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<th>Title</th>
<th>Thermal analysis of the catalytic action of colloids (I): catalytic decomposition of hydrogen peroxide by colloidal platinum</th>
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<td>Author(s)</td>
<td>水渡 英二</td>
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<tr>
<td>Citation</td>
<td>物理化学の進歩 13(3): 74-86</td>
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THERMAL ANALYSIS OF THE CATALYTIC ACTION OF COLLOIDS. (I)*

Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum.

By Eiji Surto.

Bredig and his collaborators first made comprehensive researches on the catalytic action by various colloidal solutions. They called the action of hydrosol of metal or metal oxide and hydroxide “Anorganische Fermente” because of the similarity of the action to that of enzyme. Since then, numerous investigations have been made and most of them done concerning the catalytic decomposition of hydrogen peroxide by colloidal platinum. In all of these studies chemical analysis such as titration of the solution or the measurement of the evolved oxygen has been adopted for the determination of the reaction velocity. The present author investigated the said reaction by the thermo-analytical method, which originated with Prof. S. Horiba and was successfully applicable for continued measurements of the reaction velocity, especially for the initial part of the reaction, in order to elucidate the mechanism of the decomposition and colloidal catalysis.

Experimental.

Materials.

The platinum sol was prepared by Bredig’s electric dispersion method, using a direct current (40 volts, 6 amperes) cooled in an ice-bath. After about 1 hour it became so dark brown that no electric spark was seen. The concentration then determined by precipitating with a little electrolyte was 60~80 mg. of platinum per litre. After standing for several days to permit the larger platinum particles to settle, the sol was carefully siphoned off and diluted.

* This is the English translation of the paper which appeared in Rev. Phys. Chem. Japan, 10, 251 (1936).

1) G. Bredig and co-workers, Z. physik. Chem., 31, 259 (1899); 37, 1, 323 (1901); 66, 162 (1906); 70, 34 (1909); 81, 385 (1912); Ber., 37, 598 (1894) etc.


This stock solution was so stable without any addition of a protective colloid or peptizer that no precipitate was noticed after several months; and it never coagulated after the decomposition of hydrogen peroxide.

The hydrogen peroxide solution was a diluted Merck's 'Perhydrol'.

All the water used was a conductivity water prepared thus: twice distilled water was redistilled by means of a Pyrex condenser and then the air without CO₂ was passed for several days. All the vessels used were made of 'Telex' glass⁴ and were steamed out.

Apparatus and Procedure.

In the thermal analysis in the liquid system, the measurement of the temperature change of the reaction system was made by means of a glass calorimeter as shown in Fig. 1. In the figure, A is a glass Dewar vessel holding about 100 c.c. of a solution, B a glass vessel which holds about 60 c.c., C a normal Beckmann's thermometer, D a glass stirrer rotating 300±20 times per minute, and E a heater with a platinum wire resistance movable up and down.

50 c.c. of platinum sol was introduced into A and a solution of hydrogen peroxide in B to let just 50 c.c. flow out of B'*. The lid which supports B, C, D and E was put on A tightly and then F' was connected. The whole apparatus was dipped in a thermostat at 30±0.002°C. The platinum sol in A was heated to almost the same temperature as that of the thermostat by E, and then F was drawn out to avoid the catalytic decomposition by it. After thermal equilibrium had been obtained about 1 hour later, hydrogen peroxide solution was siphoned off into platinum sol in A within 3-4 seconds, first blowing from f. Instantly they were mixed with each other and the reaction started. At the same moment, Beckmann's thermometer which was tapped automatically was read on. The initial concentration of hydrogen peroxide was determined in another flask by titration with standard potassium permanganate solution.

Calculation Method of Thermal Analysis.

The principle of the thermal analysis can be expressed by the following equation:

\[ \frac{dT}{dt} - \frac{dT'}{dt} = \frac{Q}{W} \frac{dx}{dt}, \]

where \( \frac{dT}{dt} \) is the temperature change in the reaction system, \( -\frac{dT'}{dt} \) is the cooling velocity due to the temperature difference between a reaction system and its surroundings, i.e. the thermostat, \( Q \cdot \frac{dx}{dt} \) is the heat quantity produced by the reaction per unit time (Q and \( \frac{dx}{dt} \)).

