THE STANDARD ELECTRODE POTENTIAL OF IRON AND THE ACTIVITY COEFFICIENT OF FERROUS CHLORIDE

BY MERLE RANDALL AND MIKKEL FRANDSEN

Richards and Behr[1] made a comprehensive study of the difference in potential of various kinds of iron, differing in mode of preparation and in mechanical and thermal treatment. Differences of about three centivolts were encountered. They considered pure iron, produced by reduction of iron oxide with hydrogen and subsequently fused in vacuum, as the normal or standard form of iron; with this form they found 0.76 volt for the electromotive force of the cell

$$Fe(s), FeSO_4 \; 0.5 \; M, \; KCl \; 0.1 \; M, \; HgCl(s), \; Hg(l)$$
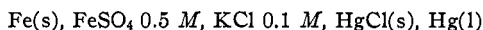
Unfortunately, the unknown activity of the ferrous ion in this concentrated solution and the unknown liquid potential involved make it impossible to calculate the standard electrode potential from this determination.

Hampton[2] used pure iron produced by reduction of iron oxide with hydrogen at about 800° as the standard form of iron, and avoided liquid potentials using the cell

$$Fe(s), FeCl_2 \; 0.1 \; M, \; HgCl(s), \; Hg(l)$$
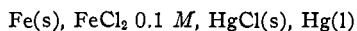
Assuming the activity of ferrous chloride to be the same as that of barium chloride, he found 0.4413 volt for the standard electrode potential of iron.

In a recent determination of the free energy of ferrous hydroxide[3] we attempted to use Hampton's standard form of iron in some alkaline cells, but did not succeed because the contact between the iron and the wire at the bottom of the cells was destroyed in a certain length of time. This difficulty was avoided by using electrolytic iron deposited upon platinum electrodes, with which satisfactory measurements were obtained. In the ensuing calculations, however, we had to use a value for the free energy of formation of the ferrous ion, and it became necessary to find out whether Hampton's value would apply to our electrolytic iron. We decided, therefore, to measure the potential of both kinds of iron in cells of the type used by him. In addition, we used a value for the activity coefficient of ferrous chloride calculated from various data given in the literature.

Apparatus and Materials

As ferrous chloride is a strong reducing agent, it is necessary to take special precautions to avoid oxidation in the cells. A cell used for iron prepared by reduction of the oxide is shown in Fig. 1. It will be noticed

[1] Richards and Behr, Carnegie Inst. Pub. No. 61 (1906).

[2] Hampton, *J. Phys. Chem.*, **30**, 980 (1926).

[3] Randall and Frandsen, THIS JOURNAL, **54**, 40 (1932).

that the two half-cells are closed glass vessels. The S-shaped in- and out-lets permit flushing and when left filled with the solution of ferrous chloride they prevent atmospheric oxygen from penetrating into the cell. The iron in the left half-cell was slipped in through the side tube before this was bent into shape.

The half-cells employed for electrolytic iron were similar to that described in our article on ferrous hydroxide.

Iron.—The preparation of both kinds of iron was described in the previous paper. After the electrolytic iron had been placed in its half-cell, adhering layers from the bath were removed by flushing with dilute hydrochloric acid and 0.1 M ferrous chloride. The iron produced by reduction was placed in the cells without ever coming in contact with air and was first submerged in the solution of ferrous chloride without preceding flushing with acid. Later, however, some samples of this iron were treated with acid as described in the following.
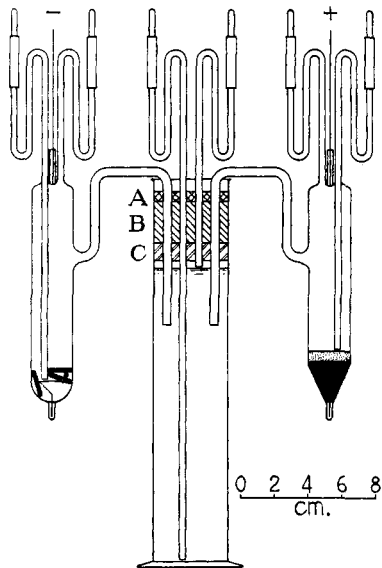
Ferrous Chloride Solution.—A large amount of 0.2 M hydrochloric acid was first made by mixing correct weights of constant boiling hydrochloric acid and conductivity water according to the method of Hulett,[4] allowance being made for the small amount of water that later escapes with the hydrogen. This solution was then allowed to react with an excess of pure iron wire in an apparatus similar to that of Richards and Behr.[1] A layer of paraffin 1 cm. thick was cast under the stopper, which was also heavily coated with paraffin on the outside to keep out oxygen.

