A STUDY OF THE ENERGY DISTRIBUTION OF THE ACTIVE CENTRES OF CATALYSTS BY THE ADSORPTION OF POISONOUS SUBSTANCES.

The Decomposition of Hydrogen Peroxide with Platinum Black poisoned by Mercuric Ion.

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Introduction.

It has frequently been suggested that catalysis does not proceed at uniform rate over the whole of an accessible catalytic surface, and the concept of "active centre" was put forward by Taylor[1], which has been extended by Schwab, Pietch and others[2], and also by Smekal[3] from various experimental evidences.

With respect to these concepts, it is probable that there are innumerable degrees in the activity of the surface atoms which compose the active centres. Therefore, it will be of great importance for making clear the mechanism of the action of a catalyst to investigate the energy distribution of these centres and the controlling factors.. From the standpoint of chemical kinetics, a number of experiments have already been carried out[4]. In the present experiment, as one of the most appropriate methods of making such an investigation as this, successive poisoning is adopted: the change of activity of the catalyst is measured in the presence of a poisonous substance which is adsorbed strongly on a catalyst and yet is indifferent to the reaction. For the higher the activity of the atoms is, the more strongly the poison is adsorbed and so by successive small additions of poisonous substances the centres will be spoiled in the order of activity.

Many studies on this line have been made and an interesting phenomenon—selective poisoning—has been discovered. For instance, Vavon and Husson[5] found that a platinum catalyst could be poisoned by addition of a small quantity of

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[1] *Proc. Roy. Soc.* [A], 108, 105 (1925); *J. Phys. Chem.*, 30, 145 (1926).

[2] *Z. physik. Chem.* [B], 1, 385 (1928); 2, 262: 5, 1 (1929); 12, 427 (1931); *Z. Elektrochem.*, 35, 573 (1929).

[3] *Physik. Z.*, 26, 707 (1925); 27, 837 (1926); *Z. Elektrochem.*, 34, 477 (1928); *Z. Physik.*, 55, 289 (1929).

[4] Horiba and Ri, *Rec. Trav.*, 51, 641 (1931); *Rev. Phys. Chem. Japan* (Japanese Edition), 4, 73 (1930).
Ri, *ibid.*, 5, 41 (1931).
Ri and Nagamitsu, *ibid.*, 9, 140 (1935).
Kubokawa, *ibid.*, 11, 82, 96 (1937).

[5] *Compt. rend.*, 175, 277 (1922).

carbon disulphide as far as its action in hydrogenation of propyl ketone was concerned, but that the catalyst was still active for hydrogenation of piperonal: addition of carbon disulphide in turn suppressed the later reaction, but the catalyst remained effective for hydrogenation of nitrobenzene. Similar studies on selective poisoning have been done by Willstätter and Hatt[6], Kubota and Yoshikawa[7], Rideal and Wright[8], and Ghosh and Bakshi[9]. These studies, however, have only shown a variety of active centres qualitatively. As to the quantitative study, some experiments were carried out by Maxted and his co-workers[10]–[17]. Their results obtained showed that only one or two kinds of centres participated in a reaction and that so long as the content of a poison was not so large, a linear relation held between the activity and the constant of a poison:

$$k=k_0(1-\alpha c),$$

where k is the activity, c the content of a poison, k_0 the activity in the absence of poison, and α a constant which they called 'poisoning coefficient'. As an example, the decomposition of hydrogen peroxide with platinum black poisoned by mercuric ion is shown in Fig. 1.[18] In many other reactions such a linear relation possessing an angular point as is seen in the figure has been found.

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[6] *Ber. Dtsch. chem. Ges.*, 45, 1471 (1912).

[7] *Sci. Paper Inst. Phys. Chem. Res.*, 3, 223 (1925).

[8] *J. Chem. Soc.*, 127, 1347 (1925).

[9] *J. Ind. Chem. Soc.*, 6, 749 (1929).

[10] The linear fall in the activity of platinum black in hydrogenation of oleic acid by the increase in the content of mercury, sulphur, arsenic or zinc was observed. Maxted, *J. Chem. Soc.*, 119, 225 (1921).

[11] The similar phenomenon in decomposition of hydrogen peroxide by the increase in the content of mercuric nitrate, mercuric chloride or lead acetate was observed. Maxted, *ibid.*, 121, 1760 (1922).

[12] It was tested that the concentration of lead or mercury adsorbed by platinum black was proportional to the concentration originally present in the system. Maxted, *ibid.*, 127, 73 (1925).

