

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

### The Effect of Temperature and Heat Treatment of Platinum Sol upon the Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum.

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In order to elucidate the mechanism of the microheterogeneous catalysis, the catalytic decomposition of hydrogen peroxide by colloidal platinum was kinetically studied by the method of thermal analysis of reaction velocity as one of the most fundamentally simple instances. In the first paper<sup>1)</sup> of this series it was reported that the reaction proceeds in two stages; *the initial stage*, which is the special part noticed at the beginning of the reaction, and *the later stage*, which is the main part of the reaction and is rightly of the first order. In that investigation, the influence of the concentrations of platinum sol and hydrogen peroxide solution was mainly studied. In the present investigation, the activation energy for this reaction was measured under varying reaction temperatures, and the cause of the initial stage was studied by examining how the reaction type varied in the case of the sol preliminarily heated, boiled or frozen.

### Experimental.

*The platinum sol* used in the present experiment was prepared by Bredig's electric dispersion method (40 volts, 6 amp., D. C.) as in the previous research.<sup>1)</sup> As the catalytic activity of such a sol increases with aging,<sup>1)</sup> the sol, whose activity got fixed after several months since its preparation, was used; its concentration was about  $10^{-8}$  g.-atom/litre. *The hydrogen peroxide solution* used was Merck's Perhydrol diluted to 0.058 g.-mol./litre. All the water used was conductivity water redistilled from alkaline permanganate solution, using a Pyrex condenser. All the vessels used were made of 'Telex glass' and were steamed out.

The apparatus and procedure were almost similar to those in the previous report.<sup>1)</sup> Namely, the reaction started at the time when 50 c.c. of platinum sol was mixed with 50 c.c. of hydrogen peroxide solution in a glass calorimeter (a Dewar vessel) dipped in a thermostat. The temperature rise,  $\Delta T$ , in the reaction system by the heat generated by the catalytic decomposition of hydrogen peroxide was measured with time,  $t$ , by means of Beckmann's thermo-

1) E. Suito, This Journal, 13, 74 (1939).

meter. From the  $\Delta T-t$  curve thus obtained,  $\frac{Q}{W} \cdot \frac{dx}{dt}$  (viz., the reaction velocity,  $\frac{dx}{dt}$ , as  $Q$  and  $W$  are constants) is obtained according to the theoretical equation of thermal analysis:

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

where  $\frac{dT}{dt}$  is the temperature change in the reaction system,  $K$  is the cooling constant,  $\tau$  is the correction term,  $Q$  is the reaction heat and  $W$  is the water equivalent of the reaction system. As the main part of the reaction is of the first order, the reaction velocity constant,  $k_1$ , is also obtained from the slope of the straight part of the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curve.

The cooling constant  $K$ , the correction term  $\tau$ , and the water equivalent  $W$  of the apparatus used were measured at various temperatures, and their mean values are tabulated in Table I.

Table I.

Temp. (°C)	$K$ (min. <sup>-1</sup> )	$\tau$ (°C)	$r^*$ (ohm)	$W$ (cal.)
25	0.0134	+0.020	0.484	119.2
30	0.0140	+0.018	0.493	119.4
35	0.0148	+0.014	0.503	119.9
40	0.0156	+0.010	0.512	120.1
45	0.0164	+0.006	0.522	119.9
50	0.0172	+0.002	0.531	119.7
55	0.0178	-0.002	0.540	120.4
60	0.0182	-0.005	0.550	119.4
				mean 119.7

\*  $r$  denotes the resistance of the platinum wire of the heater necessary to calculate  $W$ . Its change with temperatures is shown here.

From the table it is seen that the cooling constant  $K$  increases with rising temperature and that its temperature coefficient agrees well with the theoretical value<sup>2)</sup> if the cooling of such a Dewar vessel with no silver plating as used for the present experiment is assumed to depend mainly on radiation. The correction term  $\tau$  decreases with rising temperature, and this is considered to be caused by the difference between the temperature of the reaction system and room temperature. It is natural that the water equivalent  $W$  does not vary with temperature; the mean value is found to be 119.7 cal.

## Results and their Considerations.

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

Experiments were carried out under such a condition as the initial concent-

2) Unpublished.

ration of hydrogen peroxide was 0.029 g.-mol./litre, the concentration of platinum sol (No. 4) was  $4 \times 10^{-6}$  g.-atom/litre and the temperatures of the reaction system, i.e. those of the thermostat, were 25, 30, 35, 40, 45, 50, 55 and 60° C. The curve obtained by plotting  $\Delta T$  for  $t$  is shown in Fig. 1. From this curve, according to the method of thermal analysis, the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curve was obtained and is shown in Fig. 2.

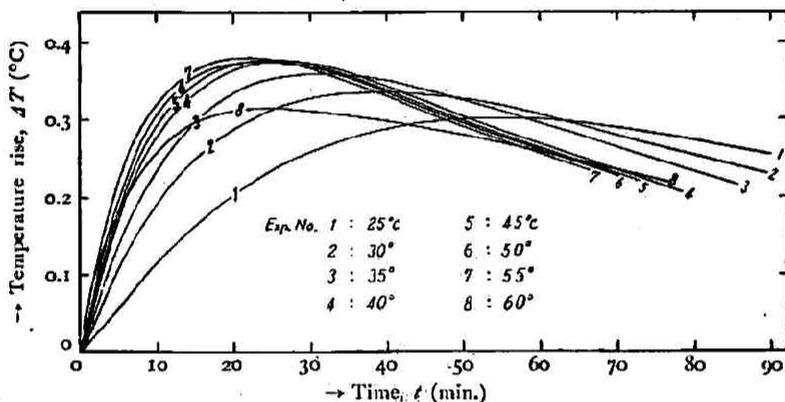


Fig. 1.  $\Delta T-t$  relation for the reactions at various temperatures.

