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# THE CATALYTIC DECOMPOSITION OF HYDRO-GEN PEROXIDE ON DIFFERENT METALS.

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Received 23rd July, 1935.

The catalytic decomposition of hydrogen peroxide into water and molecular oxygen was first studied by Thenard and has since been investigated in great detail. Bredig and his collaborators<sup>1</sup> studied the reaction on solid and colloidally dispersed metals. Though a great deal of interesting experimental material has been collected, the mechanism of this catalysis is still unexplained.

The velocity of the chemical reaction on the interface is often considerably greater than the rate of diffusion of the reacting molecules or the reaction products to or from the interface. In this case we are really measuring the rate of diffusion.<sup>2</sup> In other cases the velocity depends on

<sup>1</sup> Bredig and Müller von Bernek, Z. physik. Chem., 1899, **31**, 258; Bredig and Ykeda, Z. physik. Chem., 1901, **37**, 1; Bredig and Teletow, Z. Elektrochem., 1906, **12**, 581.

<sup>2</sup> Nernst and Brunner, Z. physik. Chem., 1904, 47, 53; 1905, 51, 95.

the adsorption of the hydrogen peroxide on the surface, and when the surface is practically saturated, the velocity becomes independent of the concentration of H<sub>2</sub>O<sub>2</sub>. Owing to these reasons it is often practically impossible to draw any conclusions about the mechanism from the dependence of velocity on concentration as in homogeneous systems.

An opportunity to investigate the problem from a new point of view arose from the work of Haber and Weiss 3 on the catalytic decomposition of  $H_2O_2$  in homogeneous systems. Here the  $H_2O_2$  is primarily attacked monovalently, yielding the radicals OH or  $HO_2(O_2^{-})$  which may further give rise to the chain reactions :

$$OH + H_2O_2 = H_2O + HO_2$$
 . . . (1)

$$O_2^- + H_2O_2 = OH^- + OH + O_2$$
 . . (2)

Recent experiments on the dependence of the catalytic decomposition on the  $H^+$  ion concentration have shown that the original equation (2) must be altered so that the radical HO<sub>2</sub> is replaced by its anion  $O_2^{-}$ . They are related by the dissociation equilibrium :

$$O_2^- + H^+ \rightleftharpoons HO_2$$
 . . . . (3)

with the equilibrium constant

$$\Gamma_{\mathrm{HO}_2} = \frac{[\mathrm{O}_2^{-}][\mathrm{H}^+]}{[\mathrm{HO}_2]}.$$

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In homogeneous systems the primary formation of the radicals with the consequent initiation of the chains can be accomplished in many different ways; for instance, by the transformation of a metal ion into one of next higher valency, as in the case of ferrous ion : 3

 $Fe^{++} + H_2O_2 = Fe^{+++} + OH^- + OH$ ,

or by reduction of a higher valent state, as in the case of the ferric catalysis : 3

$$\mathrm{Fe}^{+++} + \mathrm{HO}_2^{-} = \mathrm{Fe}^{++} + \mathrm{HO}_2.$$

Hydrogen peroxide can also be split by the action of a light quantum \*

$$H_2O_2 + h\nu = 2OH,$$

or the radicals  $HO_2$  and  $O_2^-$  may be produced by the reaction between ozone and an OH- ion 5

$$O_3 + OH^- = O_2^- + HO_2$$
.

# General Theory.

The action of the atoms of the metal surface is considered to be similar to that of metal ions where the formation of the radicals is taking place as a result of a simple electron transfer process.

According to the Pauli-Sommerfeld theory every metal can be considered as a reservoir of quasi free electrons which obey the Fermi-Dirac statistics.

The most simple assumption is that the electrons of the metal electron

<sup>3</sup> F. Haber and J. Weiss, Proc. Roy. Soc., 1934, 147A, 332, also Haber and

Weiss, Naturwiss., 1932, 20, 948.
 <sup>4</sup> Urey, Dawsey and Rice, J.A.C.S., 1929, 51, 1371; G. Kornfeld, Z. physik.
 Chem., 1935, 29B, 205. Haber and Weiss, loc. cit.<sup>3</sup>
 <sup>5</sup> J. Weiss, Trans. Faraday Soc., 1935, 31, 668.

