# ON THE OXIDATION OF FERROUS HYDROXIDE IN SODIUM HYDROXIDE SOLUTION BY MEANS OF AIR.

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The principal purpose of the previous study[1] on the oxidation of ferrous hydroxide by means of air was to know the effect of sodium hydroxide on the reaction, and the oxidation velocity in the first stage was only studied. The present research was carried out to study the reaction under almost the same conditions more completely.

**Experimental.** The experimental procedure was quite the same as that described in the previous paper,[1] only a large test-tube (diameter = 3 cm.) was used for the reacting vessel as in the case of the oxidation of sodium sulphite[2] or stannous hydroxide,[3] instead of an Erlenmeyer flask (100 cc.), which was used in the previous study.

After t-minutes the air current was stopped and the total quantity of ferrous and ferric hydroxide was dissolved in sulphuric acid in the atmosphere of carbon dioxide by Jahoda's method,[4] and the amount of ferrous sulphate thus formed was titrated with 0.1000 normal potassium permanganate solution, the volume of which is given as $v$ in the following tables. The values of $k$ were obtained by $k=\frac{1}{t}(v_0-v)$, $v_0$ being the value of $v$ at $t=0$, and the values of $v_{calc.}$ were calculated by $v_{calc.}=v_0-k\,t$, using the mean value of $k$.

TABLE 1.

Temp. = 20° C. Velocity of air = 7.78 litres per hour.

| $C_{NaOH}$ normal | $t$ min. | $v$ c.c. | $v_{calc.}$ c.c. | $k$ |
|---|---|---|---|---|
| 0.0470 | 0 | 11.87 | — | — |
| | 10 | 9.10 | 9.00 | 0.277 |
| | 15 | 7.36 | 7.56 | 0.301 |
| | 25 | 4.65 | 4.69 | 0.289 |
| | 0 | 24.00 | — | — |
| | 15 | 19.74 | 19.69 | 0.284 |
| | 30 | 16.04 | 15.39 | 0.265 |
| | 50 | 9.69 | 9.65 | 0.286 |
| | 0 | 11.47 | — | — |
| | 10 | 8.44 | 8.60 | 0.303 |
| | 20 | 5.69 | 5.73 | 0.289 |
| | 30 | 2.73 | 2.86 | 0.291 |
| | | | | Mean : 0.287 |

(1) S. Miyamoto, this journal, 2 (1927), 40.
(2) Ibid., 2 (1927), 74.
(3) Ibid., 2 (1927), 155.
(4) Lunge-Berl, "Chemisch-technische Untersuchungsmethoden", 7. Aufl., 2. Bd., S. 135.

TABLE 1. (*Continued.*)

| $C_{NaOH}$ normal | $t$ min. | $v$ c.c. | $v_{calc.}$ c.c. | $k$ |
|---|---|---|---|---|
| 0.1700 | 0 | 23.75 | — | — |
| | 15 | 19.62 | 19.55 | 0.276 |
| | 30 | 15.46 | 15.35 | 0.276 |
| | 55 | 8.07 | 8.35 | 0.285 |
| | 0 | 11.41 | — | — |
| | 10 | 8.67 | 8.61 | 0.274 |
| | 20 | 5.80 | 5.81 | 0.281 |
| | 30 | 2.81 | 3.01 | 0.287 |
| | | | | Mean : 0.280 |
| 0.5494 | 0 | 11.71 | — | — |
| | 10 | 9.39 | 9.40 | 0.232 |
| | 20 | 7.03 | 7.09 | 0.234 |
| | 30 | 4.77 | 4.78 | 0.231 |
| | 0 | 12.35 | — | — |
| | 10 | 10.08 | 10.04 | 0.227 |
| | 20 | 7.71 | 7.73 | 0.232 |
| | 30 | 5.49 | 5.42 | 0.229 |
| | | | | Mean : 0.231 |
| 1.130 | 0 | 11.59 | — | — |
| | 10 | 9.97 | 9.89 | 0.162 |
| | 20 | 8.19 | 8.19 | 0.170 |
| | 40 | 4.71 | 4.79 | 0.172 |
| | 0 | 12.35 | — | — |
| | 10 | 10.67 | 10.65 | 0.168 |
| | 20 | 8.92 | 8.95 | 0.172 |
| | 40 | 5.22 | 5.55 | 0.178 |
| | | | | Mean : 0.170 |
| 1.670 | 0 | 11.49 | — | — |
| | 15 | 9.78 | 9.61 | 0.114 |
| | 30 | 7.85 | 7.74 | 0.121 |
| | 55 | 4.23 | 4.61 | 0.132 |
| | 0 | 12.31 | — | — |
| | 15 | 10.42 | 10.43 | 0.126 |
| | 30 | 8.53 | 8.56 | 0.126 |
| | 55 | 5.09 | 5.43 | 0.131 |
| | | | | Mean : 0.125 |
| 2.260 | 0 | 11.49 | — | — |
| | 15 | 10.19 | 10.06 | 0.0867 |
| | 30 | 8.75 | 8.62 | 0.0913 |
| | 60 | 5.44 | 5.76 | 0.1008 |
| | 0 | 11.49 | — | — |
| | 15 | 10.07 | 10.06 | 0.0947 |
| | 30 | 8.55 | 8.62 | 0.0980 |
| | 60 | 5.41 | 5.76 | 0.1013 |
| | | | | Mean : 0.0955 |