---

⁴ The 'Telex' glass manufactured by Tokyo Electric Co. Ltd. is similar to 'Pyrex' in quality.
are the reaction heat and the reaction velocity respectively), and $W$ the water equivalent of the reaction system.

**Cooling Constant and Water Equivalent.**

In the calculation of the reaction velocity and reaction heat according to equation (1), it is necessary to know $-\frac{dT'}{dt}$ and $W$ which are particular to the reaction system, i.e., the apparatus. In this case the cooling follows Newton's law, that is, it is proportional to the temperature difference, $dT$, between the reaction system and the thermostat. This was empirically justified with some correction, $\theta$ or $\tau$, caused by stirring heat or others. Therefore,

$$-\frac{dT'}{dt} = K \cdot \Delta T - \theta \quad \text{........................................... (2)}$$

Thus, by the measurement of natural cooling velocity of the reaction system the cooling constant $K$ and the correction term $\theta$ or $\tau$ can be obtained.

Let $r$ represent the resistance of the platinum wire of the heater and $i$ the intensity of the electric current transmitted through it, then the heat quantity per minute $q'$ liberated by the current is

$$q' = \frac{irr \times 100}{4.184} \quad \text{(cal.)}$$

Putting $q'$ for $Q \cdot \frac{dx}{dt}$ in equation (1), we have

$$W = \frac{d\theta}{dt} + K (\Delta T - \tau) \quad \text{........................................... (3)}$$

Accordingly, the water equivalent $W$ is obtained from the measurement of the rate of the temperature rise of the reaction system by electric heating. The resistance of the heater $r$ was measured preliminarily by a potentiometric method under the same condition as in the calculation of the water equivalent and was found to be 0.493 ohm. The values of $K$ and $W$ obtained are given in Table I.

**Table I.**

<table>
<thead>
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<th>No.</th>
<th>$r$ (°C)</th>
<th>$\theta$ (°C/min)</th>
<th>$\phi$</th>
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<th>$i$ (amp)</th>
<th>$W$ (cal)</th>
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Mean values: $\tau = 0.018$, $\theta = 0.00024$, $K = 0.0139$, $W = 116.6$

5) $\theta = K$; $\theta$ is the rate of temperature rise by stirring; $r$ is the temperature difference between the reaction system and the thermostat at thermal equilibrium, being due to stirring heat.

6) The platinum wire of the heater is dipped in the solution in this case and not in case of the reaction. Consequently, the water equivalent for the reaction must be exactly $W' = 0.014$, because the weight of the platinum wire is 0.46 gm. and the specific heat is 0.0312. This correction, however, is negligible as compared with the value of $W$.

7) As to the value of $K$, $(a)$ was obtained from graphical method and $(b)$ from calculation. See, S. Horiba and K. Sato, *Rev. Phys. Chem. Jap.,* 6, 25 (1938).
Reaction Velocity.

Substituting equation \( (z') \) in the fundamental formula \( (1) \), we have

\[
\frac{dT}{dt} + K(DT - \tau) = \frac{Q}{W} \cdot \frac{dx}{dt}.
\]

As \( \frac{dT}{dt} \) is the inclination of the reaction curve \( (DT - t \ curve) \), the value of \( \frac{Q}{W} \cdot \frac{dx}{dt} \) can be easily obtained from equation \( (4) \). In this case \( W \) is known and \( Q \) can be obtained as shown below; hence the reaction velocity \( \frac{dx}{dt} \) at a certain time can be calculated. Even if \( W \) and \( Q \) are unknown, both are constants and so the plot of \( \frac{Q}{W} \cdot \frac{dx}{dt} \) for a time \( t \) makes the reaction velocity curve.

If the reaction is of the first order,

\[
\frac{dx}{dt} = k_1(a - x) = k_1a - ke^{-kt},
\]

where \( k_1 \) is the velocity constant and \( a \) is the initial concentration. Putting \( (5) \) in equation \( (4) \) and taking logarithms, we have

\[
\log \left\{ \frac{dT}{dt} + K(DT - \tau) \right\} = \log \frac{Q}{W} \cdot \frac{dx}{dt} = \log \frac{Qk_1a}{W} - \frac{k_1t}{2.303}.
\]

Accordingly, plotting the value of \( \log \frac{Q}{W} \cdot \frac{dx}{dt} \) for a time \( t \), a straight line will be obtained and the slope of this line will give \( k_1 \).

