

3. The yield is not affected by hydrogen, is probably increased by nitrogen, and very greatly increased by oxygen, in the presence of which, however, the reaction probably proceeds in a different manner.

4. A discussion of the possible mechanism leaves the exact formulation of the reaction unclear, but shows that as far as can at present be established, the results are in accord with other work, and with theoretical considerations.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## DETERMINATION OF THE FREE ENERGY OF FERROUS HYDROXIDE FROM MEASUREMENTS OF ELECTROMOTIVE FORCE

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The purpose of this investigation was to determine the standard free energy of formation of ferrous hydroxide. This was accomplished by measurements of electromotive force, and the result is compared with others obtained from diverse determinations of the solubility product.

### Apparatus and Materials

Measurements were made on a series of cells of the type



in which various samples of iron were used. In addition, a few cells of the type



were included, in which only iron deposited by electrolysis upon platinum electrodes was used. The cells were built with special care to exclude oxygen, and placed in an oil thermostat maintained at 25°. The electromotive forces were measured on the potentiometer described by Lewis, Brighton and Sebastian.<sup>1</sup>

Iron.—Four different kinds of iron were used, prepared by the following methods.

(1) Electrolytically, by the Fischer–Langbein process.<sup>2</sup> The electrolyte was prepared from c. p. hydrochloric acid, pure iron wire in excess, c. p. calcium chloride and distilled water. The iron was deposited upon bright platinum electrodes, 1.3 by 1.3 cm., and pure iron wire served as anode. The electrolysis was performed at the bottom of a U-tube with square corners which was immersed in an oil-bath maintained at 110°, at which temperature practically no hydrogen<sup>2</sup> is included in the iron depositing on the cathode. In most cases the current density was maintained at 0.15 amp. per sq. cm.

<sup>1</sup> Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2246 (1917).

<sup>2</sup> Allmand and Ellingham, "Applied Electrochemistry," Longmans, Green and Company, New York, 1924, p. 347.

of that side of the electrode which was facing the anode. It was found, however, that within wide limits the electromotive behavior of this kind of iron is independent of the current density at which the iron is deposited. About 0.25 g. of iron was deposited on each side of the platinum.

In building the half-cell shown on the left side of Fig. 1, the glass rod carrying the electrode was inserted in a rubber stopper, which, after being greased with vaseline, was forced into the cylinder. The cylinder was then clamped upside down, and molten paraffin let in through a small glass tube not shown in the figure. As soon as the paraffin had solidified under the stopper, the cylinder was placed in normal position and a solution of deKhotinsky cement in alcohol was poured on top of the rubber stopper, leaving an air-tight layer after evaporation of the alcohol. The cylinder was then flushed successively with 0.1 M hydrochloric acid, conductivity water, and 0.05 M barium hydroxide. In flushing, pure nitrogen was used each time to force liquid out of the cell. After this treatment the electrode was perfectly bright. As shown in Fig. 1 the two half-cells were connected to an intermediate vessel, which was insulated against atmospheric oxygen in a similar manner. After charging the other half-cell with mercury and mercuric oxide the whole cell with all its connections was filled with 0.05 M barium hydroxide.

By preliminary experiments it had been found that iron is passive in alkaline solution, and that the electromotive force of the cell does not correspond to a reversible reaction under these circumstances. However, passive iron becomes active when charged cathodically with hydrogen.<sup>3</sup> This kind of iron electrodes, as well as those described under (2) and (3), were therefore electrolyzed as cathode, with a platinum electrode, not shown on the figure, as anode, for ten minutes with a current of ten to fourteen milliamperes. As this caused a slight change in the concentration of the barium hydroxide, the half-cell containing iron was again flushed with fresh 0.05 M barium hydroxide. Finally, the iron electrode was completely submerged in a thick suspension of ferrous hydroxide in 0.05 M barium hydroxide. Some of this suspension left in the S-shaped in- and outlets of the cell prevented oxygen from diffusing into the cell through these.

(2) By reduction of pure iron oxide with hydrogen, according to the method of Richards and Behr.<sup>4</sup> The reduction was carried out at a temperature of 800 to 850°. The hydrogen required for the reduction was prepared and carefully purified in the cryogenic laboratory; no impurities were deposited when it was passed through a liquid air trap. The resulting samples of iron were stored in glass tubes filled with pure hydrogen.

