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STUDIES OF COLLOIDAL CATALYSTS BY THERMAL ANALYSIS OF REACTION VELOCITY. VII.

On the Permanent Poisoning of Catalysts.

By Eiji Suito.

Generally, in the poisoning of catalysts two types are recognized, "temporary and permanent". As one of the former cases, the poisoning of the catalytic decomposition of hydrogen peroxide on colloidal platinum by carbon monoxide was reported in the previous report of this series[1]. Now, as the latter case, the effect of mercuric chloride, mercuric cyanide and potassium cyanide (and, as the comparing common salt, potassium chloride) on that reaction has been investigated by the method of thermal analysis of reaction velocity[2]. Then the behaviour of the poison, the cation Hg^{++} and the anion CN^- (K^+ and Cl^- ions make no poisoning), examined and the ionic adsorption discussed.

Experimental.

The *apparatus* and the *procedure* of the thermal analysis were similar to those in the previous report[2]. Namely, 50 cc. of hydrogen peroxide solution and 50 cc. of platinum sol, to either of which a given amount of the poison was added, were mixed together in a glass calorimeter. The temperature rise, $\triangle T$, in the reaction system caused by the decomposition of hydrogen peroxide is measured with time, t. From the thermoanalytical equation,

$$\frac{dT}{dt}+K\triangle T=\frac{Q}{W}\cdot\frac{dx}{dt}$$

K: the cooling constant of the reaction system, 0.013
W: the water equivalent of the reaction system, 119.5 cal.
Q: the decomposition heat of H_2O_2, 23.9 Kcal/mol.

the reaction velocity, $\frac{dx}{dt}$, is obtained. The relation $\triangle T \sim t$ (curve (a) in the figures) and $\log \frac{dx}{dt} \sim t$ (curve (b)) show the type of the reaction. If the reaction is first order, the latter relation is expressed by a streight line and its slope

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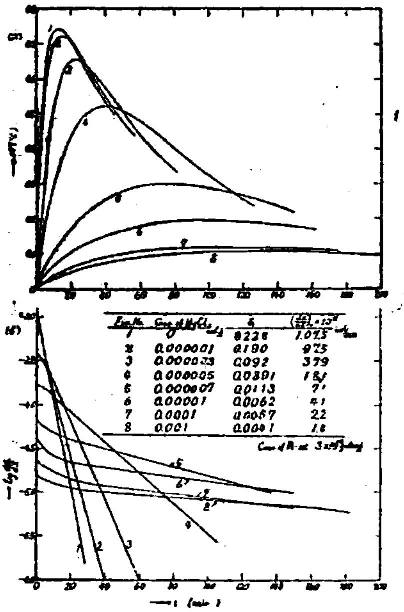
[1] Eizi Suito, *This Journal*, 18, 96, 109 (1944).
[2] Eizi Suito, *ibid.*, 13, 76 (1939). 15, 1, 155 (1941). 16, 1 (1942).

indicatesthe velocity constant. The activities of catalysts are compared by using the first order velocity constant, k, and the initial reaction velocity, $\left(\frac{dx}{dt}\right)_0$.

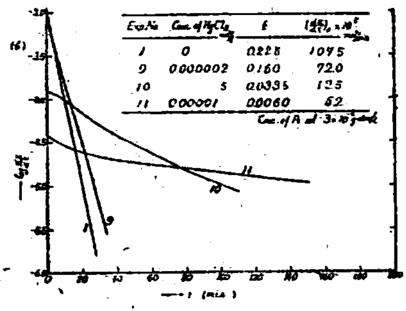
The *platinum sol* used was prepared electrically by high frequency alternating current (Svedberg method) in air and treated with hydrogen gas; the sol obtained was accordingly very stable hydrogen sol which had the surface of platinum[1] and its concentration was $3\sim6\times10^{-5}$ g-atom/l at the reaction. The amount of the poisons added was so small that the sol did not coagulate through all the experiments. (But in the case of a large amount of KCl it coagulated.) The concentration of *hydrogen peroxide* was always 0.05 mol/l at the reaction. The *temperature* of the experiments was always 25°C.



Exp. No.	Conc. of $HgCl_2$ mol/l	k	$\left(\frac{dx}{dt}\right)_0\times10$[illegible] mol/l·min
1	0	0.228	1.075
2	0.000001	0.190	975
3	0.0000033	0.092	379
4	0.000005	0.0391	181
5	0.000007	0.0113	7'
6	0.00001	0.0062	41
7	0.0001	0.0057	22
8	0.001	0.0041	1.8

Conc. of Pt-sol 3×10^{-5} g-atom/l

Fig. 1



Exp. No.	Conc. of $HgCl_2$ mol/l	k	$\left(\frac{dx}{dt}\right)_0\times10^5$ mol/l·min
1	0	0.228	1075
9	0.000002	0.160	72.0
10	5	0.0335	12.5
11	0.00001	0.0060	5.2

Conc. of Pt-sol 3×10^{-5} g-atom/l

Fig. 2

Experimental Results.