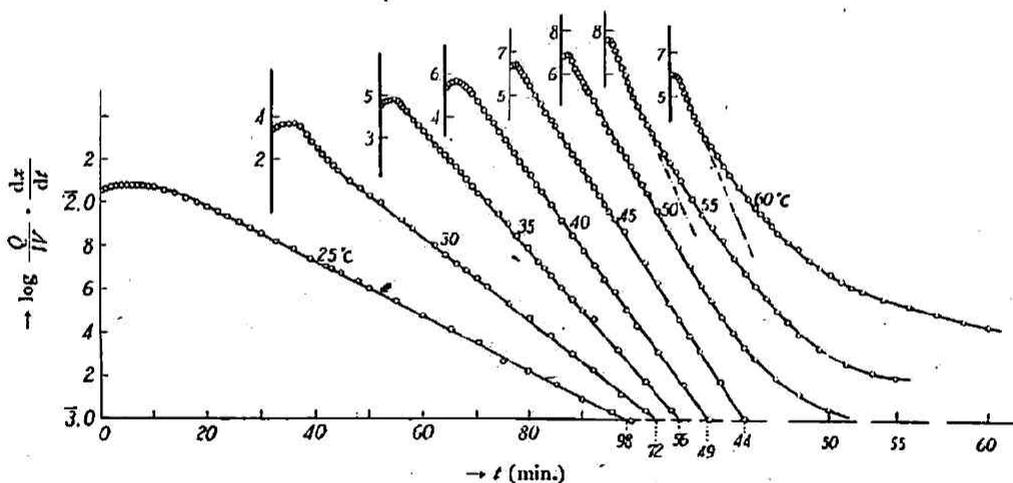


Fig. 2.  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  relation for the reactions at various temperatures.

(Note) Though the ordinate is displaced for each curve, the scale of both ordinate and abscissa is equal for each. The intersections of each reaction curve with the abscissa ( $\log \frac{Q}{W} \cdot \frac{dx}{dt} = 3.0$ ), i.e. 98, 72, 56, 49 and 44 minutes, indicate the time when the reaction has almost finished.

In Fig. 2, the initial stage particular to the reaction exists in each curve and its duration,  $\alpha$ , decreases with rising temperature, as shown in the third column of

Table II, while the initial reaction velocity,  $\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{int.}$ , increases as shown in the fourth column. At 60°C. however, both the cases are reversed. The later stage which is the main part of the reaction is exactly linear and namely of first order below 45°C. At 50°C. the final part of the curve deviates from the straight line. At 55°C. the whole part of the curve bends upwards, that is, the reaction becomes slower as they proceed, deviating from the first order. At 60°C. this bending is more remarkable. The value of  $k_1$ , the constant of the first order reaction velocity, obtained from the slope of the straight line is given in the fifth

Table II.

Initial conc. of H<sub>2</sub>O<sub>2</sub>: 0.029 g.-mol./litre, Conc. of Pt-sol (No. 4): 4 × 10<sup>-6</sup> g.-atom/litre.

Exp. No.	Temp. (°C)	a (min.)	$\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{int.}$	$k_1$ (min. <sup>-1</sup> )	E (cal.)	$k_m$
1	25	15	0.0115	0.028	16,338	0.024
2	30	10	0.0225	0.044	12,797	0.044
3	35	4	0.0294	0.063	9,154	0.058
4	40	3	0.0353	0.080	5,463	0.074
5	45	1.5	0.0435	0.092	3,005	0.083
6	50	1	0.0470	0.099		
7	55	1	0.0580	(0.110)		
8	60	2	0.0397	(0.099)		

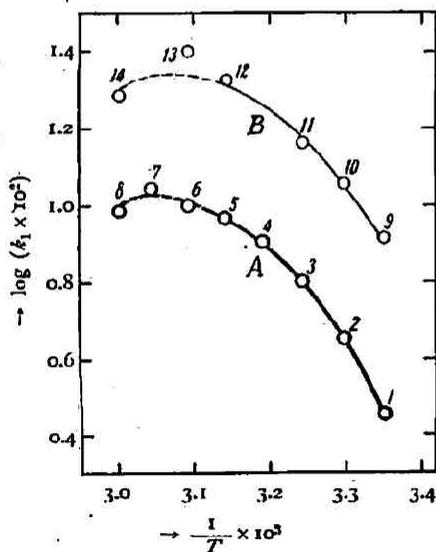


Fig. 3. Relation between the reaction velocity constant and temperature.  
Curve(A): Conc. of Pt-sol. 4 × 10<sup>-6</sup> g.-atom/litre.  
Curve(B): Conc. of Pt-sol. 8 × 10<sup>-6</sup> g.-atom/litre.

column of Table II and the relation between its logarithm and the temperature ( $\frac{1}{T}$ , the reciprocal of the absolute temperature) is drawn as Curve A in Fig. 3. As to the reactions at 50, 55 and 60°C., the value is obtained from the tangent at the initial part of the curve for the later stage of the reaction. At these high temperatures the thermal decomposition of hydrogen peroxide is also increased, but it is negligible because it merely amounts to a few hundredths of the catalytic decomposition. The relation between the initial reaction velocity  $\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{int.}$  and  $\frac{1}{T}$  is quite the same as in Fig. 3.