The half-cell used for this kind of iron was similar to the one shown on the right side of Fig. 1. The platinum lead at the bottom, however, was curled up into a ring, about one cm. in diameter, placed horizontally a little above the bottom. Several pieces of

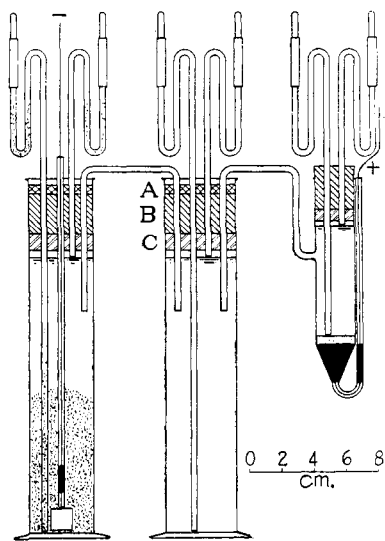


Fig. 1.—Cell containing electrolytic iron, ferrous hydroxide, 0.05 M barium hydroxide, mercuric oxide, mercury. A, de Khotinsky cement; B, rubber stopper; C, paraffin.

<sup>3</sup> Ref. 2, p. 259.

<sup>4</sup> Richards and Behr, Carnegie Inst. Pub. No. 61 (1906).

iron were thrown down upon this ring, whereby a large surface of iron in good contact with the platinum wire was obtained. When connection had been made to the half-cell containing mercury, the iron was completely submerged in a thick suspension of ferrous hydroxide in 0.05 M barium hydroxide.

(3) We are indebted to the firm of Pike and West of San Francisco for a sample of commercial electrolytic iron from their experimental unit. They reported the following impurities in the sample: carbon 0.0075%, sulfur 0.0075%, copper 0.022%.

This iron had not been prepared by Fischer's process. It contained a small amount of hydrogen, which made it somewhat brittle. All traces of rust were removed from it by filing. Some coarse filings and a few small pieces were then produced from it with a hard clean file, and placed in a half-cell similar to the one used for the iron produced by reduction of iron oxide.

(4) A small recently charged Edison cell was flushed and filled with conductivity water, allowed to stand overnight, and again emptied and filled. This was repeated several times, until the original electrolyte had been thoroughly removed. Pure nitrogen was used for displacing the liquid. The cell was then repeatedly flushed and filled with 0.05 M barium hydroxide, a rubber stopper with glass tubing was placed in its neck, and connection was made in the usual manner to a half-cell containing  $\text{Ba}(\text{OH})_2$ , 0.05 M,  $\text{HgO}(\text{s})$ ,  $\text{Hg}(\text{l})$ .

**Ferrous Hydroxide.**—About 8 g. of pure iron wire, 99.8% Fe, was placed in the 750-cc. tube, shown in Fig. 2, and the air in this displaced by pure hydrogen. Twelve

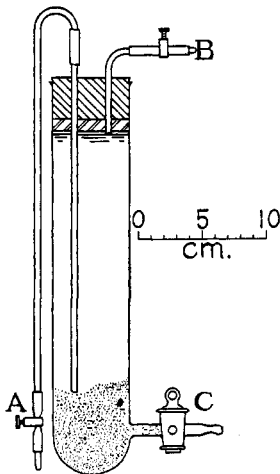


Fig. 2.—Tube for preparation of ferrous hydroxide.

cc. of concentrated hydrochloric acid, corresponding to 4 g. of iron, was diluted with an equal volume of water and charged into the tube, and the mixture was heated. The excess of iron prevented the formation of ferric ion. When the acid had been used up, 200 cc. of distilled water from which dissolved gases had been expelled by boiling was added through C and immediately followed by 200 cc. of a solution of barium hydroxide from which dissolved oxygen had been similarly removed. This solution contained enough barium hydroxide to precipitate the iron and make the mixture about 0.05 M with respect to barium hydroxide. After settling overnight about four-fifths of the solution was forced out through A with pure hydrogen coming in through B; the tube was filled again with 0.05 M barium hydroxide, and the contents thoroughly mixed. By repeating this decantation six to seven times, a thick suspension of solid ferrous hydroxide in 0.05 M barium hydroxide was obtained in the lower part of the tube.