[13] The linear fall in the activity of platinum black in oxidation of sulphur dioxide by the increase in the content of arsenic was observed. Maxted and Dunsby, *ibid.*, 1928, 1600.

[14] The similar phenomenon in decomposition of hydrogen peroxide by the increase in the content of mercuric chloride was observed. Maxted and Lewis, *ibid.*, 1933, 502.

[15] The similar phenomenon in hydrogenation of crotonic acid, oleic acid and benzoic acid by the increase in the content of mercuric chloride was observed. Maxted and Stone, *ibid*, 1934, 26.

[16] The similar phenomenon in hydrogenation of nitrobenzene, acetophenon, benzene and oleic acid by the increase in the content of mercuric chloride and carbon disulphide was observed. Maxted and Stone, *ibid.*, 1934, 672.

[17] The hydrogenation of crotonic acid with platinum black and that of oleic acid with reduced nickel were studied, and the poisoning coefficients of various substances, such as hydrogen sulphide, sulphur and others, discussed. Maxted and Evans, *ibid.*, 1937, 603.

[18] Maxted, "*Catalysis and Its Industrial Applications*," p. 136. Churchill, London (1933).

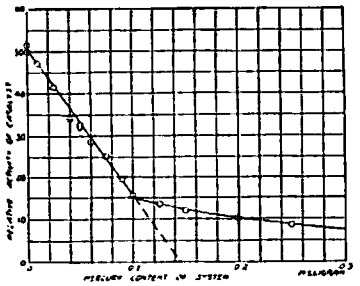

Fig. 1.

It is seen from this fact that one kind of the active centres chiefly participates in a reaction, while another kind also slightly does. But, in Pease and Stewart's experiments[19] on hydrogenation of ethylene with copper poisoned by carbon monoxide, no linear relation was observed. Therefore, the author re-examined whether the linear relation was found, as was by Maxted, with the hope of getting some information on the energy distribution of active centres.

Experimental.

The effect of mercuric ion on the decomposition of hydrogen peroxide with platinum as a catalyst was carefully examined, modifying the methods used by Maxted. Much care was taken as to the purity of the catalyst, because any poisonous substances adsorbed on the catalyst would lessen the number of the kinds of the active centres to participate in the reaction.

Hydrogen peroxide was prepared by the reaction between sodium peroxide and sulphuric acid, and distilled under reduced pressures. Mercuric chloride used as a poison was obtained from Merck. The reaction vessel was made of non-alkali glass.

Two methods for preparing platinum black used will be explained below.

(1) Experiments with Platinum Black made by Reduction from the Oxide.

Catalyst.—Platinum oxide was prepared by Voorhees and Adams' method[20] and reduced with hydrogen. According to the instructions given by these authors, a solution of platinum chloride, with 1 g. of platinum in 5 c.c. of water, was mixed with 20 g. of pure sodium nitrate in a Pyrex beaker, and the mixture was heated gently to about 500°C. After the mass was cooled, the platinum oxide was washed several times by decantation. Pure hydrogen was passed through the suspension which was heated to 100°C. Fine suspension of platinum black was obtained, the colour being changed black. The catalyst thus obtained may contain a small quantity of alkali salt, which is almost indifferent to the decomposition of hydrogen peroxide[21]. The platinum suspension used in the present experiment contained about 1 mg. of platinum in 1 c.c.

Adsorption of Mercuric Ion.—What is required in the present experiments is neither

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[19] *J. Am. Chem. Soc.*, 47, 1235 (1925).

[20] *J. Am. Chem. Soc.*, 44, 1397 (1922).

[21] Bancroft, *J. Phys. Chem.*, 21, 767 (1917). And this has been also ascertained by the experiment.

the content of poison nor the concentration, but the adsorbed amount of poison on the surface of the catalyst. Therefore, the adsorbed amount of mercuric ion was measured for a part of the suspension used.

The determination of mercuric ion was made by means of a colorimeter, using diphenyl carbazide as an indicator[22]. The sensitivity was 1×10^{-3} mg. of mercuric ion in 5 c.c. of the solution.

The experimental result obtained with 0.2 g. of platinum black in 220 c.c. of water showed that mercuric ion was adsorbed so much that 96.6% of 44.33 mg. added was adsorbed. The amount of mercuric ion added per unit weight of the catalyst in the principal experiments is smaller than that in this experiment, and so it may be assumed that in them the whole of the added quantity is adsorbed.

Adsorption equilibrium was almost established about 30 minutes after mixing mercuric chloride solution. It can not be regarded as the true equilibrium, for further adsorption continued for several days, though the amount was small. There was, however, no difference between the decomposition velocity of hydrogen peroxide measured 30 minutes after mixing and that measured after a day. It has been admitted that the chlorine ion in a mercuric chloride solution added to the suspension has scarcely any influence on the reaction[23].