Series A: The reaction between the H_2O_2-solution and the Pt-sols containing various amounts of poisons.

Series B: The reaction between the H_2O_2-solutions containing various amounts of poisons and the Pt-sol.

(1) Mercuric chloride, $HgCl_2$.

Series A (Exp. No. 1~8 shown in Fig. 1.)

The reaction type is not different from the standard reaction in the absence of poison (Exp. No. 1.) and is mainly first order, except at the initial stage which is caused particularly by the hydrogen sol. As the amount of the poison is increased, the activity, k or $\left(\frac{dx}{dt}\right)_0$, decrease.

Series B (Exp. No. 9~11 in Fig. 2.)

The reaction type and the depression of the activity is much the same as in Series A.

(2) Potassium cyanide, KCN.

Series A (Exp. No. 12~19 in Fig. 3.)

The relation between log $\frac{dx}{dt}$ and t is not linear but "S"-shaped; *viz.* the reaction is not first order. Although k is not determined, the activity indicated by $\left(\frac{dx}{dt}\right)_0$ is remarkably decreased with the increase of concentration of KCN.

Series B (Exp, No. 20~26 in Fig. 4.)

The reaction is of "S" type, being the same as in Series A, but it differs from Series A that all the log $\left(\frac{dx}{dt}\right)\sim t$ curves converge to the point $\left(\frac{dx}{dt}\right)_{0,0}$ of standard reaction when $t=0$.

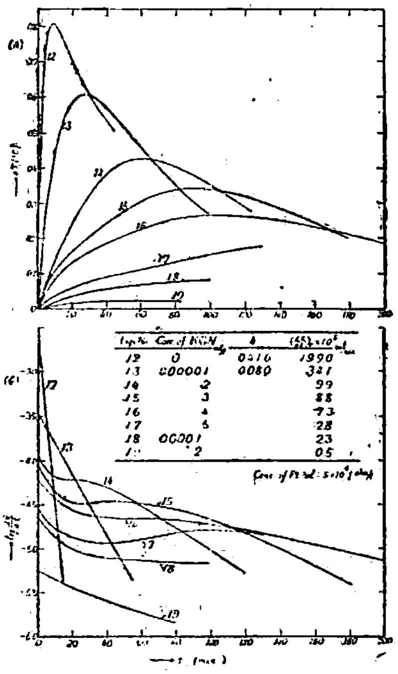


Fig. 3

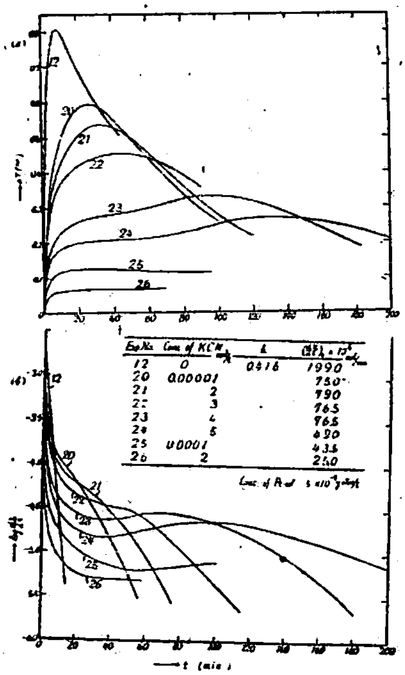


Fig. 4

(3) **Mercuric cyanide, $Hg(CN)_2$.**

Series A (Exp. No. 27~33 in Fig. 5.)

Series B (Exp. No. 34~35 in Fig. 6.)

In both Series, the reaction is of "S" type and the activity, $\left(\frac{dx}{dt}\right)_0$, is similary affected by the concentration of the poison.

(4) **Potassium chloride, KCl.**

Series A (Exp. No. 36~41 in Fig. 7.)

Series B (Exp. No. 42~45 in Fig. 8.)