**Ferric Hydroxide.**—In the tube shown in Fig. 2 a concentrated solution of ferric chloride was boiled with a little concentrated nitric acid in order to oxidize every trace of ferrous ion to ferric ion, diluted with freshly boiled distilled water, precipitated and repeatedly decanted with barium hydroxide, in order to produce a thick suspension of solid ferric hydroxide in 0.05 M barium hydroxide.

**Barium Hydroxide.**—As a solution of barium hydroxide contains no carbonate it was used in preference to sodium or potassium hydroxide. One single batch of 0.05 M barium hydroxide,<sup>5</sup> large enough for the entire investigation, was prepared at the

<sup>5</sup> All concentrations are expressed in moles per 1000 g. of water. Vacuum corrections have been applied to all weights.

start. Early in these experiments it was found necessary to remove completely dissolved oxygen. This was done by boiling the solution for half an hour in a flask fitted with a reflux condenser. In order to remove impurities such as lead and arsenic some iron wire was added before boiling. The air above the boiling solution was displaced with pure hydrogen.

**Mercuric Oxide.**—Mercuric oxide was prepared by heating c. p.  $\text{HgNO}_3 \cdot 2\text{H}_2\text{O}$  in an electric furnace to about  $500^\circ$  with stirring. The residue was ground, washed with conductivity water, and dried at  $105^\circ$ . Ordinarily, duplicates of electrodes in which this oxide was used would differ only by 0.0005 volt or less. In the final experiments the mercuric oxide electrodes were checked against a hydrogen electrode.

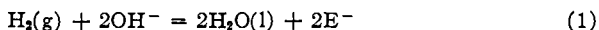
**Mercury.**—The mercury was refined by washing with dilute nitric acid in the usual manner, followed by distillation in a current of air.

**Nitrogen.**—Pure nitrogen was prepared whenever needed by gentle heating of a solution of 1 part of sodium nitrite, 1.5 parts of ammonium sulfate, and 1 part of potassium chromate in 4 parts of water. The gas was washed with a mixture of 1 volume of concentrated sulfuric acid and 5 volumes of saturated potassium dichromate solution.<sup>6</sup>

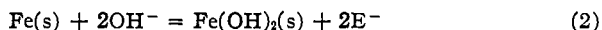
### Data and Discussion

The variation of the electromotive forces of the various cells with time is shown graphically in Fig. 3. To avoid excessive overlapping all curves but  $a_1$  have been plotted at an arbitrary distance from the vertical axis.

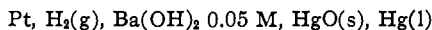
It will be noticed that the electromotive force is increasing from the start in all cells. This is ascribed to the fact that all iron electrodes, as mentioned previously, were activated by cathodic charging with hydrogen. Probably the charge of hydrogen makes them behave in part as hydrogen electrodes. It is thought that the two half-cell reactions



and



tend to occur simultaneously at the iron electrode. By checking the mercury half-cell against a hydrogen electrode, the electromotive force of the cell



was found to be 0.9266 volt, in close agreement with the values given by Brönsted and Ming Chow for similar cells.<sup>7</sup> This is, therefore, the potential corresponding to reaction (1). In course of time the charge of hydrogen is lost by diffusion, and the electromotive force of the cell approaches the value corresponding to reaction (2). The fluctuations of the cells  $a_1$ ,  $a_2$  and  $a_3$  indicate other disturbing influences in addition to hydrogen.

When it was realized that a relatively long time would be required for the establishment of equilibrium in the cells, the measurements were discon-

<sup>6</sup> See Gmelin-Kraut, "Handbuch der anorganischen Chemie," Heidelberg, 1907, Vol. I, 1, 171.

<sup>7</sup> Brönsted, *Z. physik. Chem.*, **65**, 84, 744 (1909); Ming Chow, *THIS JOURNAL*, **42**, 488 (1920).

tinued for more than one year. At the end of this period the electromotive force of Cell  $a_1$  proved to be the same as before, a value which both Cell  $a_2$  and Cell  $a_3$  by that time had very nearly attained also. In Cells  $b_1$ ,  $b_2$  and  $c$  the contact between the iron and the platinum wire had been destroyed, probably by an insulating coating of ferrous hydroxide formed on the iron during the prolonged submersion.