Fig. 1.—Cell containing iron, ferrous chloride 0.1 M, calomel, mercury, protected against atmospheric oxygen: A, de Khotinsky cement; B, rubber stopper; C, paraffin.

Calomel.—An excess of pure mercury was heated with 25 cc. of 3 N nitric acid to 50–60° for half an hour under frequent shaking, the mixture placed on a shaking machine for one hour, then poured into about twenty volumes of conductivity water, and precipitated with 1 N hydrochloric acid. The precipitate was washed repeatedly by decantation with conductivity water, and run into a 250-cc. bottle, with an inlet tube at the top and an outlet tube reaching the bottom, and containing pure hydrogen and a little pure mercury. After settling, the main part of the water was forced out with pure hydrogen and replaced with 0.1 M ferrous chloride; the bottle was rotated overnight, and the solution was decanted after settling. This was repeated about six times, whereby a suspension of calomel in 0.1 M ferrous chloride was obtained, from which the calomel cells containing pure mercury and hydrogen were charged. Half-cells prepared in this manner agreed to 0.00005 volt, and two months later with freshly prepared cells.

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

4 Hulett, THIS JOURNAL, 31, 390 (1909).

The cells were placed in an oil thermostat maintained at 25°, and their electromotive force was measured on the potentiometer described by Lewis, Brighton and Sebastian.[5] To avoid erratic results it was found necessary to shake the half-cells containing iron by gentle tapping previous to each measurement.
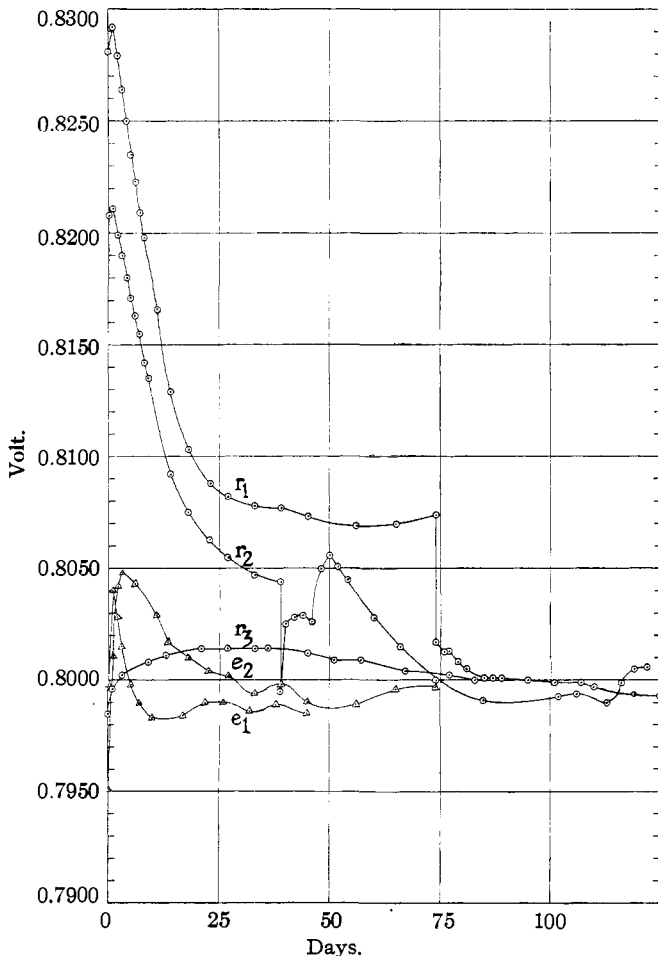
Fig. 2.—Variation of the electromotive force of cells of the type Fe(s), FeCl$_2$ 0.1 M, HgCl(s), Hg(l) with time. Cells r$_1$, r$_2$ and r$_3$ contained iron produced by reduction of iron oxide; Cells e$_1$ and e$_2$ contained electrolytic iron.

Data and Discussion

In Fig. 2 the electromotive force of various cells is shown plotted against time. It is seen that the electromotive force in all cases changes considerably during the first two weeks.

[5] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2246 (1917).

It has often been observed that the electromotive behavior of the electrolytic iron within wide limits is independent of the current density at which the iron has been deposited.   This is demonstrated again by Cells e_1 and e_2, in which the samples of iron were deposited at current densities of 1.5 and 0.15 amp./sq. cm., respectively.