From Arrhenius' equation:

$$k = Ze^{-E/RT}, \text{ or } \ln \frac{k_1}{k_2} = ER \frac{T_2 - T_1}{T_1 T_2},$$

the apparent activation energy,  $E$ , was calculated and is given in the sixth column of Table II. The value obtained by Bredig and his collaborators<sup>3)</sup> is 11,700 cal. and this corresponds to  $E$  nearly at 30°C. From the fact that the temperature coefficient of this reaction is large, it has been admitted that the reaction velocity is determined not by the diffusion process of the reacting molecules but by the reaction itself. This idea is also confirmed by the fact that there is an optimum temperature for the reaction.

In another experiment made by using platinum sol whose concentration was twice as high ( $8 \times 10^{-6}$  g.-atom/litre), the same results were obtained, as given in Table III and Curve B in Fig. 3.

Table III.

Initial conc. of  $\text{H}_2\text{O}_2$ : 0.029 g.-mol./litre, Conc. of Pt-sol (No. 4):  $8 \times 10^{-6}$  g.-atom/litre.

Exp. No.	Temp. (°C)	$a$ (min.)	$\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{\text{int.}}$	$k_1$ (min. <sup>-1</sup> )
9	25	8	0.0300	0.083
10	30	3	0.0473	0.115
11	35	2	0.0659	0.150
12	45	1.5	0.0959	0.210
13	50	—	0.1100	0.253
14	60	—	0.0830	(0.191)

## (2) On the Occurrence of the Maximum Velocity.

It is very interesting to note that, as above mentioned, there exists the maximum reaction velocity at some temperature, because such a phenomenon was found for the first time in colloidal catalysis.

The enzyme reaction has generally an optimum velocity even at a low temperature (40—50°C.), and this is considered to be due to the deactivation of enzyme by heat. The present case may be also caused by the deactivation of colloidal Pt-catalyst by sintering. Then the fact that the reactions at 55 and 60°C. proceed slowing down, deviating from the first order, must be explained by the assumption that the deactivation of Pt-catalyst is taking place during the course of the reaction. For instance, in the reaction at 60°C. (Exp. No. 8) the velocity

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

constants  $k_1$  calculated from the tangents of the curve corresponding to 5 minutes and 50 minutes were 0.099 and 0.018 respectively and their ratio was about 5 : 1. As in every experiment the reactants were left to stand in the thermostat for about 1 hour before the start of the reaction to have the thermal equilibrium of the reaction system, this ratio must show the ratio of the activities of sols which were heated at 60°C. for about 1 hour and 1½ hours respectively. But, in practice, the activity of sol hardly varies even if it is preliminarily heated for 2—3 hours at 60°C. as shown in Exp. No. 15, 16 and 17 (cf. next Section). Consequently some other cause than the deactivation of catalyst must be considered.

Let us examine, by another analytical method, the types of the reactions at 55 and 60°C., whose  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curves are not of the first order. In the kinetic study of catalysis, the catalytic mechanism has already been elucidated in the author's laboratory<sup>4)</sup> by knowing the relation between  $\frac{x}{t}$  and the apparent unimolecular constant  $k_m = \frac{1}{t} \ln \frac{a}{a-x}$  where  $a$  is the initial concentration of the reactant and  $x$  is the concentration after a time,  $t$ , later.<sup>5)</sup> This relation obtained about Exp. Nos. 1—8 is shown in Fig. 4.

The curves for 25, 30, 35, 40 and 45°C. are exactly perpendicular, but their initial parts slightly bend. In other words, the main part of each

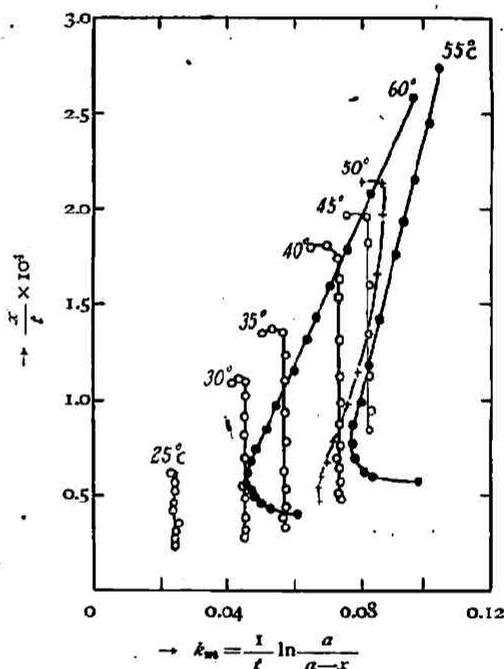


Fig. 4.  $\frac{x}{t} - \frac{1}{t} \ln \frac{a}{a-x}$  relation for the reactions at various temperatures.

4) S. Horiba and T. Ri, This Journal, 4, 123 (1930); R. Kiyama, *ibid.*, 13, 125 (1939); K. Seya, *ibid.*, 13, 137 (1939); etc.

