ON THE DISSOLUTION VELOCITY OF OXYGEN INTO SODIUM HYDROXIDE, SODIUM CARBONATE AND HYDROCHLORIC ACID SOLUTION.

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Studies on the oxidation velocities by means of air of several substances, such as ferrous hydroxide,(1) sodium sulphite,(2) stannous hydroxide,(3) and the mixture of sodium sulphite and stannous hydroxide(4) in sodium hydroxide solution, stannous chloride in hydrochloric acid solution,(5) stannous hydroxide,(6) sodium sulphite,(7) and the mixture of sodium sulphite and stannous hydroxide(8) in sodium carbonate solution, were carried out.

This kind of heterogeneous reactions can be considered to take place in three stages, firstly, a part of the molecules of oxygen, which strike the surface of air bubbles, enters into the liquid surface film, secondly, the oxidation occurs in the liquid phase (principally in the surface film), thirdly, the reacting substances in the inner liquid phase diffuse to the surface of the bubbles, and the oxygen dissolved in the surface film diffuses into the inner liquid phase. The slowest process will determine the velocities of these heterogeneous reactions. If the second or the third process be the slowest, the oxidation velocity should depend on the concentrations of the reacting substances. If sufficient reacting substances be always present to react with oxygen as soon as it enters in the surface film, that is, if the concentration of oxygen in the surface film be always kept zero, the apparent oxidation

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(1) This journal, **2** (1927), 40.
(2) Ibid., **2** (1927), 74.
(3) Ibid., **2** (1927), 155.
(4) Ibid., **2** (1927), 191.
(5) Ibid., **2** (1927), 259.
(6) Ibid., **3** (1928), 43.
(7) Ibid., **3** (1928), 76.
(8) Ibid., **3** (1928), 95.

velocity is no other than the rate of the first process, the dissolution of oxygen, and will be independent of the concentration of the reacting substances, if the partial pressure of oxygen be kept constant.

Under these conditions, the meaning of the dissolution velocity of oxygen is quite different from that of the dissolution velocity of solid substances in the liquid phase, in which case the process of diffusion governs the velocity. The oxidation velocities of the substances above described with air were almost in every case independent of the concentrations of the reacting substances under the conditions of the author's measurements, if the initial concentrations of the reacting substances be not very small. In these cases, the observed apparent oxidation velocities do not mean the true oxidation velocities of the substances, but the dissolution velocity of oxygen, the meaning of which being above described, into the liquid phase. It is then possible to calculate the approximate values of the dissolution velocity of oxygen into sodium hydroxide, sodium carbonate and hydrochloric acid solution, when air was passed into 40 c.c. of the solution in a test tube (diameter ≒ 3 cm.) through a glass tube (inside diameter ≒ 4 mm., outside diameter ≒ 6 mm.) at the rate of 7.78 litres per hour, from the results of the author's studies. The calculated values are given in Table 1. The concentrations are given in the first column and the dissolution velocities in the second, the third, and the fourth column, some of them being already given in the previous papers.

The results are also shown graphically in Fig. 1.

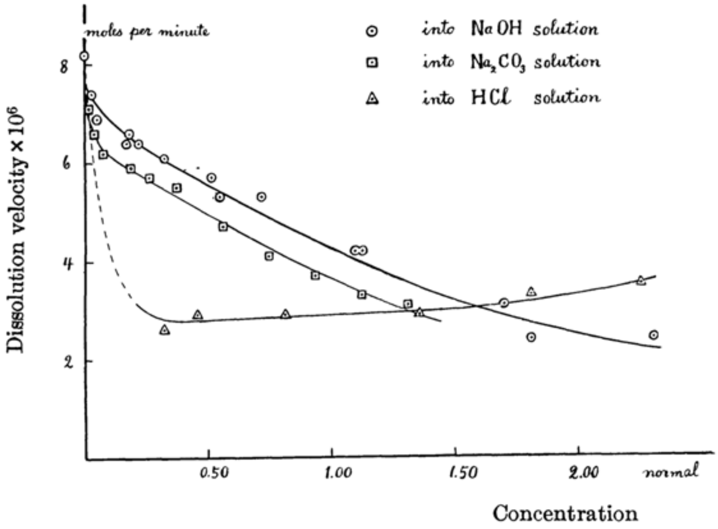

Fig. 1.

TABLE 1.

Temp. = 20°C.