Richards and Behr observed that the potential of the iron produced by reduction increased with decreasing temperature of the reduction, and ascribed this to the fact that iron produced at lower temperatures is more finely divided.   Their observation is confirmed by the potentials of Cells r_1, r_2 and r_3, the samples of iron in which were produced at 770, 800 and 850°, respectively.   Besides the temperature the rate of reduction also influences the state of subdivision of the iron, the subdivision of which decreases with increasing rate of reduction.

The iron in Cell r_3 was produced in a rapid current of hydrogen, and consisted of well-sintered pieces which did not seem to contain any fine particles.   The electromotive force of this cell is, therefore, much closer to that of electrolytic iron than those of the other cells containing iron produced by reduction.

The continued decrease in the electromotive force of Cells r_1 and r_2 is undoubtedly due to a slow disappearance of the finer particles of iron, which have a higher escaping tendency than the bulk of the iron.   To accelerate this process the iron in these two cells was treated after 74 and 39 days, respectively, with 0.2 M hydrochloric acid, and then flushed with and again submerged in 0.1 M ferrous chloride solution.   It is seen from Fig. 2 that after this treatment the electromotive force of these cells became finally almost identical with that of those containing electrolytic iron.

Equilibrium Potentials.—From the curves in Fig. 2 we find for the equilibrium potentials of Cells e_1 and e_2 the values 0.7987 and 0.7994 volt, respectively, from which the average value 0.7990 volt is obtained for the cells containing electrolytic iron.   Similarly, we find 0.8000, 0.7992 and 0.8014 volt for Cells r_1, r_2 and r_3, respectively, from which the average value 0.8002 volt is found for the equilibrium potential of the cells containing iron produced by reduction.   For both kinds of iron we shall then take $E = 0.7996 \pm 0.0010$ volt.   The close agreement of the equilibrium potential of cells containing either kind of iron with this value may be taken as strong evidence of its correctness.

The Activity Coefficient of Ferrous Chloride

The activity coefficient of ferrous chloride was calculated by the usual procedures[6] from various data given in the literature.   The freezing point data of Biltz and Meyer[7] were the most valuable source, although other

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[6] Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

[7] Biltz and Meyer, *Z. physik. Chem.*, **40**, 185 (1902).

measurements[8] also were considered.   As usual the heat of dilution was neglected in the calculations.   A plot of log γ against the square root of the ionic strength, $\mu^{1/2}$, made it possible to draw a curve representing the average of the various results.   From this curve the values given in Table I were obtained.

TABLE I

ACTIVITY COEFFICIENT OF FERROUS CHLORIDE AT THE FREEZING POINT

Molality	Log γ	Molality	Log γ
0.001	−0.048	0.05	−0.205
.002	− .065	.1	− .236
.005	− .095	.2	− .252
.01	− .124	.5	− .234
.02	− .157	1.0	− .175

Although the vapor pressure measurements of Tammann indicate that the activity coefficient of ferrous chloride decreases slightly with increasing temperature, it will cause no appreciable errors to use the values in Table I at 25° without the application of any temperature correction.

Discussion of Hampton's Results

In spite of the fact that our cell diagrammatically is identical with Hampton's, our determination of its equilibrium potential, 0.7996 volt, is considerably lower than his value, 0.8088 volt.   From a careful study of his work,[2,9] we are led to believe that in his choice of the equilibrium potential he was misled by the tendency of finely divided iron to give too high values.   Our reasons for this conclusion are the following.

(1) Treatment with acid reduces the activity of Hampton's "finely divided iron" to our value.   Our Cells r_1 and r_2 were prepared essentially in the same manner as Cells 6 and 7 of Hampton's publication, and, as shown on Fig. 2, the electromotive force of Cell r_1 was for a long time nearly constant at about 0.8072 volt, a value which differs only little from the apparent equilibrium potential, 0.8088 of Hampton's Cell 7.   The potential 0.8072 volt, however, does not correspond to a true equilibrium because Cells r_1 and r_2 after treatment of the iron with acid, which accelerates the removal of finer particles of iron, attain a nearly constant electromotive force of approximately the same value as shown by Cells e_1 and e_2, which contained compact electrolytic iron.

(2) Prolonged exposure to solutions of ferrous chloride makes the activity of Hampton's "finely divided iron" approach our value.   Some data from which this may be shown are given in Table II.

[8] (a) Goldschmidt and Syngros, Z. anorg. Chem., 5, 129 (1894); (b) Peters, Z. physik. Chem., 26, 223 (1898);   (c) Vapor pressure measurements, Tammann, Mem. Acad. Pet., [7] 35, No. 99 (1887).