5) In the thermo-analytical method, the way of calculating  $x$  is as follows:

Integrate the equation of the thermal analysis, eq. (1), from  $t=0$  to  $t=t$ , and this becomes

$$\int_0^t dT + K \int_0^t \Delta T \cdot dt - \tau K \cdot t = \frac{Q}{W} \int_0^t dx$$

$$\therefore x = \frac{W}{Q} \{ (\Delta T)_t + K \cdot S - \tau K \cdot t \}$$

Here,  $S = \int_0^t \Delta T \cdot dt$  and its value is obtained by the graphical integration of the  $\Delta T - t$  curve.  $(\Delta T)_t$  is the temperature difference at a time  $t$ .  $Q = 23.9$  cal. (the value obtained in the first report), and  $K$ ,  $\tau$  and  $W$  are given in Table I. From these values, the value of  $x$  can be calculated.

reaction is of the first order and at its initial part seems to be of the zero order. This agrees quite well with the result obtained in the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  relation (Fig. 2.), and  $k_m$  being constant, the value given in the last column of Table II fairly agrees with  $k_1$ . The curves for 55 and 60°C. are quite different from those below 45°C.: the main part of each reaction proceeds in the retarded type and at the end it changes from the first order into the zero order. The curve for 50°C. is of the intermediate type between the above two.

Thus, *below* the temperature for the maximum velocity, the main part of the reaction is of *the first order* with a *positive* temperature coefficient, but *above* that temperature it belongs to *the retarded type* with a *negative* temperature coefficient.

Generally, the catalytic reaction with a maximum activity has been found in the catalytic hydrogenation of unsaturated compounds, such as ethylene on a nickel catalyst in the case of the gas phase<sup>6)</sup> and crotonic acid and maleic acid in the acetic acid solution with a platinum black catalyst in the case of the liquid phase<sup>7)</sup>. This is explained by the reason that the decrease of the concentration of the reacting substance adsorbed, such as ethylene, with the rise of temperature overcomes the acceleration of the reaction velocity. The reaction is the bimolecular reaction of  $C_2H_4$  and  $H_2$  and its retardation is caused by the strong adsorption of  $C_2H_4$ . The present reaction is the monomolecular decomposition reaction of  $H_2O_2$  and generates  $H_2O$  and  $O_2$  as reaction products. As the reaction occurs in aqueous solution, the adsorption of  $H_2O$  on catalyst may be negligibly small. Supposing that the adsorption of the other reaction product,  $O_2$ , is very strong at *high* temperature, it may be considered that the adsorption of  $H_2O_2$  rapidly decreases and becomes a controlling factor. Accordingly, the absolute value of the negative temperature coefficient of the concentration of  $H_2O_2$  adsorbed becomes larger than that (positive value) of the true velocity constant, so that the apparent temperature coefficient of the reaction becomes negative. On the other hand, below the temperature for the maximum velocity the former is very small and less than the latter, and there is a positive temperature coefficient. Moreover, the experimental fact that the retarded type appears at higher temperatures than that corresponding with the maximum velocity is well explained as being naturally caused by the strong adsorption of  $O_2$ . For a supposed strong adsorption of  $O_2$  on

6) H. zur Strassen, *Z. physik. Chem.*, A 169, 81 (1934); O. Toyama, *This Journal*, 14, 94 (1940).

7) E. B. Maxted and C. H. Moon, *J. Chem. Soc.*, 1190 (1935).

Pt at high temperature, however, there is no evidence. It may be rather appropriate to consider that nascent oxygen generated by decomposition acts on the active center of Pt-catalyst. Even by such an inference the same result is obtained.

In short, the cause of both the retarded type and the negative temperature coefficient at high temperature is regarded as the retardation of the decomposition reaction by the action of oxygen generated by the reaction on the catalyst surface rather than as the deactivation by sintering of the colloidal catalyst surface by heat.

### (3) The Reaction with Heated Sol.

The question how far the activity of platinum sol varied when the sol was heated previous to the reaction was examined. Platinum sols (No. 4), the same ones as in the previous experiment, were heated for 2 hours at 45, 60, 80 and 95°C. respectively. Experiments were carried out at the reaction temperature 30°C., and the result obtained is given in Fig. 5 and Table IV. The sols heated

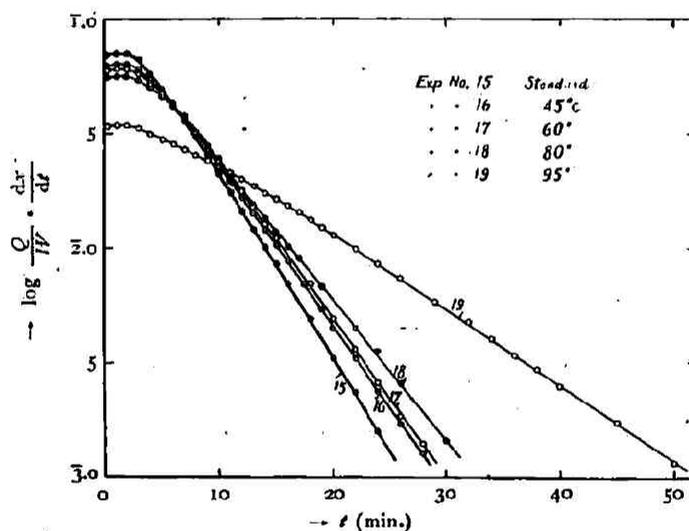


Fig. 5. The reactions with the heated sol.

at 45 and 60°C. show very little decrease in activity. (The sol heated at 60°C. for 3 hours shows the same activity as that heated for 2 hours.) The activity of the sol heated at 80°C. fairly decreases. The activity at 90°C. is below the half of that of the sol not heated. These reaction types show the characteristic curve similar to that of the sol not heated and the duration of their initial stages,  $\alpha$ , hardly varies.

Table IV.

Initial conc. of  $H_2O_2$ : 0.029 g.-mol./litre.  
 Conc. of Pt-sol (No. 4):  $9 \times 10^{-6}$  g.-atom/litre.  
 Temperature: 30°C.