Experimental Method.—A given quantity of mercuric chloride solution was mixed with 1 c.c. of the suspension in each of five tubes, and 30 minutes later 5 c.c. of hydrogen peroxide solution was added. In different lapses of time after the addition, hydrogen peroxide in each tube was titrated with potassium permanganate solution the reaction having been stopped by adding concentrated solution of mercuric chloride.

Stirring brought forth much increase in the decomposition velocity, but it did not improve the constancy of the velocity constant of the first order reaction though its rate was kept constant. The experimental results obtained without stirring are given in Results, (1).

(2) Experiments with Platinum Black prepared by Electrolysis.

A platinum plate (2 × 2 cm.) as shown in Fig. 2 was rotated in platinizing solution (3 g. of platinum chloride; 0.01 g. of lead acetate; 100 c.c. of water) so as to be covered homogeneously with platinum black by the aid of another platinum electrode when current was transmitted. The black was attached thinly but tightly for fear of its detachment due to violent evolution of gas during the period of

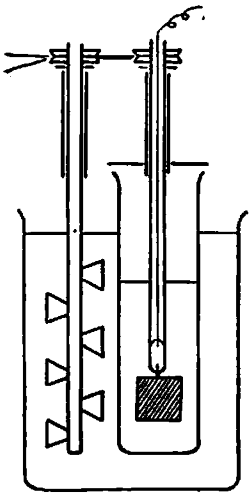

Fig. 2.

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[22] Stock and Pohland, *Z. Angew. Chem.*, 39, 791 (1926).

[23] This is evident from the fact that neither KCl nor NaCl solution has any effect on the reaction.

the reaction. The plate was thoroughly cleaned by electrolysis in dilute sulphuric acid, and then stored in pure water.

Experimental method.—A given quantity of mercuric chloride solution was mixed with 150 c.c. of water in a beaker as shown in Fig. 2 and made to adsorb on the black well by stirring. The plate was rotated about 200 times a minute. As the velocity of stirring so much affected that of decomposition, it was kept constant by means of a speed adjuster throughout the experiment. In certain lapses of time after adding 10 c.c. of hydrogen peroxide solution, 2 c.c. at a time was titrated with potassium permanganate solution. Such a series of experiments were carried out exchanging a solution for a new solution for the purpose of successive addition of the poison.

Results.

(1) Experiments with Platinum Black made by Reduction from the Oxide.

The experimental results obtained are given in Table 1. Assuming that the decomposition of hydrogen peroxide was a reaction of the first order, the velocity constant k was calculated. c_0 is the concentration of hydrogen peroxide at $t=0$ in gram molecules per 10 c.c., c the concentration at t minutes, x the number of adsorbed mercuric ions.

Table 1.

(a) $x=0$ $c_0=35.38\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
2	26.88	60.5
4	20.16	61.5
5	18.72	64.1
6	14.88	62.4
10	10.50	53.0

(b) $x=4.5\times10^{15}$ $c_0=30.24\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
5	24.15	19.5
7	23.92	14.6
10	23.23	11.5
15	17.01	16.7
20	16.31	13.4

(c) $x=9.0\times10^{15}$ $c_0=31.20\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
10	23.24	12.8
20	20.02	9.61
40	9.07	13.4
60	8.88	9.10
70	8.60	7.99

(d) $x=2.7\times10^{16}$ $c_0=30.24\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
10	26.80	5.25
25	23.04	5.91
40	16.32	8.37
55	13.92	7.66
80	10.56	6.65

(e) $x=4.5\times10^{16}$ $c_0=33.60\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
15	27.84	5.44
25	23.04	6.55
40	22.08	5.16
55	18.72	4.62
70	18.24	3.79

(f) $x=9.0\times10^{16}$ $c_0=31.20\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
10	28.01	4.69
25	26.40	3.39
40	22.13	3.75
55	21.04	3.11
70	20.16	3.16

(g) $x=1.8\times10^{17}$ $c_0=31.20\times10^{-5}$

t	$c\times10^5$	$k\times10^3$
10	30.24	1.81
25	27.84	2.63
40	26.88	2.16
55	23.52	2.97
80	20.64	2.99