Reaction heat.

From equations \( (1) \) and \( (2) \), the following equation is obtained:

\[
\frac{dT}{dt} + K(DT - \theta) = \frac{Q}{W} \cdot \frac{dx}{dt}.
\]

Integrating this equation from \( t=0 \) to \( t=t \), a certain time after the completion of the reaction, we have

\[
Q = \frac{W}{a} \left\{ \left( \int_0^t DT + K \int_0^t DT - \theta t \right) \right\}
\]

\[
= \frac{W}{a} \left\{ (DT)_{t=t} + K \cdot S - \theta t \right\}.
\]

Hence, if the value of \( S=\int_0^t DT \cdot dt \) is calculated by the graphical integration of the \( DT - t \ curve, \) the reaction heat \( Q \) can be obtained.

In the case of the first order reaction, the intersection of \( \log \frac{Q}{W} \cdot \frac{dx}{dt} \) line with the ordinate represents \( \log \frac{Qk_1a}{W} \) as seen from equation \( (6) \). Accordingly, from the initial concentration \( a \), the velocity constant \( k_1 \), and the water equivalent \( W \), the reaction heat \( Q \) can be calculated.

Experimental Results and their Consideration.

One of the results obtained is given in Table II. The curve obtained by plotting \( DT(=T - T_0) \) for \( t \) is shown as \( (a) \) in Figs. 3, 4, 6, 7 and 8.
Table II.

(a) Series I, Expt. 4. (Dec. 3, 1935)
Pt-sol 10cc.
H₂O₂ 0.029 g·mol/litre
30°C (room temp. 18—22°C)

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Tₜ=2.500

Using the values of \( \frac{Q}{W} \cdot \frac{dx}{dt} \) and \( \log \frac{Q}{W} \cdot \frac{dx}{dt} \) obtained from this curve according to equation (4), as an example in Table III, the reaction velocity curve was drawn as (b) in Figs. 3, 4, 7 and 8. And the \( \log \frac{Q}{W} \cdot \frac{dx}{dt} \sim t \) curve is seen nearly linear as (c) in Figs. 3, 4, 6, 7 and 8, and from its slope \( k \) was obtained.
### Table III.

(a)

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<th>$Q dx/W dt$</th>
<th>log $Q dx/W dt$</th>
<th>$t$ (min.)</th>
<th>$dT$ (°C)</th>
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(b)

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$k_1 = 0.0592$

$k_1 = 0.2923$
Five series of the experiments were carried out as follows (cf. Table IV):

I and II. The concentration of hydrogen peroxide was kept constant, and that of platinum sol was varied. The activity of platinum sol varied during the stock as proved in Series III. Series II were carried out on the sol, whose activity became extremely high in half a month's stock after series I.

III. The change of activity of the colloid caused with aging was examined.

IV and V. The concentration of hydrogen peroxide was changed. The time

<table>
<thead>
<tr>
<th>Series</th>
<th>Date</th>
<th>Concentration of H₂O₂</th>
<th>Concentration of Pt-sol.</th>
<th>α (min.)</th>
<th>k₁ (min⁻¹)</th>
<th>Q (Cal. / gₐm.)</th>
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<td>I</td>
<td>Dec. 5, 1935</td>
<td>3.7</td>
<td>0.029</td>
<td>1</td>
<td>0.4677</td>
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<td>Nov. 30</td>
<td>2.9</td>
<td>0.029</td>
<td>1.2</td>
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<td>24.474</td>
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<td>III</td>
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<td>3</td>
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<td>V</td>
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<td>0.029</td>
<td>4</td>
<td>0210</td>
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</table>

(Note) (1) The stock solution of Pt-sol No. 2, prepared on Nov. 12, 1935 was used for Series I, II, III & V, and No. 3 prepared on Feb. 3, 1936 for Series IV.

(2) The concentrations of H₂O₂ and Pt-sol indicate those at the reaction, i.e. those after the mixing of both solutions.
of the reaction was shortened and both series were completed within a few days to lessen the change of the activity. Series V were examined with the object of considering the initial part of the reaction.

1) Reaction Type.

