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THE MECHANISM OF THE CATALYSIS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM.

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As an explanation of the catalytic effect of colloidal platinum on the decomposition of hydrogen peroxide, Bredig[1] and his associates accept the hypothesis, originally advanced by Haber,[2] that the platinum first forms an unstable oxide, which reacts with the peroxide giving, of course, oxygen and water. The possibility of such an intermediate product has appeared more probable since the work of Grube,[3] who has shown that the evolution of oxygen from a platinized platinum cathode is preceded by the formation of PtO_3. The two stages in the reaction, according to this explanation, may be represented by the equations:

$$x\mathrm{Pt} + {}^1/_2\, y\mathrm{O}_2 = \mathrm{Pt}_x\mathrm{O}_y \qquad (1)$$

$$\mathrm{Pt}_x\mathrm{O}_y + y\mathrm{H}_2\mathrm{O}_2 = x\mathrm{Pt} + y\mathrm{H}_2\mathrm{O} + y\mathrm{O}_2 \qquad (2)$$

If the concentration of the unstable oxide remains constant, or, in other words, if the change represented by equation (1) is rapid in comparison with that represented by equation (2) the reaction would be expected to be of the first order. That this is only approximately true is evident from the typical series of determinations from the work of Bredig and Ikeda[4] given in Table I. Time in minutes is given under the columns headed t and under $(a - x)$ the concentrations of hydrogen peroxide in arbitrary units. The columns headed by k_1 contain the value of the expression: $1/t \log a/(a - x)$ the first order "constant." In this formula

Table I.

t.	$a-x$.	$k_1 \times 100$.	$K_m \times 100$.	t.	$a-x$.	$k_1 \times 100$.	$K_m \times 100$.
0	12.54	..	..	0	11.80	..	..
4.12	8.57	4.01	2.96	3.90	8.30	3.93	2.87
7.37	6.19	4.15	2.97	7.90	5.70	4.00	2.81
12.25	3.68	4.37	2.95	11.96	3.70	4.22	2.84
19.75	1.52	4.62	2.89	16.55	2.04	4.60	2.94

t.	$a-x$.	$k_1 \times 100$.	$K_m \times 100$.
0	10.50	..	..
3.82	7.43	3.93	2.80
9.29	4.50	3.95	2.68
15.37	2.27	4.26	2.74
19.80	1.37	4.45	2.70

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[1] "Anorganische Fermente," *Z. physik. Chem.*, 31, 258 (1899) and 37, 5 (1901).

[2] *Z. anorg. Chem.*, 18, 40 (1898).

[3] *Z. Elektrochem.*, 16, 621 (1910).

[4] *Z. physik. Chem.*, 37, 5 (1901).

a represents the concentration of the peroxide at the beginning of the reaction. It is apparent that the value of the first order "constant" increases as the reaction proceeds. This slow increase of k_1 is also quite evident in fifty other series in the paper from which these figures are taken.

That this shift in the value of k_1 is not caused by a slow saturation of the catalyzer with oxygen is definitely shown by some experiments of these authors, the data of which are given in Table II. The colloidal platinum used in Series B had already been used in Series A and contained, presumably, the full quantity of the unstable oxide. A similar increase in the value of k_1 can be observed in both series. This means, of course, that if the reaction takes place in the stages represented by equations (1) and (2) the process represented by equation (1) is much the more rapid. We must, therefore, seek another explanation of this interesting variation.

Table II.

	Series A Conc. Pt 0.000014				Series B Conc. Pt 0.0000084		
t.	$a - x$.	$100k_1$.	$K_m \times 100$.	t.	$a - x$.	$100k_1$.	$K_m \times 100$.
0	$26.\dot{3}$	..	..	0	39.6	..	..
5.93	15.8	3.72	3.45	5.9	29.2	2.25	2.07
10.90	9.3	4.13	3.30	12.5	19.1	2.54	2.25
16.00	4.8	4.62	3.46	18.4	13.1	2.61	2.25
				25.1	7.9	2.79	2.28
		Mean,	3.40	30.3	5.3	2.89	2.28
						Mean,	2.23.

As the colloidal platinum presents a very large surface to the liquid it seems possible that an adsorption of the peroxide on this surface influences the rate of reaction. It is also probable that the reaction is confined to a layer next the solid-liquid boundary.[1] Such an adsorption would be expected to follow the usual isotherm

$$x/m = \alpha(c - x)^n, \qquad (3)$$

in which x, c and m are respectively the amount of adsorbed solute, the total concentration of solute and the concentration of the colloid, and α and n are constants. The term $(c - x)$ represents the concentration of solute in equilibrium with the adsorbed quantity x. It can easily be seen that if the exponent n is less than 1, which is the case in adsorption isotherms which have been directly measured, a relatively larger portion of the total amount of the solute will be adsorbed from dilute solutions, and if the reaction takes place in the adsorbed layer, the adsorbing medium will be more effective as a catalyst as the concentration decreases, as is observed in the case under discussion.