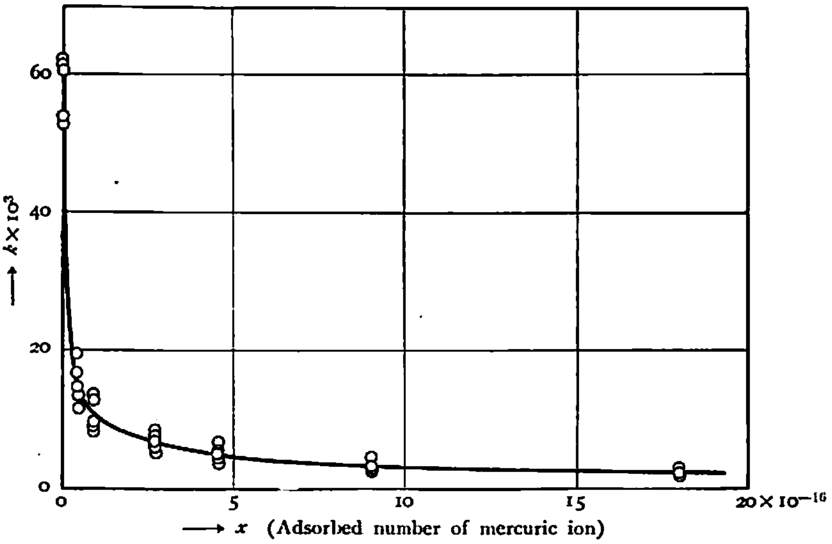

Fig. 3.

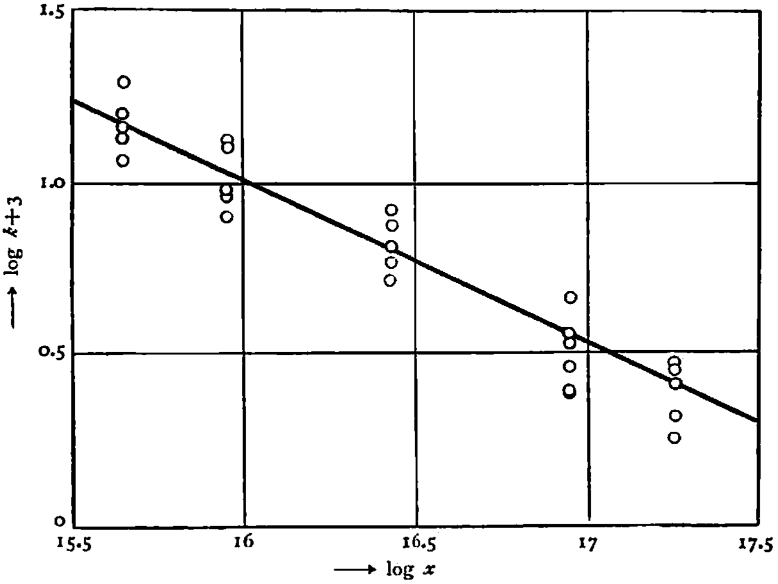

Fig. 4.

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Table 1 is graphically shown in Fig. 3, where x is the number of mercuric ions adsorbed. Fig. 4 shows that the relation between log k and log x is linear.

(2) Experiments with Platinum Black prepared by Electrolysis.

The velocity constant k which was also calculated is given in Table 2 and Fig. 5. c denotes the c.c. of a potassium permanganate solution consumed.

Table 2.

(a) $x=0$

t	c	$k\times 10^3$
9	5.8	—
15	5.0	10.7
20	4.4	11.1
25	3.9	10.5
30	3.5	9.39
35	3.1	10.5

(b) $x=0.9\times 10^{17}$

t	c	$k\times 10^3$
5	6.1	—
10	5.7	5.90
15	5.4	4.68
20	5.0	6.68
25	4.6	7.26
30	4.3	5.84

(c) $x=5.4\times 10^{17}$

t	c	$k\times 10^3$
10	5.1	—
15	4.85	4.36
20	4.6	4.58
25	4.4	3.88
30	4.2	4.04
35	4.0	4.24

(d) $x=14.4\times 10^{17}$

t	c	$k\times 10^3$
10	6.0	—
15	5.8	2.94
20	5.6	3.04
25	5.35	3.98
30	5.1	4.14
35	4.9	3.48

(e) $x=18.9\times 10^{17}$

t	c	$k\times 10^3$
10	6.5	—
15	6.25	3.67
20	6.0	3.56
25	5.75	3.68
30	5.55	3.12
35	5.35	3.18

Fig. 6 shows the relation between log k and log x.

As is seen in Figs. 3 and 5, neither the linear relation between k and x nor an angular point is observed, while the linear relation is seen between log k and log x in Figs. 4 and 6.