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gas are able under certain circumstances to split the  $H_2O_2$  molecules present at the interface metal/solution according to :

$$H_2O_2 + \epsilon_{metal} = OH^- + OH \qquad . \qquad . \qquad (4)$$

Here the hydrogen peroxide is acting as an oxidising agent being itself reduced monovalently by an electron from the metal.

In alkaline solutions of  $H_2O_2$  which contain a larger quantity of the anion  $HO_2^-$ , the process :

$$HO_2^{-} = HO_2 + \epsilon_{metal} \quad . \qquad . \qquad . \qquad (5)$$

may become important where the anion gives an electron to the metal. Here the hydrogen peroxide is acting as a reducing agent in the form of its anion  $HO_2^{-}$ . This is related to the  $H_2O_2$  by the dissociation equilibrium :

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad . \quad . \quad . \quad (6)$$

with the dissociation constant

$$K_{\rm H_2O_2} = \frac{[\rm HO_2^{-}]]\rm H^+]}{[\rm H_2O_2]}.$$
 (20° C.)

Processes (4) and (5) clearly show the two different types of reactions which hydrogen peroxide can undergo; namely reduction and oxidation.

We will here deal with reaction (4) in detail. The important point is. that OH radicals are formed when  $H_2O_2$ is attacked monovalently so that one electron is transferred. The following experiments indicate that the simultaneous formation of two OH<sup>-</sup> ions according to the reaction

$$H_2O_2 + 2\epsilon_{metal} = 2OH^{-1}$$

is obviously not taking place to a great extent. This fact can be easily explained on the basis of the Franck-Condon principle.

In the figure the potential curves are reproduced schematically for two OH radicals, one OH radical and one OH<sup>-1</sup> ion, and for two OH<sup>-1</sup> ions. One can understand that the formation of OH<sup>-1</sup>

ion and OH radical from  $H_2O_2$  molecule  $(a \longrightarrow b)$  is, from energy reasons alone, very much favoured compared with the simultaneous formation of two OH<sup>-</sup> ions  $(a \longrightarrow c)$ . This is due to the strong Coulombic repulsive energy between the two OH<sup>-</sup> ions; even if we assume a value of 2 Å. for the distance between the OH in the  $H_2O_2$  molecule, this is of the order of  $\sim 7$  volts.

A potential barrier at the metal surface prevents the electrons from escaping from the metal. Transfers of electrons are essentially possible only between levels of equal energy.

We will denote by  $\Phi$  the work function of the metal under the given conditions, *i.e.*, the negative energy of the highest occupied level in the metal, by  $E_{OH}$  the electron affinity of the OH<sup>-</sup> ion and by  $D_{H_2O_2}$  the dissociation energy of  $H_2O_2$  into two OH radicals.  $\Delta A$  stands for the difference of the adsorption energies between the initial state  $(H_2O_2)$ and the final state (OH + OH<sup>-</sup>) on the metal surface under consideration



the potential curves.

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 $(\Delta A \text{ will practically always have a positive value because of the strong})$ adsorption of the free radical OH). Then the energy necessary for the electron to split the  $H_2O_2$  is given by  $E = D_{H_2O_2} - E_{OH} - \Delta A$ . This value of E must lie in the continuum of the occupied electronic levels within the metal, *i.e.*, the relation :

$$E_{\mathbf{OH}} + \Delta A - D_{\mathbf{H}_{2}\mathbf{O}_{2}} > \boldsymbol{\Phi} \qquad . \qquad . \qquad (7)$$

must be fulfilled.

Equation (7) can be tested experimentally since it is possible to alter both  $\boldsymbol{\Phi}$  and  $\Delta A$  arbitrarily.