[9] Hampton, Manuscript Thesis, University of California, Berkeley, California, 1921.

TABLE II

Fe(s), FeCl₂(aq.), HgCl(s), Hg(l) AT 25°

Cell	m(FeCl₂)	E	$\mu^{1/2}$	Log γ + const.
Hampton's Thesis No. 33	0.5	0.7474	. . .	. . . . . .
Hampton's Thesis No. 33	2.245	.6592	. . .	. . . . . .
Hampton's Thesis No. 33	0.1	.8000	0.5477	−8.2173
Hampton's Publication No. 5	0.1	.8087	.5477	−8.3154
Hampton's Publication No. 5	.0865	.8136	.5095	−8.3077
Hampton's Publication No. 5	.050	.8278	.3873	−8.2297
Hampton's Publication No. 5	.0095	.8826	.1688	−8.1260
Hampton's Publication No. 7	.1	.8088	.5477	−8.3154
Hampton's Publication No. 7	.01	.8790	.1732	−8.1077
Randall and Frandsen	.1	.7996	.5477	−8.2128

In each cell the iron was successively left in contact with various solutions of ferrous chloride, the molalities of which are given in the second column in the order in which they were applied, until the electromotive force had become approximately constant. Values of the electromotive force, E, and the square root of the ionic strength, $\mu^{1/2}$, are included in the table. The values of log γ + constant have been calculated by the equation[10]

$$\log \gamma + \text{constant} = -\frac{E}{0.088725} - \log m_{\pm}$$

in which $m_{\pm}$ is the stoichiometric mean molality. The constant is equal to $-E^{\circ}_{298}/0.088725$, from which E°_{298}, the electromotive force of the cell when the ions of the solute are at unit activity, may be found as soon as the value of the constant has been determined.

The figures in the last column of Table II are shown plotted against the square root of the ionic strength in Fig. 3. Superimposed upon this plot is shown
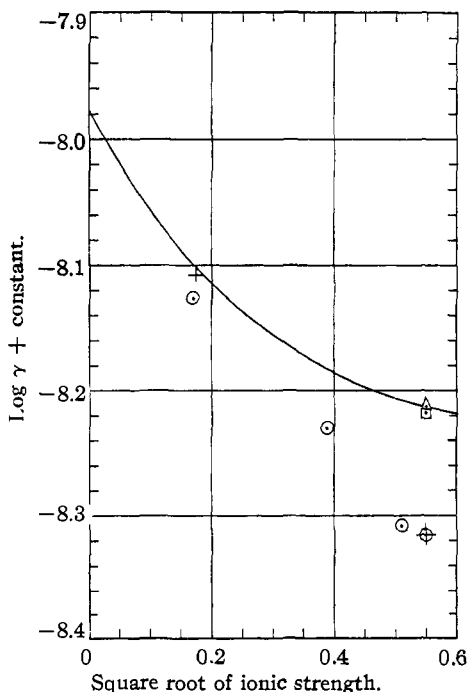

Fig. 3.—Activity coefficient function of ferrous chloride. Solid curve obtained mainly from freezing-point data: □, Hampton Cell 33; ⊙, Hampton Cell 5; +, Hampton Cell 7; △, Randall and Frandsen.

the curve from the previously mentioned plot of log γ against the square

[10] Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

root of the ionic strength, which has been drawn, parallel to its original position, through the point corresponding to $E = 0.7996$ for 0.1 M ferrous chloride. As the measurements in the more dilute solutions were made last, it is seen that the longer Hampton's iron in each case had been in contact with solutions of ferrous chloride, the closer is the agreement between his determinations and ours. The reason for this is undoubtedly the progressive elimination of very fine particles of iron. Hampton's Cell No. 33 is in agreement with ours because its iron first was treated with other solutions of ferrous chloride as shown in Table II.

(3) Hampton's measurements of the equilibrium

$$Fe(s) + 2TlCl(s) = Fe^{++} + 2Cl^- + 2Tl(s)$$

indicate that his value for the electromotive force is too high. The data in Tables V and VI of his publication give evidence that his approach to the equilibrium from the left was much closer than that from the right. Nevertheless, his value for the electromotive force agrees better with the result of his approach to the equilibrium from the right. In the following calculations it will be shown that our value for the electromotive force nearly coincides with the result of his approach to the equilibrium from the left.