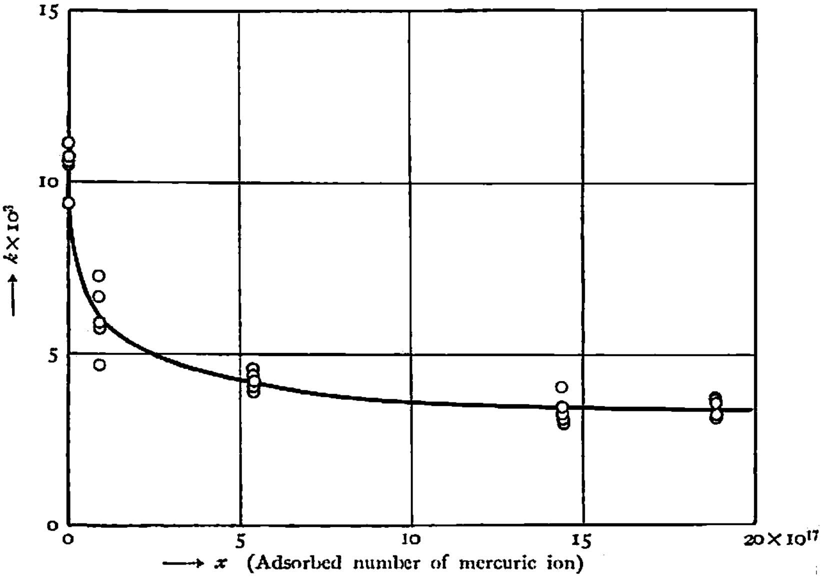

Fig. 5.

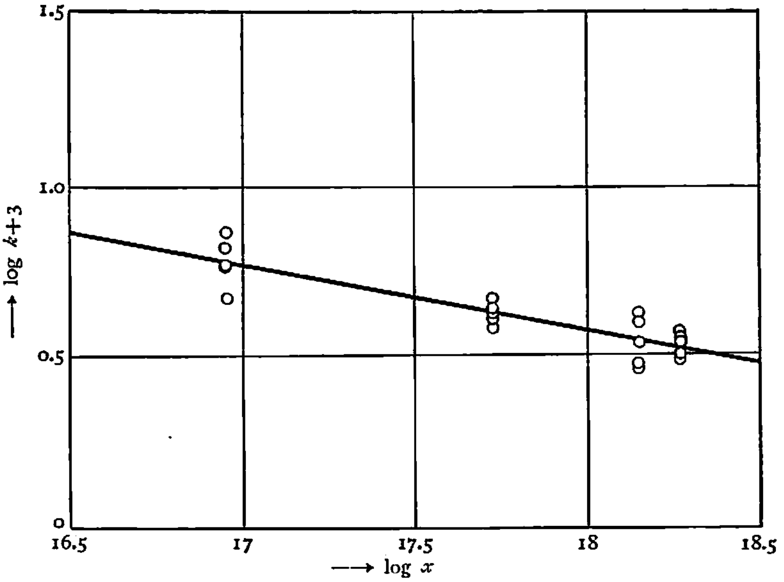

Fig. 6.

It should be noted in these results that k was not so satisfactorily constant, especially when the amount of poison was small, even though the experiments were carefully carried out[24].

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[24] In the case of the decomposition of hydrogen peroxide with colloidal platinum the results obtained are relatively uniform. (e.g. Bredig and Ikeda, *Z. physik. Chem.*, **31**, 324 (1899). Suito, *Rev. Phys. Chem. Japan* (Japanese Edition), **10**, 251 (1936).) Colloidal platinum, however, is inappropriate to the present experiment, because it is coagulated by mercuric ion.

Discussion.

General Treatment of Successive Poisoning.

The velocity constant k of a catalytic reaction in a heterogeneous system is expressed as the summation of the velocity constant κ of each atom of the centres. If there are m kinds of centres which participate in a reaction,

$$k=\sum_{i=1}^{m} n_i \kappa_i \,, \tag{1}$$

where n_i is the number of the surface atoms composing the centres of each kind.

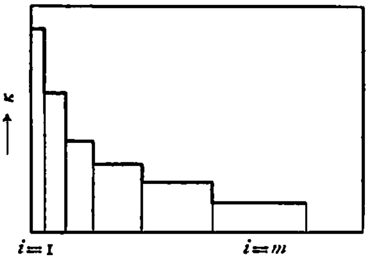

Fig. 7.