#### Catalytic Decomposition by Electrolysis.

The most simple and direct method to alter  $\Phi$  is to apply a negative potential  $(-V_c)$  to the metal surface concerned. This negative potential will decrease the work function of the metal to the value of the order

$$\Phi' = \Phi - \epsilon V_{c_1}$$

and will therefore favour the electron transfer.<sup>6</sup>

Mercury and bright platinum are not effective catalysts for the decomposition of H<sub>2</sub>O<sub>2</sub> in acid solution. But if we favour, by cathodic polarisation, the escape of the electrons from the metal, we find an entirely new effect, which could hardly be expected on earlier views. We get a much stronger catalytic decomposition than on the unpolarised metals under the same conditions.

The experiments were made in an apparatus of the following description. It consisted essentially of a glass bell in a glass beaker, provided with a cooling spiral for the regulation of temperature, which could be read on the thermometer and kept constant to  $\pm \frac{1}{2}^{\circ}$  C. The cathode, Pt or Hg (amalgamated platinum), was built in the form of a rapid stirrer which was introduced through an air-tight joint.

The gas evolved was collected in a gas burette and hydrogen and oxygen determined in the usual way after a qualitative test to show the absence of other gases. The cathodic gases contain either pure hydrogen, mixtures of hydrogen and oxygen, or pure oxygen. The surprising result is the appearance of oxygen on the cathode. Some of the experimental results are collected in Table I.

We see that in the most favourable case about 4 mols  $O_2$  per I Faraday can be obtained. These high values are however not always easily reproducible as the individual processes are very dependent on the state of the metal surface. But values of about 2 mols O<sub>2</sub> per I Faraday are always easily obtained (see Table I.).

We have here, probably for the first time, a very noticeable departure from Faraday's law caused by secondary processes. This corresponds to the well-known apparent break-down of the Einstein law in photochemistry.

In Table II. some results have been calculated from the older work of Tanatar.' But Tanatar was working only with low values of the ratio  $[H_2O_2]$ 

 $\gamma = \gamma$  (see experiments Tables I. and II.), so that he did not find the [H2SO4]

effect which we have observed. However, as he made no analysis of his cathode gas, the assumption that it was pure H<sub>2</sub> is open to doubt.

For the sake of completeness we should mention briefly the anode process in the electrolysis of hydrogen peroxide. As in the experiments of Tanatar," which we have confirmed in acid solutions, one always obtains a maximum value of 1 mol. O2 per Faraday. Since the formation of OH

<sup>6</sup> Cf., R. W. Gurney, Proc. Roy. Soc., 1932, 137A, 134. <sup>7</sup> S. Tanatar, Ber., 1903, **36**, 199.

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Nr.	[H2O2] Mols./ltr.	[H <sub>2</sub> SO <sub>4</sub> ] Mols./ltr.	$\gamma = \frac{[H_2O_2]}{[H_3SO_4]}.$	Current Amps./cm².	Volume Per Cent. O <sub>2</sub> in Cathode Gas.	Mols. O2 • Per 1 Faraday.	Remarks.
	0:445	0.110	3.74	0.023	34	$7.54 \cdot 10^{-3}$	
2	0.407	0.110	3.45	0.026	16	5.70.10-2	platinum
2	0.482	0.013	41.6	0.013	88	2.03.10-1	cathode
4	0.360	0.0625	5.76	0.020	19	1.0 . 10-1	15
5	0.350	0.0625	5.65	0.040	10	5.0.10-2	
6	0.210	0.110	18.10	0.010	20	3.0.10-2	
7	0.233	0.0110	19.60	0.040	13	3.0.10-2	
8	0.200	0.0115	43.5	0.010	60	6.0.10-2	morener
9	0.232	0.0112	46.3	0.030	82	2.7.10-1	mercury
10	0.800	0.0111	72.1	0.030	100	1.5.10-1	(amal
II	0.941	0.0002	1882	0.0040	100	3.93	gam pla-
12	0.941	0.0002	1882	0.0042	100	2.23	tinum)
13	0.470	0.0002	940	0.0062	100	2.10	( cinam)
14	0.470	0.002	94	0.024	100	o·44	
15	0.020	0.001	50	0.002	100	0.10	
16	0.051	0.002	4.2	0.023	practically	no gas on	
					the ca	athode	IJ
	1	1					

TABLE I.—Electrolysis of Hydrogen Peroxide in Sulphuric Acid Solution  $(20^\circ\ \text{C.})$ 

\* The values are corrected for the oxygen obtained in blank experiments without current. This correction can be practically disregarded for mercury cathodes.