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[1] Freundlich ["Kapillarchemie" (p. 382)] has suggested adsorption and diffusion through the adsorbed layer as an explanation of this variation.

If the adsorbing material is very dilute, the amount of adsorbed substance x may be neglected where it occurs in the difference $(c - x)$. The adsorption isotherm then takes the form:

$$x/m = \alpha c^n \qquad (4)$$

Solving for x and substituting it in the place of the active concentration c in the differential equation of a reaction of the first order, $dc/dt = K'c$, we obtain:

$$dc/dt = K'm\alpha c^n \quad \text{or} \quad dc/c^n = K'm\alpha dt$$

Integrating between the time limits zero and t the expression becomes:[1]

$$C_o^{1-n} - C_t^{1-n} = [(n - 1)K'm\alpha]t,$$

and collecting all the constants in the term K we have

$$C_o^{1-n} - C_t^{1-n} = (Km)t, \qquad (5)$$

in which C_o and C_t are the concentrations of peroxide at the beginning of the reaction and after the elapse of the time t, respectively.

The amount of substance adsorbed will depend on the extent of the surface of the adsorbing medium exposed to the solution. The surface will, of course, vary with the concentration of the adsorbent (m of Eq. 3) and its degree of dispersion, a factor which influences the value of α in the same equation. Since the term Km (of Eq. 5) is a product containing α as one of its factors it would, in general, be a constant for more than one series only when a given concentration of the identical preparation of colloid is used in all the runs. There is, however, no such restriction as to the constancy of the term n for its value depends only on the nature of the substances involved. If Equation 5 is based on correct assumptions the value of this constant found for one series of determinations should hold also for any other series. Calculations, by the author, based on the work of Bredig and Ikeda have shown that this is the case. A single value (0.8) for the adsorption exponent has been found sufficient to ex-

TABLE III.

C_{Pt} 0.0000103.

t.	$a - x$.	100 k_t.	100 (Km).
0	24.8	...	..
2.32	20.25	3.8	(3.28)
4.52	16.4	4.0	3.34
7.62	11.82	4.2	3.44
9.67	9.38	4.4	3.48
12.2	7.3	4.4	3.42
14.7	5.4	4.5	3.40
17.2	3.55	4.9	3.56
19.0	2.8	5.0	3.54
22.0	1.91	5.1	3.46

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[1] Bodenstein and Stock (*Ber.*, **40**, 570) have applied a similar equation to the catalysis of gas reactions.

press the experimental results of these investigators, even though the concentration of the colloid and the initial concentration of the hydrogen peroxide vary through rather wide limits. A glance at the columns headed *Km* in Tables I, II and III which contain values of this product will indicate how closely the equation expresses the results.

The values of *Km* found in Table II are particularly interesting since they afford another test of the validity of the assumptions contained in the derivation of Equation 5. As will be recalled, the same sample of colloid was used in Series A and B but at different concentrations. In this case the ratio of the two constants $(Km)_B/(Km)_A$ should be the same as the ratio of the concentrations of the colloid $(m_B)/(m_A)$. The values actually observed are:

$$\frac{(Km)_B}{(Km)_A} = \frac{2.23}{3.40} = 0.65 \text{ and } \frac{m_B}{m_A} = \frac{0.0000084}{0.0000140} = 0.60,$$

which agree as closely as could be expected.

An equation that does not involve the neglecting of the term x, where it occurs in the difference $(c - x)$, in the adsorption isotherm, can be derived, but it is, in its simplest form, a three-constant expression. As we have no independent means of evaluating the extra constant, the use of such an equation would give no further light on the mechanism of the reaction. The great dilution of the catalyst (not over 0.000031 mol per liter in any case investigated) lends support to the supposition that we are dealing with a rapid reaction in an adsorption layer which involves only a small portion of the total concentration.

In the foregoing, only the series in which pure hydrogen peroxide and the colloid are in solution are considered. Equation 5 does not describe the results of experiments in which "poisons" such as prussic acid, iodine or hydrogen sulfide are present, since there are a number of ways in which such substances may influence the reaction, such as chemical combination of the "poison" with the platinum or with the peroxide, selective adsorption of the "poison," etc. It is interesting to note that the reaction under consideration is one of the very few in which this test for adsorption can be used, since practically all other reactions give rise to products which will change the system as the reaction proceeds.

It also seems probable in the light of these calculations that the diffusion of the peroxide to the surface of the colloid, *i. e.*, the velocity of adsorption, is more rapid than the rate with which the decomposition takes place. The Brownian movement of the particles and the stirring effect of the bubbles of evolved oxygen undoubtedly have the effect of bringing fresh solution into contact with the colloidal particles, thus maintaining a saturated adsorption layer.

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