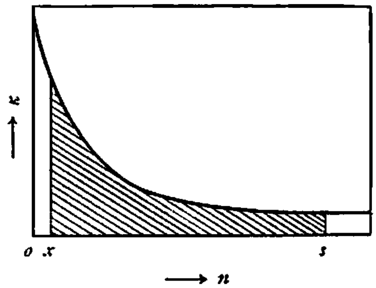

Fig. 8.

When κ and n are placed in the order of i as shown in Fig. 7, k will be represented by the area surrounded by discontinuous lines. As already mentioned in Introduction, it is supposed that there are innumerable degrees in activity of the centres, and so κ may be regarded as a continuous function of n; hence $k=\int_0^s \kappa dn$, where s denotes the least active centre which is the atom at the s'th position from that of the most active centre. Suppose that the ion or molecule of a poison covers the centre in the order of activity when it was added successively. The integration, therefore, should be performed from x, the adsorbed number of atoms of the poison, to s to obtain the velocity constant of the surface left free by the poison; hence

$$k=\int_x^s \kappa dn \,. \tag{2}$$

k is shown by the area indicated by oblique lines in Fig. 8.

According to Arrehenius' equation let q represent the heat of activation for a certain reaction, and κ will be written as

$$\kappa=a\cdot e^{-q/RT}, \tag{3}$$

where a is a constant, while q differs according to the kind of centre[25].

The energy distribution of the active centres must be known to perform the integration of equation (2). Constable[26] considered that the strain energy E of the metastable atoms of the active centres varies according to their mutual distance. Applying the normal law of errors, the following relation is obtained:

$$dn=f\cdot e^{-E/h}dE\,, \qquad (4)$$

where h is a constant named "distribution constant" to be determined by the condition of preparing the catalyst, for example, by the reduction temperature in the case of reduced metal, and f another constant. The strain energy E measures the magnitude of the external field, which in turn causes the lowering of the critical increment q from the maximum value q' on the reaction centre. Thus we have

$$q'-q=cE\,,$$

where c is a constant. Therefore taking β as a new constant, we have

$$dn=\beta\cdot e^{q/h}dq\,. \qquad (5)$$

Cremer and Schwab[27], taking E as the excessive energy of the active centre from the energy of an atom in the surface of the normal lattice, obtained the similar results. If the surface of a catalyst is in statistical equilibrium with the temperature of preparation θ, we have, according to Boltzmann's principle,

$$dn=f\cdot e^{-E/R\theta}dE. \qquad (6)$$

Taking q_h as the activation energy of the reaction in a homogeneous system and λ_a as the adsorption heat of the reactant in an activated state on a normal lattice atom, we have, according to Schwab,

$$E=q_h-\lambda_a-q.$$

Thus, the relation (5) also proves to hold.

Integrating equation (5), c being the integration constant, we have

$$n=\beta h\cdot e^{q/h}+c\,. \qquad (7)$$

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[25] a contains the term of the mean life of a reacting molecule on the surface, but it is considered to be not so much varied by the kind of the centre as compared with the term of the heat of activation as considered by Constable. (See the next note.)

[26] *Proc. Roy. Soc.* [A], **108**, 355 (1925).

[27] Cremer, *Z. physik. Chem.* [A], **144**, 231 (1929).
Cremer and Schwab, *ibid.*, **144**, 243 (1929).
Schwab, *Z. physik. Chem.* [B], **5**, 406 (1929); "*Katalyse*," p. 196~7, Springer, Berlin (1931).

Taking logarithms of (7), c being neglected[28], we have

$$\log n = q/h + \log \beta h$$

or

$$q = h(\log n - \log \beta h).$$

Substituting the relation in (3) and then (2) we obtain

$$k = a\int_x^s e^{-h(\log n - \log \beta h)/RT}\, dn\,.$$

Putting $h/RT \equiv \gamma$ and $h/RT \cdot \log \beta h \equiv \delta$, we have

$$\begin{aligned} k &= a\int_x^s e^{-\gamma \log n + \delta}\, dn \\ &= a\int_x^s e^{\delta} \cdot e^{\log n^{-\gamma}}\, dn \\ &= a \cdot e^{\delta}\int_x^s n^{-\gamma}\, dn \\ &= \frac{a \cdot e^{\delta}}{-\gamma+1} \cdot n^{-\gamma+1}\Big|_x^s \\ &= \frac{a \cdot e^{\delta}}{-\gamma+1}\left(s^{-\gamma+1} - x^{-\gamma+1}\right). \end{aligned}$$

Now putting $\frac{a \cdot e^{\delta}}{\gamma - 1} \equiv c$ and $\frac{a \cdot e^{\delta}}{\gamma - 1} \cdot s^{-\gamma+1} \equiv c'$, we have

$$k = \frac{c}{x^{\gamma-1}} - c'. \tag{8}$$

Equation (8) gives the relation between the adsorbed amount of the poison x and the velocity constant k. In the case where the content of poison is small ($x \ll s$), c' becomes negligible in the right hand side of equation (8); hence

$$\log k = \log c - (\gamma - 1) \log x. \tag{9}$$

This equation shows the linear relation between log k and log x as shown in Figs. 4 and 6.