TABLE II.—ELECTROLYSIS OF HYDROGEN PEROXIDE IN SULPHURIC ACID SOLUTION (20° C.).

Nr.	[ <b>H</b> 2O2] Mols./ltr.	[H2SO4] Mols./ltr.	$\gamma = \frac{[H_2O_2]}{[H_2SO]_4}.$	Current in Amps.	Mols. $H_2$ per I Faraday on the Cathode.	Mols. O <sub>2</sub> per 1 Faraday on the Anode.	Remarks.
1	0·44	1.53	0·287	0·268	0·4	0.85	} platinum
2	0·88	1.53	0·574	0·146	0·15	1.0	} elec-
3	1·76	1.53	1·148	0·201	0·003	1.02	trodes

radicals on the anode can be assumed, the process may be represented by the reaction

$$_{2OH} = H_{2O} + O$$

which was found for the gaseous state by Bonhoeffer and Pearson.<sup>8</sup> This is followed by the decomposition of  $H_2O_2$  by oxygen atoms :

$$H_2O_2 + O = O_2 + H_2O.$$

In alkaline solutions where  $HO_2^-$  ions can also be discharged on the anode we should still expect short chains. Some experiments in this direction seem to confirm this, but we will not discuss these further here.

The primary process on the platinum cathode (as also for the mercury in acid solution) is represented by equation (7). The OH radicals thus formed can initiate the chain reactions (r and 2) which proceed on the surface of the metal causing the decomposition of  $H_2O_2$  into molecular oxygen and water.

<sup>8</sup> Bonhoeffer and Pearson, Z. physik. Chem., 1931, 14**B**, 1; also Rodebush and Wahl, J. Chem. Physics, 1933, 1.

There are also some chain breaking processes which we have to take into account. The following processes :

$$OH + \epsilon_{metal} = OH^{-}$$
 . . . . (8)

as well as reaction (4) are favoured by a negative potential.

Owing to the comparatively high concentration of the radicals on the surface, chain breaking by the interaction of two radicals, e.g.,

$$OH + HO_2 = O_2 + H_2O + 70 \text{ K cals.}$$
 (10)

may assume an important part. From all these considerations we have to expect only short chains on the surface, and is in agreement with experiment.

A mechanism for the catalytic decomposition of hydrogen peroxide has been assumed which involves chain reactions occurring in the adsorbed phase on the surface of the catalyst. Due to the high adsorption energy of free radicals, a diffusion of the chains from the surface into the solution (at the comparatively low temperatures used) is very improbable. This could only occur appreciably if the surface became saturated with radicals. There is, however, no experimental evidence for this effect. There seems to be no theoretical objection to the assumption of surface chains and the application of the method of stationary concentrations which has already been discussed in a previous paper by J. A. Christiansen.<sup>9</sup>

Reactions (4), (8) and (9) may also be regarded as an intermediate formation of positive ions on the metal surface according to :

 $Me = Me^+ + \epsilon$ .

The electrons used up are replaced by the electric current.

From the reactions (I), (2), (4), (8), and (9) one can derive an expression for the rate of evolution of oxygen in the stationary state on the cathode during electrolysis.