The reaction always proceeds as shown schematically in Fig. 2: it proceeds in the two stages—the initial stage (ab) and the later stage (cde). The later stage, which is the main part of the reaction, is exactly of the first order (for the line c'd'e' is straight), and before this stage a special stage appears.

It has been admitted that the catalytic decomposition of hydrogen peroxide by metallic colloids is either of the first order or nearly of the first order with some deviation. Even in the present experiments, if \( k_1 \) is calculated by an ordinary method \( (k_1 = \frac{1}{t} \ln \frac{a}{a-x}) \) neglecting the initial stage, it does not become constant and the reaction does not exactly appear to be of the first order over the whole region. By the ordinary titration method the initial stage will never be noticed, because this stage is too short for the time interval of measurements. But it is interesting to mention that by the thermo-analytical method the initial stage was found, which will be discussed later.

2) The Effect of Concentration of Platinum Sol.

From the experimental results of Series I and II as shown in Figs. 3 and 4, the duration of time of the initial stage \( a \) (the 7th column in Table IV) is decreased as the concentration of the sol is increased. The reaction velocity constant \( k_1 \) is nearly proportional to the square of the concentration of the sol, as seen in Fig. 5.8)

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8) The deviation of the plots of Expts. 1 and 2 from the straight line of Series I can be explained by taking into account the increase in the activity with aging and that Expt. 2 was carried out first and Expt. 1 last in this series.
Generally speaking, in the case of colloidal catalysis, the reaction velocity is not proportional to the amount of catalyst, i.e., the concentration of the sol, and the following relation holds, that is,

$$\frac{k}{k'} = \left(\frac{c}{c'}\right)^n$$

where \(k\) and \(k'\) are the velocity constants for \(c\) and \(c'\), the concentrations of the sol. For the values of \(n\), Bredig and his co-workers\(^9\) have obtained 1.3~1.6, 1.1~1.4 and 1 in the decompositions of hydrogen peroxide by Pt-sol, Au-sol and Ir-sol respectively. In the present experiment, it was as high as 2.

\(^9\) loc. cit.
(3) The Change in the Activity of the Colloid with Time.

In the comparison between the experimental results Series I and II obtained with 5 c.c. and 10 c.c. of the sol, it was found that the reaction velocity was larger in Series II than in Series I. To make clear this change in the activity, the experimental results with some addition are shown in Fig. 6 as Series III. It was found that the activity of colloid increased with aging, reached the maximum and then diminished. And it is to be noted that the duration of the initial stage $a$ tends to become short with the time.

It is interesting that in colloidal catalysis the activity does not gradually diminish as in the common case of heterogeneous catalysts but rather increases to the maximum. This result G. Rocasolano\(^{10}\) has attributed to the effect of oxygen contained in the sol. S. Rusznyak\(^{11}\) has found in the decomposition of hydrogen peroxide by Ag-sol that when the dispersity is high, i.e. the size of the colloidal particle is small, the activity is also low. This relation between the particle size and activity can not be applied as a general rule to colloidal catalysis, because his experiments were carried out with the sol which was prepared chemically by reducing method and seemed to contain many other substances acting as a poison; but if we regard his results as applicable to our case, we may think that the increase in activity with aging is due to the growth of the colloid particles. However, it is probably inferred that the phenomena is rather due to the change in the surface nature of the colloid.

A more definite interpretation of this phenomenon will require further experiments. And the relation between the size of the particle of a colloid and its activity is an interesting question in the colloidal catalysis. The fact that the activity falls off after a long time as in Expt. 4 may be ascribed to the decrease in the concentration of the sol by precipitation.

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\(^{10}\) G. Rocasolano, *Compt. rend.*, 170, 1502; 171, 301 (1920).

(4) The Effect of Concentration of Hydrogen Peroxide Solution.

The experimental results (Series IV and V) obtained with various concentrations of hydrogen peroxide are shown in Figs. 7 and 8.\textsuperscript{12}

\[ \text{Fig. 7.} \]

\[ \text{Fig. 8.} \]

It is seen from the reaction velocity curve that the initial reaction velocity is nearly proportional to the initial concentration of hydrogen peroxide, and that

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each reaction ends almost at the same time. Next, that the linear part of the
\[ \log \frac{Q}{W} \cdot \frac{dx}{dt} \sim t \] curve runs in parallel shows that the reaction velocity constant
\( k_1 \) agrees well with one another. The duration of the initial stage \( a \) is about 1
min. in Series IV and 2–3 min. in Series V.