As is seen in Table 1, the oxidation velocity of ferrous hydroxide is independent of the amount of ferrous hydroxide present in the reacting vessel, and the values of the velocity constants are almost the same as those of the velocity constants of the oxidation of sodium sulphite(1) or stannous hydroxide(2) in sodium hydroxide solution under the same conditions. The coincidence of the values of their velocity constants is shown in Table 2 and graphically in Fig. 1. It can be considered, from the above results, that the oxidation velocity of ferrous hydroxide under the conditions of the author's measurements is no other than the dissolution velocity of oxygen when air was passed into sodium hydroxide solution.

Strictly speaking, the presence of solid phase in the solution will have some effect on the dissolution velocity of oxygen, but the experimental error of the present experiment will be too great to discuss it precisely.

TABLE 2.

Temp. = 20° C.

| $C_{NaOH}$ Normal | $k$ | | | $k_{calc.}$ ($=0.278-0.0942\,C_{NaOH}$) |
|---|---|---|---|---|
| | $Na_2SO_3$ | $Sn(OH)_2$ | $Fe(OH)_2$ | |
| 0 | 0.330 | — | — | — |
| 0.02888 | 0.298 | — | — | 0.275 |
| 0.0470 | — | — | 0.287 | 0.274 |
| 0.05173 | 0.276 | — | — | 0.273 |
| 0.1700 | — | — | 0.280 | 0.262 |
| 0.1706 | — | 0.257 | — | 0.262 |
| 0.1810 | 0.265 | — | — | 0.261 |
| 0.2204 | — | 0.259 | — | 0.258 |
| 0.3252 | — | 0.246 | — | 0.248 |
| 0.5173 | 0.231 | — | — | 0.229 |
| 0.5494 | — | — | 0.231 | 0.226 |
| 0.5500 | — | 0.215 | — | 0.226 |
| 0.7219 | 0.213 | — | — | 0.210 |
| 1.1011 | 0.169 | — | — | 0.174 |
| 1.130 | — | 0.168 | 0.170 | 0.172 |
| 1.670 | — | — | 0.125 | 0.121 |
| 1.704 | — | 0.126 | — | 0.117 |
| 1.810 | 0.0989 | — | — | 0.107 |
| 2.260 | — | — | 0.0955 | — |
| 2.312 | — | 0.0998 | — | — |

(1) Loc. cit.

(2) Loc. cit.

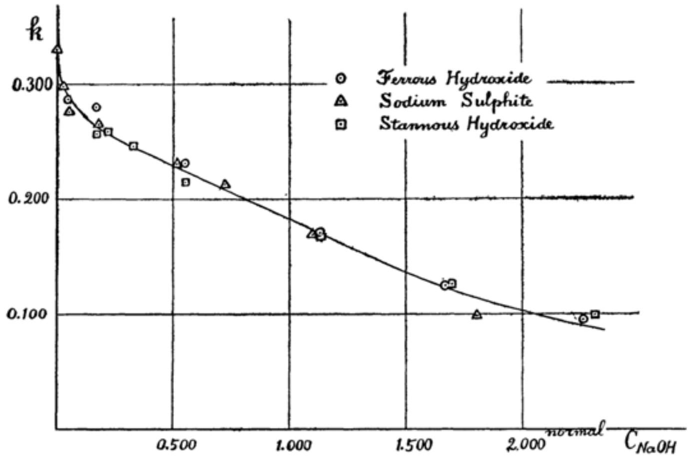


Fig. 1.