For the oxygen evolved per 1 Faraday (F) we obtain the differential equation :

$$\frac{\mathrm{d}(\mathrm{O}_{2})}{\mathrm{dF}} = \frac{k_{2}[\mathrm{O}_{2}^{-}]}{2k_{4} + k_{2}[\mathrm{O}_{2}^{-}]\left\{\mathrm{I} - \frac{[\mathrm{H}^{+}]}{\Gamma_{\mathrm{HO}_{2}}}\right\}},$$

If  $2k_4 \gg k_2[O_2^-] + \left\{I - \frac{[H^+]}{\Gamma_{HO_2}}\right\}$  which practically always is the case in acid solution, then:

$$\frac{\mathrm{d}(\mathrm{O}_2)}{\mathrm{d}\mathrm{F}} \sim \mathrm{prop} \; \frac{[\mathrm{H}_2\mathrm{O}_2]}{[\mathrm{H}^+]} \sim \mathrm{prop} \; \frac{\mathrm{I}}{\gamma}.$$

One can see from Table I. that this relation is confirmed qualitatively by the experiments. The amount of oxygen liberated per I Faraday decreases with the ratio  $\gamma$ .

In more acid solutions ( $\gamma$  small) the reactions which we have considered above are not sufficient to describe completely the cathodic process. The experiments show that the discharge of hydrogen ions and the recombination of the hydrogen atoms to hydrogen molecules becomes important and thus with decreasing  $\gamma$  we obtain a mixture of O<sub>2</sub> and H<sub>2</sub> up to practically pure H<sub>2</sub>.

<sup>9</sup> J. A. Christiansen, Z. physik. Chem., Bodensteinfestband, 1931, 69.

In these cases a smaller or greater part of the hydrogen peroxide is reduced to water without evolution of any gas, according to the equations :

$$H_2O_2 + H = H_2O + OH + 61$$
 K cals.  
OH + H = H\_2O + 115 K cals.

#### Catalytic Decomposition on Silver.

The reaction on solid silver has been studied by McIntosh<sup>10</sup>; Wiegel<sup>11</sup> has investigated the catalytic decomposition in the presence of colloidal silver. We have here the same type of reactions. The colloidal metal partly dissolves in hydrogen peroxide without appreciable evolution of gas according to the equations:

$$Ag + H_2O_2 = Ag^+ + OH^- + OH$$
$$Ag + OH = Ag^+ + OH^-.$$

Hydrogen peroxide is here acting as an oxidising agent. As the colloidal silver is increased and is finally present as a solid phase, the reaction

$$Ag^+ + HO_2^- \rightleftharpoons Ag + HO_2$$
 . (12)

can take place to a considerable extent, so that silver and  $HO_2$  radicals are produced. The latter start the chain reactions (2) and (1) and give rise to a strong catalytic decomposition of the  $H_2O_2$ . The silver formed deposits on the colloidal particles present and by increasing their size changes the colour of the solution. Reaction (12) is independently confirmed by the well-known reducing action of  $H_2O_2$  on silver salts in alkaline solutions.

For the stationary state :

$$\frac{\mathrm{d}[\mathrm{HO}_2]}{\mathrm{d}t} = \mathrm{O},$$

so that when silver is present as a solid phase we get from equation (12) the relation

$$[Ag^+][HO_2^-] \cong const.$$

This relation was proved experimentally by Wiegel, but this author could not give a satisfactory explanation of his results.

### Catalytic Decomposition on Platinum, Gold and Palladium.

The following five reactions, already represented by equations (I), (2), (4), (5) and (8), are sufficient to describe the catalytic decomposition on these noble metals in the solid and colloidal states (M = Pt, Au, Pd)

(oxidation)  $M + H_2O_2 = M^+ + OH^- + OH$ ,

chain reactions (I) and (2)

(reduction) 
$$M^+ + HO_2^- \rightleftharpoons M + HO_2$$
  
chain breaking  $M + OH = M^+ + OH^-$ .

We obtain according to the above equations for the rate of catalytic decomposition in the stationary state the relation :

$$-\frac{\mathrm{d}a}{\mathrm{d}t} = 4k_4 \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] - \Gamma_{\mathrm{HO}_2}} ]\mathrm{H}_2\mathrm{O}_2] \quad . \qquad . \qquad (13)$$

<sup>10</sup> D. M. McIntosh, J. Physic. Chem., 1902, **6**, 15. <sup>11</sup> B. Wiegel, Z. physik. Chem., 1929, 143A, 81.