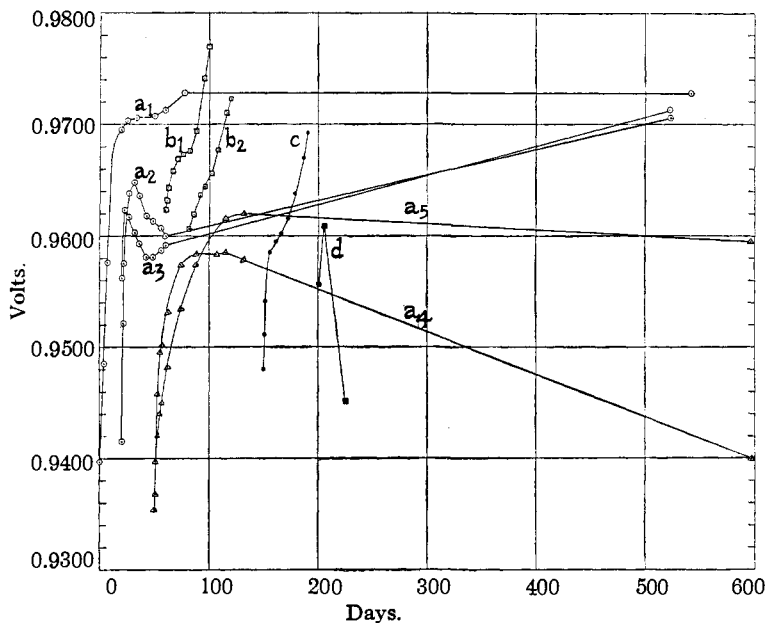


Fig. 3.—Variation of the electromotive force of cells of the type  $\text{Fe}(s)$ ,  $\text{Fe}(\text{OH})_2(s)$ ,  $\text{Ba}(\text{OH})_2$  0.05 M,  $\text{HgO}(s)$ ,  $\text{Hg}(l)$  with time. Cells  $a_1$  to  $a_5$  contained electrolytic iron; Cells  $b_1$  and  $b_2$  iron produced by reduction; Cell  $c$ , commercial electrolytic iron; Cell  $d$ , iron from an Edison cell. Cells  $a_4$  and  $a_5$  contained ferric hydroxide instead of ferrous hydroxide.

The electromotive forces of the cells containing iron produced by reduction of iron oxide, namely, Cells  $b_1$  and  $b_2$ , seem to approach a higher value than the others. This is in accord with observations made by Hampton,<sup>8</sup> and by Richards and Behr,<sup>4</sup> who state that the higher escaping tendency of this kind of iron probably is due to the presence of very finely divided particles of iron.

From Cells  $a_4$  and  $a_5$  it is seen that the presence of ferric hydroxide around the iron electrode lowers the electromotive force of the cell, and prevents it from assuming a constant, reproducible value. A similar phenomenon is observed in Cell  $d$  into which air was admitted accidentally when its electromotive force had reached a value of 0.9609 volt. The ensuing decrease

<sup>8</sup> Hampton, *J. Phys. Chem.*, **30**, 980 (1926).

of the electromotive force was probably due to formation of ferric hydroxide around the iron.

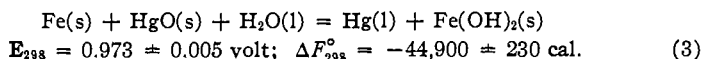
On the whole, the agreement between the various ferrous hydroxide cells containing different kinds of iron is not bad when the sluggish nature of these cells is taken into consideration. The fact that Cells  $a_1$ ,  $a_2$  and  $a_3$  in the end show very nearly the same electromotive force is very gratifying, and we feel justified in selecting

$$E_{298} = 0.973 \pm 0.005 \text{ volt}$$

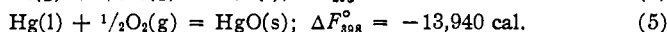
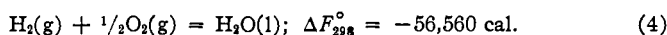
for the final equilibrium potential of the ferrous hydroxide cells.