TABLE 3.

Air=7.78 litres per hour.

| Temp. | $C_{NaOH}$ Normal | $t$ min. | $v$ c.c. | $v_{calc.}$ c.c. | $k$ |
|---|---|---|---|---|---|
| 30° C. | 0.0470 | 0 | 13.27 | — | — |
| | | 10 | 10.39 | 10.31 | 0.288 |
| | | 20 | 7.22 | 7.35 | 0.303 |
| | | 30 | 4.56 | 4.39 | 0.290 |
| | | 0 | 14.37 | — | — |
| | | 10 | 8.36 | 8.41 | 0.301 |
| | | 15 | 6.89 | 6.93 | 0.299 |
| | | 25 | 4.01 | 3.97 | 0.294 |
| | | | | | Mean : 0.296 |
| 30° C. | 0.5494 | 0 | 13.25 | — | — |
| | | 10 | 10.70 | 10.87 | 0.255 |
| | | 20 | 8.40 | 8.49 | 0.243 |
| | | 35 | 5.04 | 4.92 | 0.235 |
| | | 0 | 11.23 | — | — |
| | | 10 | 8.78 | 8.85 | 0.245 |
| | | 20 | 6.57 | 6.47 | 0.233 |
| | | 30 | 4.67 | 4.09 | 0.219 |
| | | | | | Mean : 0.238 |
| 40° C. | 0.0470 | 0 | 13.15 | — | — |
| | | 10 | 10.08 | 10.12 | 0.307 |
| | | 20 | 7.24 | 7.09 | 0.296 |
| | | 30 | 4.28 | 4.06 | 0.296 |
| | | 0 | 11.16 | — | — |
| | | 10 | 8.16 | 8.13 | 0.300 |
| | | 15 | 6.55 | 6.61 | 0.307 |
| | | 25 | 3.41 | 3.58 | 0.310 |
| | | | | | Mean : 0.303 |

TABLE 3. (*Continued.*)

| Temp. | $C_{NaOH}$ Normal | $t$ min. | $v$ c.c. | $v_{calc.}$ c.c. | $k$ |
|---|---|---|---|---|---|
| 40° C. | 0.5494 | 0 | 12.96 | — | — |
| | | 10 | 10.25 | 10.29 | 0.271 |
| | | 20 | 7.59 | 7.62 | 0.269 |
| | | 30 | 5.20 | 4.95 | 0.259 |
| | | 0 | 12.87 | — | — |
| | | 10 | 10.15 | 10.20 | 0.272 |
| | | 20 | 7.46 | 7.53 | 0.271 |
| | | 30 | 5.06 | 4.86 | 0.260 |
| | | | | | Mean : 0.267 |

**The Effect of Temperature.** The results of the measurements at 30° C. and 40° C. are given in Table 3. The effect of temperature was small, as can be expected.

$$\frac{k_{30^\circ}}{k_{20^\circ}} = \frac{0.296}{0.287} = 1.03, \quad \frac{k_{40^\circ}}{k_{30^\circ}} = \frac{0.303}{0.296} = 1.03$$

when $C_{NaOH} = 0.0470$ normal

$$\frac{k_{30^\circ}}{k_{20^\circ}} = \frac{0.238}{0.231} = 1.03, \quad \frac{k_{40^\circ}}{k_{30^\circ}} = \frac{0.267}{0.238} = 1.12$$

when $C_{NaOH} = 0.5494$ normal

## Summary.

(1) The velocity of the oxidation of ferrous hydroxide by means of air was studied. The rate of the oxidation was independent of the quantity of ferrous hydroxide present in the reacting vessel, and the values of the velocity constants were almost the same as those of the velocity constants of the oxidation of sodium sulphite or stannous hydroxide under the same conditions.

(2) The effect of temperature was small.

(3) Sodium hydroxide decreases the velocity of the oxidation, the mechanism of which will be explained by the considerations that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen under the conditions above described, and that sodium hydroxide decreases the dissolution velocity of oxygen into the solution.

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