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where a denotes the analytical concentration in mols./litre of hydrogen peroxide present in the solution. Its relation to the real concentration  $[H_2O_2]$  is given by:

$$[H_2O_2] = \frac{a[H^+]}{K_{H_2O_2} + [H^+]}$$

Equation (13) can be tested by experiment in various ways.

One of the most striking features of the catalytic decomposition on these colloidal and solid noble metals is the fact that there is a maximum rate of decomposition for a certain optimum hydrogen ion concentration. This is in the range of about  $p_{\rm H} \sim 12$ . In stronger acid or alkaline solutions the  $H_2O_2$  is rather stable.

The hydrogen ion concentration was plotted against the time required for a 50 per cent. change in  $H_2O_2$  concentration (for a given concentration of  $H_2O_2$ ). In Table III. the values which can be obtained from these curves for the optimum H<sup>+</sup> concentration are summarised.

ΤA	BL	Æ	I	11	i.

Metal.	Optimum [H+] Conc. [H+]max.	Conc. [H <sub>2</sub> O <sub>2</sub> ] Mols./ltr.	Author.	
Platinum (colloidal) 3·3 · 10 <sup>-6</sup> mols/ltr.	5.0 × 10 <sup>-13</sup>	0.022	Bredig and Müller v. Berneck	
Platinum (platinised sheets)	3·2 × 10 <sup>-13</sup>	0.122	Rius 18	
Gold (colloidal) 1·25 . 10 <sup>-5</sup> mols/ltr.	бю × 10 <sup>-13</sup>	0.042	Bredig and Reinders <sup>13</sup>	
Palladium (colloidal) 1·10 <sup>-5</sup> mols/ltr.	1.6 × 10-13	0.100	Bredig and Fortner 14	

The existence of an optimum  $H^+$  concentration can easily be deduced theoretically. Differentiating equation (13) with respect to the [H<sup>+</sup>] and putting the first differential quotient equal to zero we obtain :

$$[\mathrm{H}^+]_{\max} = \frac{K_{\mathrm{H}_2\mathrm{O}_2} \Gamma'_{\mathrm{H}\mathrm{O}_2}}{K_{\mathrm{H}_2\mathrm{O}_2} - \Gamma'_{\mathrm{H}\mathrm{O}_2}} \qquad . \qquad . \qquad (14)$$

Assuming that the dissociation constant of hydrogen peroxide has about the same value in the adsorbed phase as in the homogeneous phase  $(K_{\rm H_{2}O_{2}} = 1.2 \times 10^{-12} (20^{\circ} \text{ C.})$  we can calculate the constant of electrolytic dissociation for the HO<sub>2</sub> radical in the adsorbed phase from the equation (14). We obtain :

$$\Gamma'_{\rm HO_2} \sim 10^{-13} \, (20^{\circ} \, {\rm C.}).$$

This differs appreciably from the dissociation constant in homogeneous aqueous solution which has been shown to be 15

$$\Gamma_{\rm HO_2} \sim 10^{-6} \, (20^{\circ} \, \text{C.}).$$

<sup>12</sup> A. Rius, Z. Electrochem., 1930, 36, 149.

- <sup>13</sup> Bredig and Reinders, Z. physik. Chem., 1901, **37**, 323.
  <sup>14</sup> Bredig and Fortner, Ber., 1904, **37**, 798.
  <sup>15</sup> J. Weiss, Trans. Faraday. Soc., 1935, **31**,

This difference can easily be explained as the free radical  $HO_2$  is certainly more strongly adsorbed on the surface than the ions  $H_3O^+$  and  $O_2^-$  so that the equilibrium (3) is displaced towards the undissociated product.<sup>16</sup>

According to equation (14) [H<sup>+</sup>]<sub>max.</sub> should (to a first approximation) be independent of the concentration of  $H_2O_2$  and of the nature of the These conclusions are in good agreement with experiment (see metal. Table III.).

According to what has already been said we are able, by changing  $\pmb{\Phi}$ or  $\Delta A$ , to alter the rate of transfer of electrons (rct. 4) and thus to influence the velocity of decomposition.