Exp. No.	Temp. of Heat Treatment (°C)	$\alpha$ (min.)	$\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)_{int.}$	$k_1$
15	(standard)	2	0.0700	0.180
16	45	2	0.0620	0.160
17	60	2	0.0600	0.159
18	80	2	0.0568	0.140
19	95	2	0.0340	0.071

Maxted and Moon<sup>8)</sup> reported that, when a Pt-black catalyst was heated at 250—400°C., its activity in the hydrogen peroxide decomposition decreased to 23—2.6%, and that the activation energy of the reaction did not vary even by such a sintered catalyst. In the study of hydrogen overvoltage of platinized-Pt electrode, Frumkin and Slygin<sup>9)</sup> also observed sintering on the electrode surface by heating the electrode at 40—300°C. for 2 hours in hydrogen gas; even at so low a temperature as 40°C. the sintering was somewhat recognizable, and at 60°C. it was fairly remarkable, and at 300°C. the activity became 1/30. These are the instances of macroheterogeneous catalysis in liquid. Even in such a microheterogeneous catalysis as the present experiment, the decrease in activity by heating is properly considered to be due to the sintering on the surface of colloidal particles rather than to the growth of colloidal particles, that is, the decrease in the degree of their dispersion. This is clear from the fact that the sol does not coagulate and apparently shows no variation by heating.

#### (4) The Reaction with Boiled Sol.

The decomposition of hydrogen peroxide observed with platinum sol which was once boiled was of a different reaction type. The initial stage usually seen in the relation of  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  disappeared and an exactly straight line was obtained as shown in Fig. 6. This means that the reaction proceeds exactly in the first order from beginning to end.<sup>10)</sup> Let us call such a type 'the linear type'

8) E. B. Maxted and C. H. Moon, *J. Chem. Soc.*, 393 (1935).

9) A. Frumkin and A. Slygin, *Acta Physicochim. U. R. S. S.*, 5, 828 (1936).

10) In the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  relation, when the reaction is of the first order, the intersection of the straight line with the ordinate denotes  $\log \frac{Qk_1 a}{W}$  (see first report, p. 77), and from this value the reaction heat,  $Q$ , can be calculated. The values of  $Q$  thus obtained were equal to 23.9 Cal. per g.-mol. obtained in the first report.

and the former type 'the standard type'.

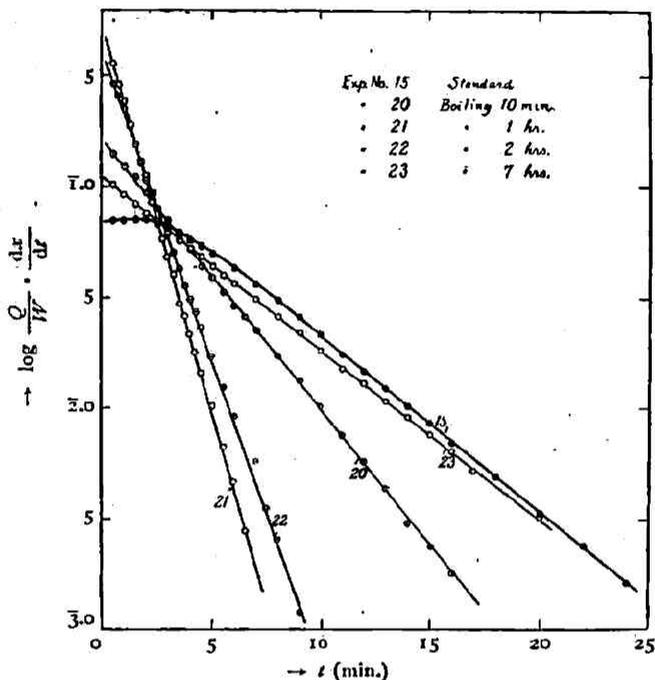


Fig. 6. The reactions with the boiled sol. (a).

Table V.

Initial conc. of  $H_2O_2$ : 0.029 g.-mol./litre.

Temperature: 30°C.

(a) Conc. of Pt-sol (No. 4):  $9 \times 10^{-6}$  g.-atom/litre.

Exp. No.	Treatment of Sol	$a$ (min.)	$(\frac{Q}{W} \cdot \frac{dr}{dr})_{int.}$	$k_1$	Coagulation
15	(Standard)	2	0.070	0.180	not
20	10 min. Boiled	0	0.150	0.262	not
21	1 hr. "	0	0.410	0.808	not
22	2 hrs. "	0	0.310	0.606	not
23	7 hrs. "	0	0.109	0.175	coag.

(b) Conc. of Pt-sol (No. 4):  $3 \times 10^{-6}$  g.-atom/litre.

24	(Standard)	7.5	0.011	0.023	not
25	1 hr. Boiled	0	0.026	0.038	not
26	1 hr. Boiled, 3 hrs. Air	0	0.010	0.020	not

The activity of the sol was increased by boiling. For instance, the activity of the sol boiled for 1 hour in a reflux condenser was four times as high as standard

(Exp. No. 21). The sol was stable for boiling, apparently showing neither variation nor coagulation. However, on further boiling the activity decreased again and the sol coagulated (Exp. No. 23). The reason why the initial stage disappears and the activity is increased by boiling will be explained later. The decrease in activity by long boiling will be ascribed to the growth of colloidal particles. A close examination under an ultramicroscope shows that in the sols boiled either for 10 minutes or for 1 hour the degree of dispersion was hardly varied, but that in the sol boiled for 4 hours it was reduced to about a half.