It is the first order reaction. In comparison with the case of poison, the

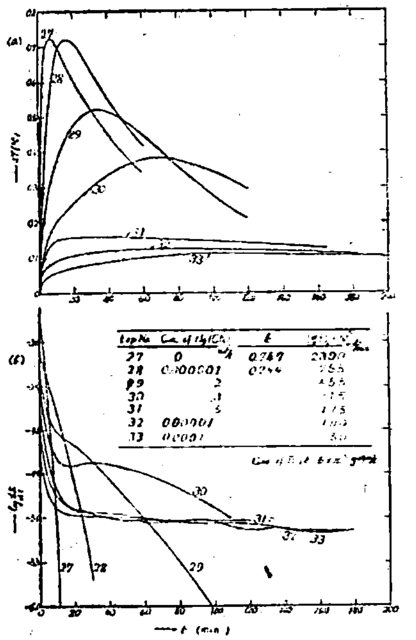


Fig. 5

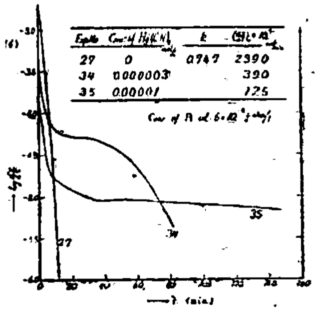


Fig. 6

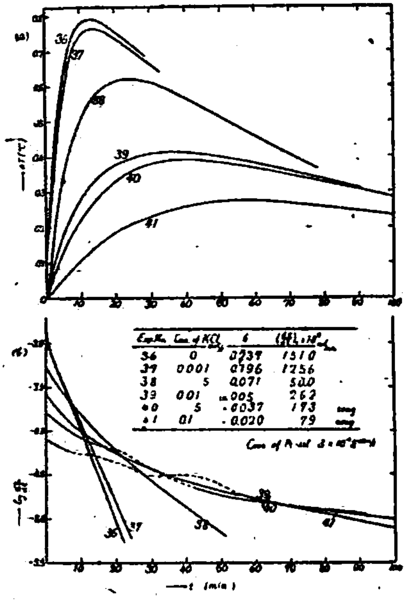


Fig. 7

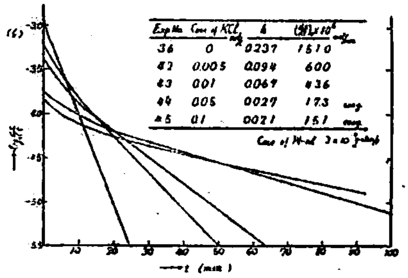


Fig. 8

depression of the activity is attended by the addition of so large amounts of the salt, that sol coagulates in the concentration of KCl above 0.05 mol/l.

Considerations.

Reaction type.

In the case of $HgCl_2$ (and KCl), the reaction type has not changed, being the first order. This fact demonstrated that the Hg^{++} ion once adsorbed on the catalyst does not react with the reactant, H_2O_2, and is a completely permanent poison. In the cases of KCN and $Hg(CN)_2$, on the other hand, the " S " type reaction may rather indicate that the activity of the catalyst diminishes slowly as the reaction proceeds according to the influence of the reactant on the poison CN^- ion ; than that two kinds of first order reaction with the constant k_1 and k_2 ($k_1 > k_2$) consecutively proceed.

Toxicity of various poisons.

The ratio of the first order reaction constant at various concentration of a poison to that in absence of the poison, k_c/k_0, conincides with the same ratio of the initial reaction velocity, $\left(\frac{dx}{dt}\right)_{0,c}\Big/\left(\frac{dx}{dt}\right)_{0,0}$, in the case of $HgCl_2$ and KCl. As the concentration of the catalyst, C, in a series is slightly different from each other, the ratio of the concentrations of poison to that of Pt-sol in each series, $c' = c/C$, indicates the relative amounts of poison through all series. The relation between the relative activity, k_c/k_0 or $\left(\frac{dx}{dt}\right)_{0,c}\Big/\left(\frac{dx}{dt}\right)_{0,0}$ and the relative amount of poison, c', is shown Fig. 9. In the case of $HgCl_2$, $Hg(CN)_2$ and KCl, the curves of Series A and B fall on each other. The order of toxicity is $Hg(CN)_2 > HgCl_2 > KCN$ ($\gg$KCl) as indicated by the relative amounts of poison to reduce the relative activity to 1/2 and 1/10. (see Table I). Obviously KCl does not act as a poison, and K^+ and Cl^- ions, therefore, can be neglected in the discussion of poisoning effect.

