom in foot note: for  $Q = 23.9$  cal. read  $Q = 23.9$  Kcal.

*Paper by REIICHI KONDO and EIJI SUIITO, Vol. XV, p. 145 (1941).*

Page 148, line 4 from bottom: for  $85 \pm 0.2^\circ\text{C}$ . read  $85 \pm 2^\circ\text{C}$ .

Page 153, line 3 from top: for  $T = 373^\circ\text{C}$ . read  $T = 373^\circ\text{K}$ , i.e.,  $T = 100^\circ\text{C}$ .