ON THE OXIDATION OF FERROUS HYDROXIDE BY AIR.—SUPPLEMENT.

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A study on the oxidation velocity of ferrous hydroxide in sodium hydroxide solution of various concentrations under certain conditions by means of air was reported in the previous papers.(1) Recently A. Krause carried out an excellent research(2) on the same subject under quite different conditions, and he refered the author's experimental results in his discussion on the inorganic chemistry of iron oxides.

The discussion, given by Krause, seems to be excellent except his consideration on the real meaning of the oxidation velocity, observed by the author. The observed oxidation velocity, given in the author's papers, were treated in his discussion, as if it means the real reaction velocity, but, as was described in the second paper of the author, it is no other than the dissolution velocity of oxygen into the solution.

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(1) This Bulletin, 2 (1927); 40; 3 (1928), 137; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 35; 9 (1928), 203.

(2) Alfons Krause, *Z. anorg. allgem. Chem.*, **174** (1928), 145.

The difference of the experimental conditions will sometimes give quite a different meaning on the observed reaction velocity of a heterogeneous chemical reaction, and the author considers that it may be necessary to give the following interpretations on the author's experimental results to prevent further misunderstanding.

C. C. Palit and N. R. Dhar have found that the oxidation velocity of some carbohydrates, induced by the oxidation of ferrous hydroxide, increases as the concentrations of sodium hydroxide increases.(1) A study, the results of which being published in the author's first paper, was undertaken to ascertain the expectation that the oxidation velocity of ferrous hydroxide will also increase with the increase of the concentration of sodium hydroxide under almost the same conditions, as those adopted by Palit and Dhar in their study, above cited. Quite unexpected result was obtained; the observed oxidation velocity of ferrous hydroxide decreases as the concentration of sodium hydroxide increases under the experimental conditions.

It was thus ascertained in the author's first paper that the increase of the velocity of the induced reaction with the increase of the concentration of sodium hydroxide, found by Palit and Dhar, is not due to the increase of the reaction velocity of the primary reaction. It will be difficult to explain the phenomenon by an usual consideration that only the increase of the velocity of the primary reaction causes the increase of the velocity of the induced reaction.

The author proposed to interprete the phenomenon by a new theory of induced reaction.(2) The theory means that a chemical reaction, whose velocity is extremely small, may be induced, when the molecules of the reacting substances are suitably activated by the direct transference of the active states of the molecules of the reaction products of some independent chemical reaction.

If we consider, according to this theory, that the induced reaction does not only depend upon the velocity of the primary reaction, but also upon the process of the transference of active states, the effect of sodium hydroxide on the induced reaction above described can easily be explained.

For the derivation of this conclusion, it is quite unnecessary to ascertain whether the observed oxidation velocity of ferrous hydroxide is the true reaction velocity or not.

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(1) *J. Phys. Chem.*, **29** (1925), 799.

(2) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 259.

By comparing the oxidation velocity of sodium sulphite(1) and stannous hydroxide,(2) observed under the same conditions, with that of ferrous hydroxide, it was found that it is quite probable to consider the observed oxidation velocity to be the dissolution velocity of oxygen into the solution. The author's second study on the same subject was carried out to confirm this consideration by a little modified method.

As was shown in the author's papers,(3) the observed oxidation velocity of ferrous hydroxide decreases as the concentration of sodium hydroxide increases under the conditions of the author's experiments. It only means that the dissolution velocity of oxygen into the solution decreases with the increase of the concentration of sodium hydroxide. Whether the true reaction velocity will also decrease with the increase of the concentration of sodium hydroxide, or, not, is a problem to be solved by the further studies.

A. Krause found the effect of temperature on the oxidation velocity, which was negligible in the author's measurements, to be very great.(4) It is not curious: it is only due to the great difference between his experimental conditions and mine, which will give quite a different meaning to the observed velocity of this heterogeneous chemical reaction. The effect of temperature on the oxidation velocity, observed under the conditions of the author's experiments, is no other than that on the dissolution velocity of oxygen into the solution, while the result, observed by A. Krause, will have quite a different meaning.

The effect of temperature or the effect of the increase of the concentration of sodium hydroxide on the true reaction velocity, the study of which was not the purpose of the author's papers, above cited, may perhaps be obtained by a similar method under some suitable conditions, but it was left for the later studies.

The fact, that the real meaning of the observed reaction velocity of a heterogeneous chemical reaction may sometimes be quite different, if the experimental conditions be not the same, causes the necessity to adopt nearly the same experimental conditions, under which the measurements of Palit and Dhar were carried out, for the purpose of the discussion on the mechanism of the induced reaction, found by Palit and Dhar. It is the reason why such experimental conditions, under which the results do not give the real reaction velocity but the dissolution velocity of air, were adopted by the author.

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(1) S. Miyamoto, this Bulletin, 2 (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 40.
(2) S. Miyamoto, this Bulletin, 2 (1927), 158; *Seientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 192.
(3) Loc. cit.
(4) Loc. cit.

According to the considerations above described, it will be clear that it is quite meaningless to compare the results of the author's experiments with those observed under quite different conditions, if the latter do not mean the dissolution velocity of oxygen into the solution.

Summary.

(1) An interpretation on the real meaning of the observed oxidation velocity of ferrous hydroxide under the conditions of the author's experiments was given to prevent misunderstanding of the author's papers.

(2) The reason, why the experimental conditions, under which the author's measurements were carried out, were adopted, was described.

(3) It was discussed that the oxidation velocity of ferrous hydroxide, observed by A. Krause under quite different conditions, will have quite a different meaning as that, observed by the author. The difference of the real meaning of the observed reaction velocity, caused by the difference of the experimental conditions, will explain why the effect of temperature, which was negligible under the author's conditions, was found by A. Krause to be very great.

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