Application of the Treatment to Another Reaction.

Let us apply the relation (9) to Pease and Stewart's data of the hydrogenation of ethylene at 0°C. with a copper catalyst poisoned by carbon monoxide,—

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[28] Equation (7) may be rewritten as

$$n - c = \beta h \cdot e^{q/h}.$$

In this equation $n - c$ is always positive, even though n tends to zero in case q approaches zero. The values of n in the present experiment are always larger than $1 \cdot 10^{16}$, so that c may be negligible.

a famous experiment for its elucidation of amazing actions of catalytic poison. They found that the addition of 0.05 c.c. of carbon monoxide to the copper catalyst which had an adsorptive capacity of 1 c.c. of hydrogen (at 1 mm. pressure) lowered the activity by over 90%. Their data are given in Table 3. The relation between the activity and the content of poison was expressed by a smooth curve. x in the table is the number of adsorbed CO molecules which has been calculated assuming that the whole of CO added should be adsorbed.[29] The main parts of their velocity curves were represented by straight lines, i.e. the reaction was regarded as of the zero order. Therefore, from the slope of the straight line k was calculated by the author; k in the absence of poison was taken as 1. The relation between k and x is shown in Fig. 9, and the linear relation between log k and log x in Fig. 10.

Table 3.

Volume of CO in c.c.	x	log x	k	log k+3	b
0	0	—	1.000	—	—
0.05	1.35×10^{18}	18.130	0.120	2.09	147
0.08	2.16 "	18.334	0.108	2.03	103
0.33	8.93 "	18.951	0.085	1.93	33
0.69	18.67 "	19.271	0.072	1.86	19
1.97	53.31 "	19.727	0.060	1.78	8
9.14	—	—	—	—	—

Let us suppose that every atom in the active surface of copper has equal adsorptive capacity. Then, as the fraction left open by the adsorbed molecules of CO brings about the hydrogenation of ethylene, we have, according to Langmuir's isotherm[30],

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[29] The adsorbed amount of CO is unknown, but it can be approximately calculated from the adsorption isotherm of CO on the same catalyst measured by them. The volume of the dead space of the vessel used seems less than 100 c.c., and so when the adsorbed amount is 9 c.c., the amount in the gas phase is to be less than 0.66 c.c. from their isotherm. Therefore, when 9.66 c.c. is introduced more than $\left(1-\frac{0.66}{9.66}\right)\times100=93\%$ is adsorbed. The curve of the isotherm almost touches the axis of the adsorbed amount when the amount is less than 5 c.c. Therefore, the value of x in Table 3 which was calculated from the amount introduced can be regarded as the adsorbed amount except the data at the bottom of the table.

[30] σ_{CO}, the fraction of the surface covered by CO, can be written as $\sigma_{CO}=\frac{bp}{1+bp}$, so that the reaction velocity will be proportional to $1-\sigma_{CO}=\frac{1}{1+bp}$. The constant of proportion was included in k.

$$k=\frac{1}{1+bp},$$

where b and p are the adsorption coefficient and the equilibrium pressure of CO respectively. Hence we can calculate the value of b, assuming that p is proportional to the volume of CO, which is given in the last column of Table 3 including the constant of proportion. If the active surface be homogeneous, the adsorption coefficient b would be constant; but in fact b decreases