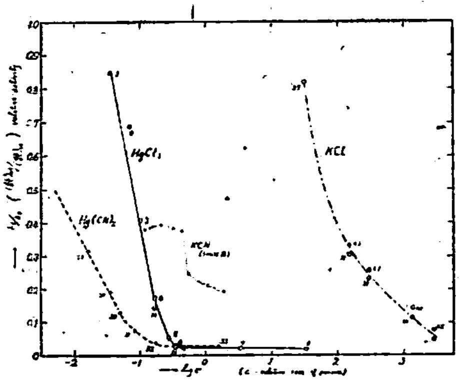


Fig. 9

Table I.

poison	toxisity		comparison of $\left(\frac{dx}{dt}\right)_0$ in series A and B	Reaction type
	$c'_{1/2}$	$c'_{1/10}$		
$HgCl_2$	0.008	0.02	A=B	first order
$Hg(CN)_2$	0.0008	0.008	A=B	"S" type
KCN		(0.03)	A<B	"S" type
KCl	10	250	A=B	first order

The curves of $HgCl_2$ and $Hg(CN)_2$ in Fig. 9. are linear, bending at $c' = 0.5$ mol. For the cause of this point, Maxted[3] attributed it to two kinds of active centre on the catalyst. But the author thinks that it is equivalent to the saturation value of adsorption that all parts of the catalyst surface is covered by the poison, Hg^{++}. Now, let us calculate the area of the catalyst surface. If a particle of the

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[3] E. B. Maxted, *J. Chem. Soc.*, 119, 225 (1926), 121, 1760 (1922), 127, 73 (1925).
E. B. Maxted & G. J. Lewis, *ibid.*; 502 (1933).

platinum colloid is a sphere of 2 mμ radius (sp. wt. of Pt is 214); the number of colloid particle is 3×10^{20} and its total surface area is 1.5×10^{8} cm^2 per 1 g-atom. As the radius of Hg^{++} ion (Hg atom) is 1.1 (1.5) Å, its number to cover completely the total surface of the catalyst as monomolecular film is 3×10^{23} (1.7×10^{23}) and namely 0.5 (0.3) mol. This value coincides with the above value of c'. Of course, it is assumed that the surface of the catalyst is smooth, because its colloidal particles have primary stability.

On the ionic adsorption.

It is sure that the falling of activity is due to strong adsorption of the poisons on the surfaces of colloidal platinum. Generally, there are two types of adsorption in solution,

(a) Molecular adsorption—non-polar adsorption (non-electrolyte)
(b) Ionic adsorption—polar adsorption (electrolyte).

And the latter can be divided into 4 cases as follow:

(1) True adsorption of electrolyte (Gibb's adsorption)
(2) Adsorption of potential determining ion.
(3) Exchange adsorption of counter ion.
(4) Exchange adsorption of lattice ion.

It is recognized that the adsorption isotherm is expressed by Freundlich equation $\log x = a \log c$ in the case (1) and $x = a + b \log c$, which is led from the Nernst-equation, in the (2).

As seen in Fig. 9. in the case of HgCl$_2$ and Hg(CN)$_2$ the activity of catalyst is in proportion to the logarithm of the poison concentration, *viz.* $\frac{k_0}{k_c} = a - b \log c'$, below its saturation value. In the case of KCl, on the otherhand, the relation between k_0/k_c and $\log c'$ is not linear, that between $\log k_0/k_c$ and $\log c'$ being linear. Accordingly in the case of KCl which does not act as a poison, it seems that neither K$^+$ nor Cl$^-$ ion has special affinity and can be selectively adsorbed on platinum surface, but the accumulation of the electrolyte—both cation and anion—retards the reaction velocity. (case (1)). It is quite natural that the influence comes out only when the concentration of the electrolyte is very high as compared with the other cases. On the otherhand, owing to the special affinity of mercury to platinum, Hg^{++} ion will be strongly adsorbed on the surface of the catalyst and never desorbed by any cause. (case (2)). Thus, this ionic adsorption causes phenomena of permanent poisoning. In this case, both HgCl$_2$ and Hg(CN)$_2$ have very small ionization values (HgCl$_2$ is regarded as a non-electrolyte), but the dissociation will be increased by the strong ionic adsorption. After the saturation concentration of poison to cover the total surface of catalyst, the hydrogen peroxide is not to decompose, but practically it decomposes a little. This fact seems to show that the decomposition occurs on the surface of mercury which is adsorbed and deposited out on platinum, namly, by the Hg-sol. (It was tested that H_2O_2 was never decomposed by $HgCl_2$ alone).

In the case of CN poison, it may be attributed to the molecular adsorption of HCN rather than to the ionic adsorption of CN^- ion, became HCN is easily formed by hydrolysis of KCN in solution. And, as HCN is a very weak acid (ionization const. is 7.2×10^{-10}), its dissociation degree will be changed by H_2O_2 (an acid), and then this seems to cause " S " type reaction.

That the initial reaction velocities in Series A and B are equal to each other, shows that the ionic adsorption just discussed need very short time to reach its equilibrium state.

In closing, it is the author's pleasant duty to acknowledge his sincere thanks to Professor S. Horiba for his valuable guidance during the course of this research.

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