Concentrations normal	Dissolution Velocity of Oxygen × 10^6 moles per min.		
	in NaOH	in Na_2CO_3	in HCl
0	8.2(1)	8.2(1)	8.2(1)
0.01875	—	7.1(1)	—
0.02888	7.4(1)	—	—
0.03750	—	6.6(1)	—
0.05173	6.9(1)	—	—
0.0750	—	6.2(1)	—
0.1706	6.4(2)	—	—
0.1810	6.6(1)	—	—
0.1875	—	5.9(1)	—
0.2204	6.4(2)	—	—
0.2625	—	5.7(1)	—
0.3235	—	—	2.6(3)
0.3252	6.1(2)	—	—
0.3750	—	5.5(1)	—
0.4587	—	—	2.9(3)
0.5173	5.7(1)	—	—
0.5500	5.3(2)	—	—
0.5630	—	4.7(1)	—
0.7219	5.3(1)	—	—
0.750	—	4.1(1)	—
0.8151	—	—	2.9(3)
0.938	—	3.7(1)	—
1.1011	4.2(1)	—	—
1.125	—	3.3(1)	—
1.130	4.2(2)	—	—
1.313	—	3.1(1)	—
1.360	—	—	2.9(3)
1.704	3.1(2)	—	—
1.810	2.4(1)	—	—
1.811	—	—	3.3(3)
2.262	—	—	3.5(3)
2.312	2.4(2)	—	—

(1) The values calculated from the oxidation velocity of sodium sulphite.
(2) " " " " " stannous hydroxide.
(3) " " " " " stannous chloride.

Ferrous hydroxide in sodium hydroxide solution and stannous hydroxide in sodium carbonate solution exist as solid phase in the system and the mechanism of the oxidation of them will be more complex, and the experimental results are not sufficient to discuss it precisely, but from the experimental results, the apparent oxidation velocity of the former seems to be the dissolution velocity of oxygen and that of the latter the reacting velocity.

The author has an opinion to explain some catalysis and induced reaction by the transference of active states.(1) It was ascertained that the increase of the velocity of the induced oxidation of some carbohydrates in the presence of ferrous hydroxide or sodium sulphite with the increase of

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(1) *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 257.

the concentration of sodium hydroxide, studied by C.C. Palit and N. R. Dhar,(1) is not due to the increase of the velocity of the primary reaction; the oxidation velocity of ferrous hydroxide(2) or sodium sulphite(3) decreases with the increase of the concentration of sodium hydroxide. The phenomenon can easily be explained by the transference of the active states of the molecules of the products or the reacting substances of the primary reaction to the molecules of the reacting substances of the secondary reaction.

As was discussed already in the previous papers, the oxidation of the mixture of stannous hydroxide and sodium sulphite can be regarded as a kind of negative induced reactions; the oxidation velocity of sodium sulphite is extremely small in the presence of stannous hydroxide.

According to the author's opinion, some negative induced reactions are explained by the transference of the active states of the molecules of the reacting substances of the secondary reaction to the molecules of some reacting substances or reaction products of the primary reaction, and the oxidation velocity of the mixture studied can be explained by the transference of the active states of the molecules of sodium sulphite to the molecules of stannous hydroxide. The transference of the active states of the molecules of sodium sulphite to the molecules of other substances seems to occur easily, which will be the cause of the existence of many negative catalysers(4) on the oxidation of sodium sulphite.

The catalytic effect of inert gases on some reactions under the influence of alpha-particles, studied by S. C. Lind and D. C. Bardwell,(5) is an experimental result favourable to the author's theory. The phenomenon can be explained as the result of the transference of active states of the molecules of inert gases, excited by alpha-particles, to the molecules of the reacting substances.

Summary.

1. The dissolution velocity of oxygen when air was passed into sodium hydroxide, sodium carbonate and hydrochloric acid solution under some conditions was calculated from the oxidation velocities of sodium sulphite, stannous hydroxide and stannous chloride.
2. The mechanism of some negative induced reactions was discussed.

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(1) *J. Phys. Chem.*, **29** (1925), 799; **30** (1926), 939

(2) Loc. cit.

(3) Loc. cit.

(4) S. L. Bigelow, *Z. physik. Chem.*, **26** (1898), 493; A. Titoff, *Z. physik. Chem.*, **45** (1903), 641; S.W. Young, *J. Am. Chem. Soc.*, **24** (1902), 297.

(5) *J. Am. Chem. Soc.*, **48** (1926), 1575.