The poisoning influence of substance such as KCN, Na<sub>2</sub>S CO can also These substances probably form a sort of cobe easily explained. ordination surface compound, with the metal atoms on the surface. Then we know from magnetic researches on the halides and complex compounds of platinum and palladium that "inert gas" electron shells are often formed.<sup>17</sup> The separation of an electron from these now completed electron shells of the metal atom on the surface requires a high energy of the order of magnitude of the ionisation potential of an inert gas. This practically prevents the occurrence of electron transfer processes so that the decomposition of  $H_2O_2$  is no longer possible.

# Catalytic Decomposition on Zinc.

When, in addition to its catalytic action, the metal is attacked to an analytically determinable amount, it is necessary to supplement these more physical considerations by chemical ones. Since the investigations of Schönbein<sup>18</sup> and M. Traube<sup>19</sup> on the

formation of hydrogen peroxide in the autoxidation of Zn, Cd, Fe, etc., in the presence of water, it has been a generally accepted fact that these base metals-in contradistinction to the noble metals-have no catalytic effect in the decomposition of  $H_2O_2$ . This fact would be very difficult to understand from our theoretical point of view. But as shown by the following experiments, this conclusion is by no means generally true.

In investigating the reaction between metallic zinc and hydrogen peroxide in neutral and (sulphuric) acid solutions, we were able to detect, under suitable conditions, a decided catalytic decomposition of  $H_2O_2$ Hydrogen peroxide formed in the autoxidation of zinc and other metals has been found only in small concentrations. This is now to be understood as the stationary state resulting from the formation and decomposition reactions. Some characteristic cases, selected from a larger number of experiments, are given in Table IV.

The experiments were carried out as follows : a definite quantity of pure zinc (granules) was added to a neutral or acid solution of hydrogen peroxide in a suitable shaking apparatus equipped with a gas-outlet, and shaken in a thermostat. The gaseous reaction products were collected in a gas burette and hydrogen and oxygen were determined in the usual Hydrogen peroxide and the free acid were titrated. On varying the way. experimental conditions it is possible to obtain as the gaseous products either practically pure  $H_2$  (small ratios  $\gamma$ ), various mixtures of  $H_2$  and  $O_2$ , or no gas at all. In the solution we find as reaction products water,

<sup>&</sup>lt;sup>16</sup> Cf. Deutsch, Z. physik. Chem., 1928, 136, 353; H. Freundlich, Kapillarchemie, II Aufl. (1931).

<sup>&</sup>lt;sup>17</sup> Stoner, Magnetism and Matter (Methuen & Co. Ltd., London, 1934).

 <sup>&</sup>lt;sup>18</sup> Schönbein, J. prakt. Chem., 71, 285; 78, 63; 79, 65.
 <sup>19</sup> M. Traube, Ber. deutsch. Chem. Ges., 1893, 26, 1474; 1885, 18, 1894.

 $Zn^{++}$  — ions (ZnSO<sub>4</sub>), and at low H<sup>+</sup> — concentrations a white precipitate, found to be essentially Zn(OH)<sub>2</sub>. According to the above considerations the surface reaction between zinc and H<sub>2</sub>O<sub>2</sub> can be written in the form :

TABLE IV .--- REACTION BETWEEN HYDROGEN PEROXIDE AND ZINC METAL.