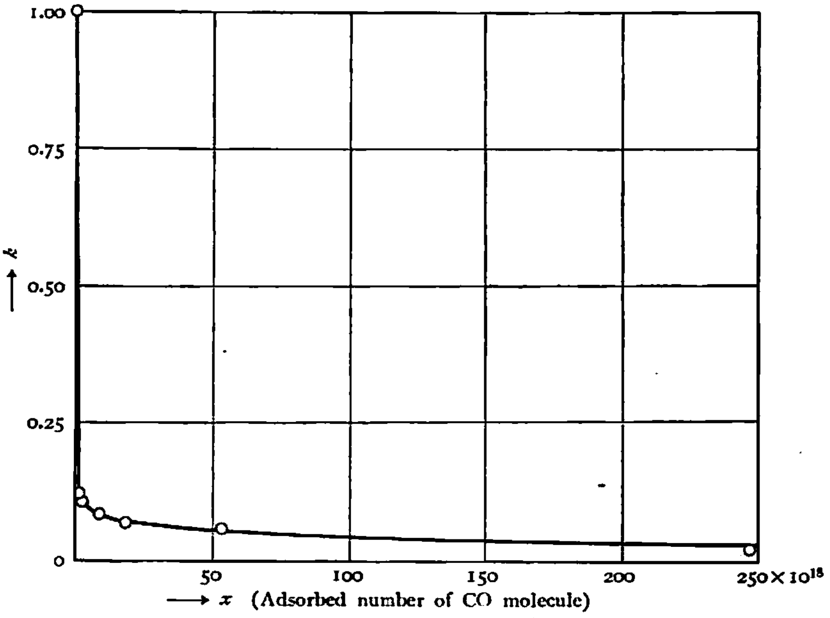

Fig. 9.

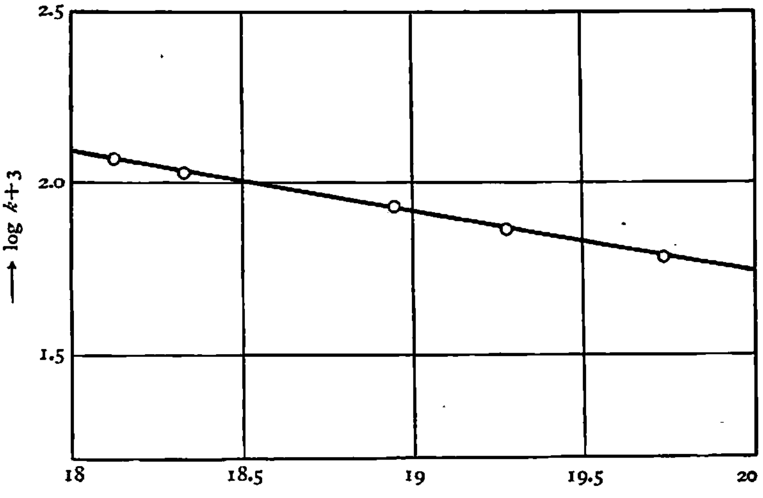

Fig. 10.

remarkably with the increase in the volume of CO added.[31] From this evidence, it is considered that the active surface is by no means homogeneous, and that the adsorption of the poison proceeds from the most active centres to the less active ones.

The Distribution Constant h.

The distribution constant h can be calculated from the linear relation between log k and log x in Figs. 4 and 6: the slope of the straight line gives $\gamma-1$, or $h/RT-1$.

The values of h for two kinds of platinum black used in the decomposition of hydrogen peroxide were as follows:

(1) $h_1=8.90$ (obtained by reduction of platinum oxide with hydrogen at 100°C.),

(2) $h_2=7.15$ (prepared by electrolysis at 30°C.).

The distribution constant h can be put as

$$h=R\theta$$

from equations (4) and (6). According to Schwab, θ is equated to the temperature of preparation of the catalyst; hence we have $\theta_1=170°\mathrm{C}.$ from (1) and $\theta_2=80°\mathrm{C}.$ from (2). These values do not coincide strictly with the temperature of preparation, but both the order and the relation $\theta_1>\theta_2$ are in good agreement.

Further quantitative studies on the relation between the distribution constant and the characteristic temperature of a catalyst as well as on the variation in the activation energy of a reaction with progressive poisoning are in progress.[32]

Summary.

(1) The decomposition of hydrogen peroxide by platinum black has been studied with successive small additions of mercuric ion as catalytic poison. The linear relation with an angular point which had been reported by Maxted has never been ascertained between the reaction velocity and the adsorbed amount of poison.

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31) Constable pointed out the heterogeneity of the surface from a similar calculation. *Proc. Cambridge Phil. Soc.*, 23, 832 (1927).

32) Maxted has reported that the temperature coefficient of the decomposition of hydrogen peroxide did not vary with the content of poison. If the temperature coefficient, however, is related to the activation energy of the reaction as usual, it is not probable from the theoretical ground,

(2) A linear relation has been found between the logarithm of the reaction velocity and that of the adsorbed amount of poison, and a similar one also found in the data of Pease and Stewart.

(3) It has been discussed that the energy distribution of the active centres can be elucidated by the experiments of progressive poisoning. The distribution has been treated as according to Boltzmann's principle, which has given the above mentioned relation.

(4) From the experimental results the distribution constant h has been obtained and the characteristic temperature of the catalyst calculated, being compared with the temperature of preparation.

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