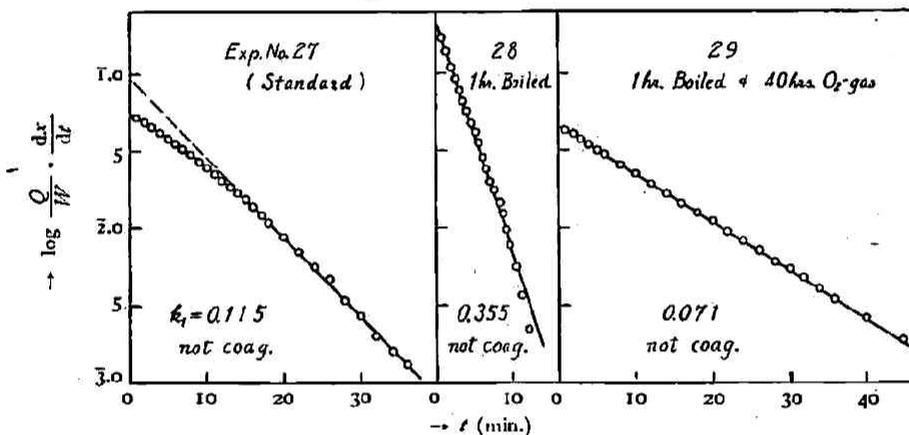


Fig. 7. The reactions with the boiled-sol. (c). Initial conc. of  $H_2O_2$ : 0.029 g.-mol./litre. Conc. of Pt-sol. (No. 5):  $10 \times 10^{-6}$  g.-atom/litre. Temperature: 25°C.

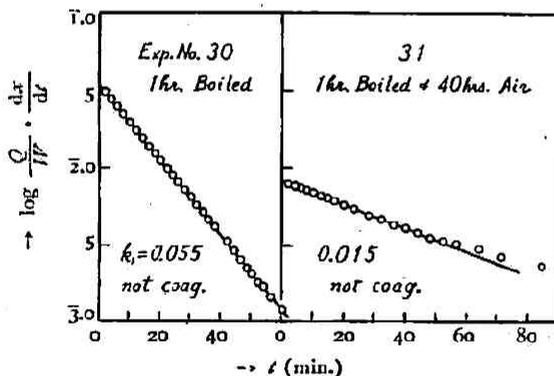


Fig. 8. The reactions with the boiled sol. (d). Initial conc. of  $H_2O_2$ : 0.029 g.-mol./litre. Conc. of Pt-sol. (No. 5):  $5 \times 10^{-6}$  g.-atom/litre. Temperature: 25°C.

Even in an experiment carried out with the sol diluted to 1/3, the activity was increased and the initial stage disappeared by boiling (Exp. No. 24 and 25 in Table V (b)). The above facts were confirmed by further experiments made with another sample of platinum sol (No. 5) prepared by the same method (Exp. No. 27 and 28 in Fig. 7).<sup>11)</sup>

Using the sol through which air or oxygen gas (washed with

11) In platinum sol No. 5, the maximum point of velocity did not appear in the initial stage of the  $\log \frac{Q}{W} \cdot \frac{dx}{dt} - t$  curve, but the curve deviated clearly from the straight line. Let  $\alpha'$  represent the time needed to reach the straight line, and then, for instance,  $\alpha' = 15$  minutes in Exp. No. 27. There exists  $\alpha'$  even in platinum sol No. 4; for instance,  $\alpha' = 2$  minutes and  $\alpha' = 8$  minutes in Exp. No. 15.

concentrated KOH solution and soda lime) was bubbled after such boiling, the reaction was found to be of 'the linear type', never turning back to 'the standard type' (Exp. No. 26, 29 and 31). The decrease in activity in this case is attributed to poisoning caused by the impurities present in the gas.

An experiment was made with the solution remaining after the reaction, that is, with the sol once made to react, the concentration of which was naturally reduced to  $1/2$ . The result obtained was that the sol belonging to 'the standard type' still showed the same standard type (Exp. No. 32) and the sol belonging to 'the linear type' showed the same linear type (Exp. No. 33) as shown in Fig. 9. From these facts it is inferred that at such a low temperature ( $25^{\circ}\text{C}.$ ) no variation caused by the reaction is recognized on the surface of the sol.

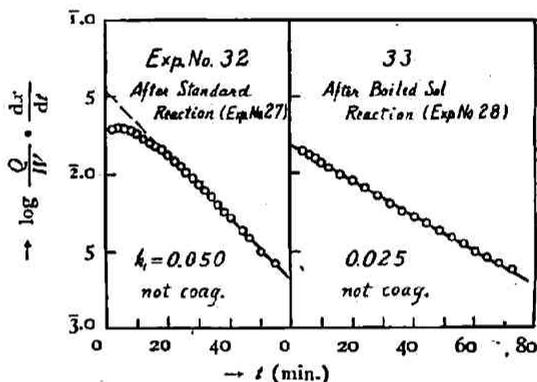


Fig. 9. The reactions with the sol once reacted. Initial conc. of  $\text{H}_2\text{O}_2$ : 0.029 g.-mol./litre. Conc. of Pt-sol. (No. 5):  $5 \times 10^{-6}$  g.-atom/litre. Temperature:  $25^{\circ}\text{C}.$

##### (5) The Reaction with Frozen and Remelted Sol.

As above mentioned, platinum sol is fairly stable for boiling, but unstable for freezing, coagulating instantly. By placing a container of the sol in the freezing mixture ( $-21^{\circ}\text{C}.$ ) consisting of NaCl and ice, the sol begins to freeze from its surroundings, expelling vigorously dissolved gas (air). The freezing proceeds gradually into the inner part of the sol. At the same time the concentration of the sol increases till the sol coagulates and the platinum particles are suspended as black flocculates, which all gather in the centre of the ice. A large number of gas bubbles, which have been included in the ice, burst out when the ice is melted. The solution when melted is no longer of brown colour which is characteristic of platinum sol, but is a suspended solution of platinum particles which are very minute but visible. The reaction with the solution thus obtained is 'the linear type' similar to the case with the boiled sol, as shown in Fig. 10. Its activity was, of course, remarkably decreased (Exp. No. 35). Though oxygen gas was bubbled through the once frozen sol, the type did not change into 'the standard type' as in the case with the boiled sol (Exp. No. 37).