(5) The Heat of Decomposition of \( \text{H}_2\text{O}_2 \).

The reaction heat \( Q \) calculated according to equation (7) is 23.9±0.5 Cal.
per 1 g.-mol, being in considerably good agreement as shown in the last column
of Table IV.

Let us compare this result with those of other investigators. Matheson and Mass,\(^{13}\)
obtained 23.45 Cal. as the decomposition of hydrogen peroxide solution with small particles
of \( \text{MnO}_2 \) by means of adiabatic calorimeter. Roth, Gran and Meichsner\(^{14}\) obtained 23.42
Cal. (at 20°C) for a 97.27% solution and 22.64 Cal. for 0.33% solution. From thermo-chemical
data\(^{15}\), \(-22\sim-25\) Cal. was calculated as the heat of formation from water and oxygen gas.
In comparison with these values it is seen that the author's value is proper.

(6) The Initial Part of the Reaction.

As to the initial part of the reaction, the deviation of the curve from the
first order is very slight. But it is ascribed not to the errors of the apparatus,
such as the time lag of Beckmann's thermometer, absorption of heat by the calorimeter,
etc., but to the reaction itself as is clear from the following three points.

(1) The deviation can not be noticed in the case of electric heating.

(2) When the reaction heat was calculated from the intersection of the ex-
tension of the straight part in the log \( \frac{Q}{W} \cdot \frac{dx}{dt} \sim t \) curve with the ordinate under
the assumption that the reaction proceeds according to the first order from the
beginning, the value obtained is generally larger than that obtained before, and
there is no agreement in the value of each experiment.

(3) As to the duration of the initial stage \( a \), inspecting from the results of
Series I and II, it is found that the higher the concentration of the sol is, the
shorter the duration becomes. If the difference among the duration is to be
regarded as due to the initial reaction velocity, that is, the rate of temperature
rise, the error to be caused by the apparatus also should be taken into account.
But, as seen from the results of Series IV and V, even though the initial reaction
velocity is different, when the concentration of the sol is definite, \( a \) is nearly

\(^{15}\) M. Belthelot, Compt. rend., 90, 331, 897 (1880); R. de Forcrand, Ibid., 130, 1250 (1900); J.
Thomson, Thermochimische Untersuchungen, etc.
constant. Moreover, in comparison between the results of these two series it is found that variation in the concentrations of the sol leads to the different value of $a$ even in the same initial velocity. Therefore, it is inferred that $a$ is affected not by the rate of temperature rise but by the reaction itself, and probably it is related to the amount of the colloid.

The reaction velocity curve of the initial stage is indefinite in each experiment, being not always linear. Therefore, the nature of the reaction of this stage cannot be made clear. The appearance of this stage may depend upon the adsorption of hydrogen peroxide on the surface of colloid, namely, to reach the adsorption equilibrium in liquid system may need a considerable time, which will be the duration of initial stage $a$. And in colloidal system the electric double layer of its surface will play an important role for the adsorption (diffusion). This presumption is not certain and theoretical consideration on this colloidal catalysis will be required.

Summary.

1) By the method of thermal analysis the catalytic decomposition of hydrogen peroxide solution by platinum sol has been studied, especially the effect of the concentration of platinum sol and that of hydrogen peroxide.

2) It has been found that the reaction proceeds in two stages: the initial stage and the later stage. The duration of the initial stage is practically independent of the concentration of hydrogen peroxide and is nearly in inverse proportion to concentration of the sol. The later stage, which is the main part of reaction, is of the first order with respect to hydrogen peroxide and the reaction velocity constant is proportional to the square of the concentration of the sol, i.e.,

$$\frac{dx}{dt} = k_1 (H_2O_2), \quad k_1 \propto (Pt-sol)^2. $$

3) The activity of the colloidal catalyst increases at first with aging.

4) The value of the decomposition heat of hydrogen peroxide has been found to be 239 Cal. per g.-mol.

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

The Laboratory of Physical Chemistry,
Kyoto Imperial University.

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