Calculation of the Standard Electrode Potential

From the intercept of the curve in Fig. 3 on the vertical axis the value of the constant is found to be -7.977. Substituting this value in the equation

$$\text{Constant} = -\frac{E^{\circ}_{298}}{0.088725} \tag{1}$$

we find the electromotive force at unit activities E°_{298}, for the cell reaction

$$Fe(s) + 2HgCl(s) = Fe^{++} + 2Cl^- + 2Hg(l); \quad E^{\circ}_{298} = 0.7078 \text{ v.};$$
$$\Delta F^{\circ}_{298} = -32,660 \text{ cal.} \tag{2}$$

whence with the value of the potential of the hydrogen–calomel cell obtained by Randall and Young[11]

$$Fe(s) = Fe^{++} + 2E^-; \quad E^{\circ}_{298} = 0.4402 \text{ v.}; \quad \Delta F^{\circ}_{298} = -20,310 \text{ cal.} \tag{3}$$

From Hampton's measurement of the equilibrium approached by the action of iron upon thallous chloride at $25°$, $m(Fe^{++}) = 0.0453$, $m(Tl^+) = 0.0042$, $m(Cl^-) = 0.0948$, whence $\log m_{\pm} = -1.1301$, and $\mu^{1/2} = 0.3743$. Assuming the principle of the ionic strength for the equilibrium mixture, we find from Table I $\log \gamma = -0.2020$; whence $\log a_2 = -3.9963$, and

$$Fe(s) + 2TlCl(s) = Fe^{++} + 2Cl^- + 2Tl(s); \quad \Delta F^{\circ}_{298} = 5455 \text{ cal.} \tag{4}$$

With the accurate measurements of Gerke[12]

$$Tl(s) + AgCl(s) = TlCl(s) + Ag(s); \quad E^{\circ}_{298} = 0.7790; \quad \Delta F^{\circ}_{298} = -17,975 \text{ cal.} \tag{5}$$
$$Ag(s) + {}^1/_2Cl_2(g) = AgCl(s); \quad \Delta F^{\circ}_{298} = -26,220 \text{ cal.} \tag{6}$$

[11] Randall and Young, THIS JOURNAL, 50, 989 (1928).

[12] Gerke, ibid., 44, 1684 (1922).

and the preliminary revised value of the free energy of formation of chloride ion ($-31,345$), we find

$$\text{Fe(s)} = \text{Fe}^{++} + 2E^{-}; \quad E^{\circ}_{298} = 0.4387 \text{ v.}; \quad \Delta F^{\circ}_{298} = -20,245 \text{ cal.} \quad (7)$$

In making these measurements Hampton used powdered reduced iron. The treatment with thallous chloride undoubtedly had the same effect as our treatment with hydrochloric acid of first removing the finer particles of iron; the residual iron might, therefore, be expected to give identical results in the two cases. The small difference between the values in Equations 3 and 7 is explained by the fact that complete equilibrium hardly was attained in Hampton's experiments. The measurements of Hampton in which the equilibrium was approached from the action of ferrous chloride upon thallium do not agree with these measurements, but the reaction is very slow and undoubtedly equilibrium was not attained.

Summary

1. Iron prepared in pure form by electrolysis is shown to have the same potential as pure iron produced by reduction of iron oxide, in ferrous chloride solution.

2. The standard single potential of iron at 25° is found to be 0.4402 volt, and the free energy of formation of ferrous ion to be $-20,310$ calories.

3. The new potential is shown to agree with the equilibrium experiments of Hampton.

4. A table of values of the activity coefficient of ferrous chloride at the freezing point has been calculated.

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THE HEATS OF "ADSORPTION" OF OXYGEN ON NICKEL AND COPPER CATALYSTS

BY W. WALKER RUSSELL AND OSBORNE C. BACON[1]

It is well known that oxygen has no action on nickel or copper[2] in the massive state at ordinary temperatures. When these metals are sufficiently finely divided to be catalytically active, however, they do take up oxygen readily and may even become pyrophoric.[3] Oxygen may also serve as a poison[4] for the catalytic activity of nickel and copper. A study of the action of oxygen on such surfaces might, therefore, be expected to

[1] From a thesis submitted in May, 1931, by Osborne C. Bacon to the Graduate School in partial fulfilment of the requirements for the degree of Master of Science.

[2] Dunn, *Proc. Roy. Soc.* (London), A111, 210 (1926).

[3] Tammann and Nikitin, *Z. anorg. allgem. Chem.*, 135, 201 (1924).

[4] Benton and Emmett, THIS JOURNAL, 48, 637 (1926); Pease and Taylor, *ibid.*, 44, 1637 (1922).