2 , 10<sup>6</sup> H2SOA] Mols./ltr.  $\frac{\Delta(H_2SO_4)}{\Delta t} \cdot 10^{5}$ Mols./ltr./min. [H<sub>a</sub>O<sub>2</sub>] Mols./ltr.  $\underline{\Delta(H_{2}O_{2})}, \underline{10^{5}}$ ∆t J<sub>Zn</sub>(OH), Mols./ltr./min.  $\frac{\Delta(H_3)}{\Delta^f} \cdot 10^5$  Mols./ltr./min. Als./ltr./min ∆<sup>t</sup> <sup>J</sup>H<sub>2</sub>O` Mols./ltr./min Mols./ltr./min [H<sub>0</sub>O<sub>1</sub>] <u>∆(0</u>,  $\Delta(H_2O_2)$ Z,  $\frac{\Delta(H_2O_3)}{\Delta l}$ - A(H2O2) Ħ 0.808 3.68 0.9 0.18 I 4.75 1.15 0.802 0.105 157.2 4.96 0.12 2 9·51 3.40 3.40 0.037 11.75 3 0.200 27.0 19.7 4.12 11.75 3.83 0.10 5.2 10.8 9.87 0.0965 0.037 0.488 9.87 0.423 0.042 4 3.8 0.813 0.416 308 308 0.252 5 6 32.6 5.20 5.25 0.010 ĭ·8 0.189 389 0.395 400 454 4.44 54.2 0.011 0.805 in water free ether solution no observable change after 144 hours. 7 8 0.825 in water free amyl alcohol solution no observable change after 24 hours.

$$Zn + H_2O_2 \rightleftharpoons Zn^+ + OH^- + OH$$
 . . (15)

Assuming the monovalent course of the reaction, univalent zinc ions are formed.<sup>20</sup>

Despite the relatively high ionisation potential of the second valency electron, it is well known that the monovalent  $Zn^+$  ions cannot be detected in the solution. Obviously they disappear and so cause the strong observed attack of the Zinc (according to equilibrium 15).

One can think of many processes by which the primarily formed  $Zn^+$  can undergo further reaction with the formation of  $Zn^{++}$ .

The reaction of  $Zn^+$  with  $H_2O_2$  or OH is sufficiently exothermal, and this is also true for the reaction  $2Zn^+ = Zn^{++} + Zn$ .

The results obtained with solutions of hydrogen peroxide in dry ether and amyl alcohol (see Table V., experiments 7 and 8) which gave no noticeable attacks even after 144 hours, show that great importance should be attributed to the decomposition with water (or perhaps with the  $H_3O^+$  ions of the water) according to:

$$Zn^+ + H_2O = Zn^{++} + OH^- + H + Q_{16}$$
 . (16)

 $Q_{16}$  can be calculated from a cyclic process, and yields a value of  $Q_{16} \sim 54$ K cal., so we see that reaction (16) is sufficiently exothermal. Here again the ratio  $\gamma = \left(\frac{[H_2O_2]}{[H_2SO_4]}\right)$  is important in deciding the course of the process, as can be seen from Table IV.

The circumstances here are very similar to those which have been discussed for the electrolysis of  $H_2O_2$  and need not be considered in further detail.

#### Summary.

1. The initial process of the catalytic decomposition of hydrogen peroxide by metals involves an electron transfer from the metal to the  $H_2O_2$ .

<sup>20</sup> Cf. A. MacAulay, Nature, 1930, 126, 914; S. V. Bodfors, Z. physik. Chem., 1932, 160A, 115; 1931, 153A, 83.

adsorbed on the interface. The hydrogen peroxide is thereby attacked monovalently (*i.e.*, one electron is transferred), resulting in the formation of the radicals OH or HO<sub>2</sub>. The chain reaction of the catalysis can then proceed. The catalytic decomposition can be described in this way by assuming only very simple elementary processes in the adsorbed phase.

2. The two principal reactions involved are :

(a) . . . 
$$H_2O_2 + \epsilon_{metal} = OH^- + OH$$

where the  $H_2O_2$  is acting as an oxidising agent.

(b) . . . 
$$HO_2^- = HO_2 + \epsilon_{metal}$$

where the  $H_2O_2$  is acting as a reducing agent.

3. The following fact constitutes strong evidence in favour of this mechanism: the catalytic decomposition becomes considerably greater if the electronic work function of the metal is decreased (*i.e.*, reaction (a) is favoured) through cathodic polarisation.

4. The catalytic decomposition on platinum, gold, palladium, silver and zinc metal has been investigated in detail and discussed from the abovementioned points of view.

In conclusion, I would like to thank Professor F. G. Donnan, F.R.S., very heartily for his continuous interest in this work, and Professor H. Freundlich for valuable discussions.

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