### Calculations

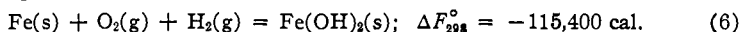
From the preceding measurements we find for the cell reaction



From the tables of free energy<sup>9</sup> we obtain



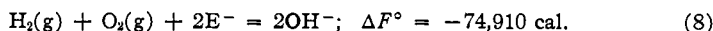
Adding Equations (3), (4) and (5) we obtain



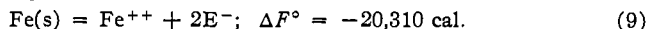
For comparison the free energy of formation of ferrous hydroxide may be calculated from data obtained by other methods. We have for the reaction



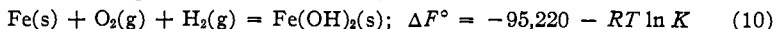
where  $K$  is the solubility product of ferrous hydroxide. From the free energy table we obtain



and in the following paper we shall find



By addition of Equations (7), (8) and (9) we then have

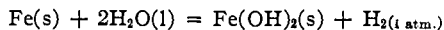


Diverse values of the solubility product  $K$ , determined in various ways, are given in Table I together with corresponding values of the free energy calculated by means of Equation (10).

It is seen that our value, 115,400 calories, is in good agreement with the average result of these determinations.

Calculating backwards from our result we find for the solubility product of ferrous hydroxide,  $K = 1.45 \times 10^{-15}$ .

In conclusion, we shall use our determination to calculate whether the reaction



<sup>9</sup> "International Critical Tables," Vol. VII, 1930, pp. 232, 258.

TABLE I

CALCULATION OF THE FREE ENERGY OF FORMATION OF FERROUS HYDROXIDE FROM ITS

Solubility product	SOLUBILITY PRODUCT Method of determining solubility product	Authority	$-\Delta F^\circ$ , calories
$1.64 \times 10^{-14}$	Calculated from Bodländer's formula, <i>Z. physik. Chem.</i> , <b>27</b> , 56 (1898)	(1)	114,000
$8.7 \times 10^{-14}$	From activities of the ions in 20% KOH solution; (Fe <sup>++</sup> ) from e. m. f. measurements	(2)	113,000
$9.84 \times 10^{-15}$	Conductivity measurements	(3)	114,300
$7.93 \times 10^{-15}$	$P_H$ measurements	(4)	114,500
$3.2 \times 10^{-14}$	$P_H$ measurements	(5)	113,600
$1.6 \times 10^{-13}$	Calculated from $P_H$ measurements of Britton, <i>J. Chem. Soc.</i> , <b>127</b> , 2118 (1925)	(6)	120,900
$4.8 \times 10^{-16}$	$P_H$ measurements	(7)	116,100
	Average		115,200

(1) E. Müller, *Z. Electrochem.*, **14**, 77 (1908). (2) P. Krassa, *ibid.*, **15**, 490 (1909). (3) A. B. Lamb, *THIS JOURNAL*, **32**, 1214 (1910). (4) Shipley and McHaffie, *Can. Chem. Met.*, **8**, 121 (1924). (5) Whitman, Russell and Davis, *THIS JOURNAL*, **47**, 70 (1925). (6) W. J. Sweeney, *Trans. Am. Electrochem. Soc.*, **53**, 317 (1928). (7) L. W. Elder, *ibid.*, **57**, 383 (1930).

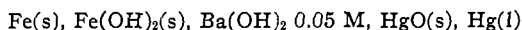
according to which iron is corroded by pure water, is thermodynamically possible. For the free energy of this reaction we find

$$\Delta F_{298}^\circ = 2 \times 56,560 - 115,400 = -2280 \text{ cal.}$$

Hence it is seen that iron and pure water actually have a small tendency to form solid ferrous hydroxide and free hydrogen.

### Summary

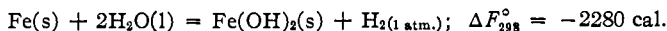
1. The electromotive force of the cell



in which pure iron prepared in different ways was employed, was found to be  $0.973 \pm 0.005$  volt at  $25^\circ$ .

2. From this determination the standard free energy of formation of ferrous hydroxide is calculated to be  $-115,400$  calories, in good agreement with the average of values calculated from diverse determinations of the solubility product.

3. Hence we find



which shows that iron and pure water have a small tendency to form ferrous hydroxide and free hydrogen.

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