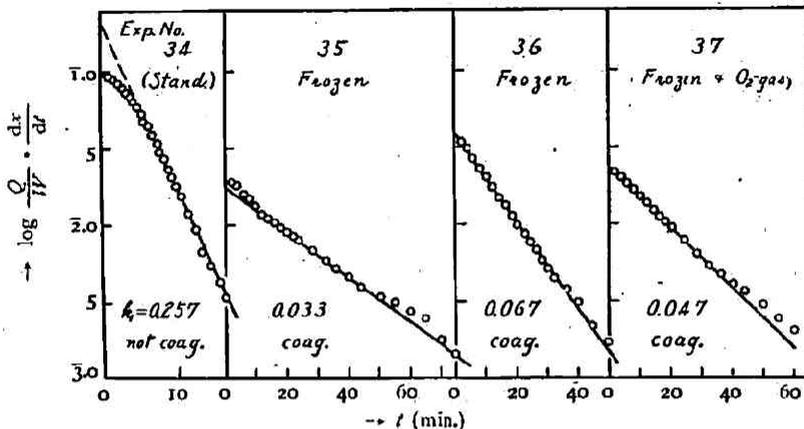


Fig. 10. The reactions with the frozen sol. ( $-20^{\circ}\text{C}$ ).  
 Initial conc. of  $\text{H}_2\text{O}_2$ :  $0.029$  g.-mol./litre.  
 Conc. of Pt-sol. (No. 5):  $15 \times 10^{-6}$  g.-atom/litre for Exp. No. 34, 35.  
 $30 \times 10^{-6}$  g.-atom/litre for Exp. No. 36, 37.  
 Temperature:  $25^{\circ}\text{C}$ .

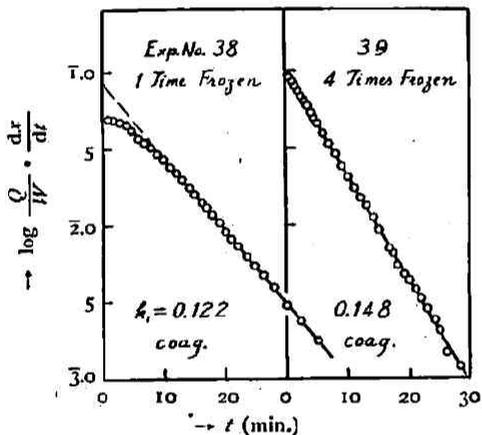


Fig. 11. The reactions with the frozen sol. ( $-78^{\circ}\text{C}$ ).  
 Initial conc. of  $\text{H}_2\text{O}_2$ :  $0.029$  g.-mol./litre.  
 Conc. of Pt-sol. (No. 5):  $30 \times 10^{-6}$  g.-atom/litre.  
 Temperature:  $25^{\circ}\text{C}$ .

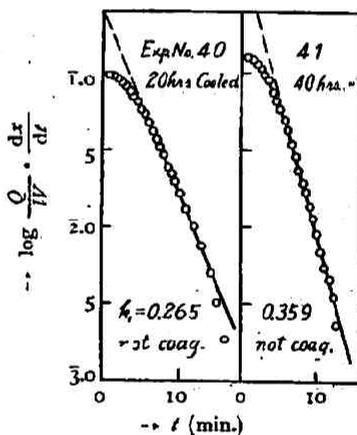


Fig. 12. The reactions with the cooled sol.  
 Initial conc. of  $\text{H}_2\text{O}_2$ :  $0.029$  g.-mol./litre.  
 Conc. of Pt-sol. (No. 5):  $15 \times 10^{-6}$  g.-atom/litre.  
 Temperature:  $25^{\circ}\text{C}$ .

When the sol was frozen in the freezing mixture ( $-78^{\circ}\text{C}$ .) consisting of dry ice and alcohol, it froze with a loud crash but expulsion of gas is little because of too sudden freezing. The reaction with the sol frozen once only showed 'the standard type' (Exp. No. 38), but when frozen four times, coagulating completely, the reaction clearly indicated 'the linear type' (Exp. No. 39).

Even if the sol is left to stand for a long time at a temperature near  $0^{\circ}\text{C}$ . it does not coagulate and the reaction shows 'the standard type' (Exp. No. 40 and 41).

**(6) On the Initial Part of the Reaction.<sup>12)</sup>**

The initial stage noticed in the standard type reaction, that is, the reaction with ordinary sols which are not previously treated, disappears when the sols are boiled or frozen, but it does not disappear when they are merely heated or cooled. It is natural that oxygen gas dissolved in the solution is expelled by boiling; the expulsion by freezing has been mentioned above. From these facts the initial stage seems to be attributable to the oxygen present in such a liquid; but it is not really so because the initial stage does not appear again even when oxygen gas is bubbled through the sol subjected to boiling or freezing and also because the initial stage does not disappear in the reaction with the sol boiled at a low temperature under reduced pressure (ca 30°C., 20 mmHg).<sup>13)</sup> However, the cause seems to be something related to oxygen.

Pennycuick<sup>14)</sup> and Pauli<sup>15)</sup> investigated into Bredig's platinum sol in detail. Both of them regard colloidal particles not as pure platinum but as platinum partly oxidized. Pennycuick regards the component of sol as  $[3.9 \text{ Pt} \cdot 1.16 \text{ Pt O}_2 \cdot 1.0 \text{ H}_2 \text{ Pt (OH)}_6]_n$  and maintains the existence of hexahydroxyplatinic acid as the surface ionogen. Pauli declares the existence of bivalent platinum oxide, PtO, and considers it to be reactive. Pennycuick found, from the measurement of conductivity of sol, that hexa-acid combining with platinum micelle gradually leaves into intermicellar liquid as free electrolyte by boiling. Bach and his collaborators<sup>16)</sup> are studying the structure of the electrically dispersed sol, preparing hydrogen-platinum and oxygen-platinum sols and measuring their conductivity, cataphoretic velocity, etc. They treat each colloidal particle as a small gas electrode because platinum sol and platinum electrode resemble each other in the state of electric charge and adsorption ability. They also coagulated the sol by freezing and measured its conductivity before and after the coagulation. In hydrogen platinum sol the conductivity of the original sol increases with the increase in concentration of sol, but that of the frozen sol

12) In the first report (Ref. 1, page 85) it was made out from the three points that 'the initial part' is ascribed not to the errors of the apparatus but to the reaction itself. This is justified by the fact that the initial part sometimes appears, sometimes disappears in the same apparatus as in the present experiment. (Especially, compare Exp. No. 15 with Exp. No. 23 in Fig. 6.)

13) Unpublished data.

14) S. W. Pennycuick, *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).

15) W. Pauli u. T. Schild, *Koll. Z.*, 72, 165 (1935); W. Pauli u. A. Baczewski, *Monatsh. Chem.*, 69, 204 (1936).

16) N. Bach u. N. Balaschowa, *Acta Physicochim. U. R. S. S.*, 3, 79 (1935); N. Bach and A. Rakow, *ibid.*, 7, 85 (1937); N. Balaschowa and N. Bach, *ibid.*, 7, 899 (1937); A. Zimin and N. Bach, *ibid.*, 11, 1 (1939).

becomes constant, independent of the concentration of sol. The difference of both conductivities corresponds to the colloid's own conductivity and the liquid obtained by remelting the frozen sol is exactly the same as the intermicellar liquid. Accordingly, hydrogen sol consists merely of platinum particles and hydrogen ion atmosphere. In oxygen sol, however, the difference between the frozen sol (coagulated sol) and the original sol, which is constant with respect to every sol concentration, is caused not by the conductivity of colloid itself, but by the existence of some other electrolyte. Though it is uncertain whether this electrolyte is such soluble platinum oxide as Pennycuik and Pauli presume, or the impurities contained in platinum, oxygen sol is not so simply constructed as hydrogen sol. Besides, air sol is similar to oxygen sol.

Thus, platinum sol is generally admitted to be a kind of acidoid sol. It is, therefore, certain from the experimental results above mentioned that, in the air sol used in the present experiment, an electrolyte is combined with the colloidal surface, forming an electrical double layer, and it leaves into the intermicellar liquid by boiling or freezing. It also seems probable that oxygen combines with a part of colloid surface and forms oxide film, either  $\text{PtO}_2$  or  $\text{PtO}$ . Accordingly, let us suppose that by boiling or freezing treatment the surface ionogen is desorbed and at the same time the combining oxygen also becomes free, being influenced by the expulsion of oxygen in liquid as already mentioned. The increase in activity by boiling mentioned in Section (4) is well explained by the removal of surface oxygen which is considered to retard such a reaction (*see* Section (2)). The decrease in activity by too long boiling has been observed to be due to the growth of colloidal particles, and in fact it is also well explained by the progress of crystallization caused by the desorption of surface ionogen.

Then the retardation of reaction recognized in the initial part of the standard type reaction should be ascribed to such combined oxygen and surface ionogen. This agrees with the fact, which will be reported in another paper, that the initial stage appears distinctly in the case of oxygen sol prepared in the atmosphere of oxygen, but that it does not exist in hydrogen sol prepared in hydrogen. Why, then, does the initial stage appear only in the presence of combined oxygen and surface ionogen? This question will be discussed some time in future. It is interesting to note that the structure of the colloid surface is closely related to the reaction. Elucidation of the structure leads to that of the mechanism of such colloidal catalysis and hence all the mechanisms of heterogeneous catalysis in solution will be made clear.

**Summary.**

(1) By the thermo-analytical method of reaction velocity, the catalytic decomposition of hydrogen peroxide by platinum sol has been measured at various temperatures (25, 30, 35,.....60°C.). The optimum temperature is recognized to be about 50°C. Above this temperature the reaction is not of the first order but of the retarded type.

(2) The surface of platinum colloid is sintered by heat treatment and its catalytic activity decreases.

(3) The sol is stable for boiling and its activity increases. But it is unstable for freezing and coagulates instantly, and its activity falls.

(4) In the reaction with the sol once boiled or frozen, the retardation at the initial stage is not observed and the whole reaction is exactly of the first order. The cause of the initial stage is discussed from the consideration of the structure of the sol.

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.

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**ERRATUM.**

*First paper of this series by EIJI SUI TO, Vol. XIII, p. 74 (1939).*

Page 83; line 15 from bottom: *for Ag-sol read Au-sol.*