[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Standard Electrode Potential of the Iron–Ferrous Ion Couple at 25°

BY W. A. PATRICK AND W. E. THOMPSON

RECEIVED MARCH 31, 1952

An experimental study of the standard electrode potential of iron has been described under conditions which completely removed oxygen from the electrolyte. A new value (+ 0.409 v.) was obtained, and variations from this value are due to the presence of atomic hydrogen in the metal.

The purpose of the following investigation is to submit experimental proof of the existence of atomic hydrogen in iron as the principal cause of the variations in the standard potential of the Fe, Fe^{++} half-cell. Since the addition of hydrogen is found to raise the iron half-cell potential, the effect must be caused by the presence of atomic rather than molecular hydrogen.

These measurements must be made in the complete absence of oxygen, for the disturbing effect of even traces of this gas is very pronounced with electrodes whose combination with oxygen is accompanied by a large decrease in free energy.

This work was undertaken as part of a study of the effect of hydrogen on the corrosion of iron, made under the auspices of the Office of Naval Research.

Richards and Behr[1] in 1906, ran measurements on the system

$$Fe \mid FeSO_4\ (0.5\ M) \mid KCl\ (0.1\ M)\ Hg_2Cl_2\text{–}Hg$$

They were unable to calculate a standard potential for this cell because of the unknown liquid potential and the high concentration of ferrous sulfate. However, they did point out the very significant fact that iron prepared electrolytically or by reduction of the oxide with hydrogen gave an average potential 0.02–0.03 v. higher than vacuum fused iron. This, they attributed to hydrogen in some "active form."

Hampton[2] measured the potential of the cell

$$Fe \mid FeCl_{2(aq)} \mid Hg_2Cl_2\text{–}Hg$$

using two types of iron electrodes; the first, a finely divided iron prepared by reducing the oxide with hydrogen and the second, an iron amalgam prepared by electrolyzing a solution of ferrous sulfate using a mercury cathode. An average value of 0.4413 v. was calculated as the standard potential.

Randall and Frandsen,[3] using the same type cell, obtained an average standard potential of 0.440 v.

It is important to note that Hampton and also Randall and Frandsen used iron that was prepared either electrolytically or by the reduction of the oxide with hydrogen. Also the measurements were made with some oxygen present.

For the work presented in this paper hydrogen-free iron was prepared by the thermal decomposition of the pentacarbonyl under vacuum. The powder thus obtained was used directly as electrode material. In addition, massive iron electrodes were prepared by vacuum fusion of the metal powder.

Special care was taken to remove all traces of oxygen from the cells, using a new process developed by Patrick and Wagner.[4]

Thus, it is believed that the procedure followed has eliminated all effects due to atomic hydrogen or to oxygen gas contamination.

Experimental Methods

A. **Apparatus.**—E.m.f. measurements were made on a Leeds and Northrup Type K potentiometer using a wall galvanometer of a sensitivity of 0.49 mv. per millimeter (at 1 meter) and a resistance of 11.6 ohms. An Eppley standard cell was used and temperature was read on a Beckmann thermometer. Both were checked and calibrated by the Bureau of Standards. The oil thermostat was maintained at a temperature of 25 ± 0.02° by a mercury regulator and thyratron control.

Deoxygenating Apparatus.—The apparatus for deoxygenating the water was essentially that described by Patrick and Wagner[4] with the addition of a side arm for distilling the water into the cell. The complete assembly is shown in Fig. 1.

Cells.—H-Shaped cells were used as shown in Fig. 1 with the right arm of approximately three times the volume of the left. A bridge between the two arms was made by means of a mercury seal stopcock (not shown). The tops of the arms were equipped with 29 × 42 standard taper caps through which the cells were loaded. The electrodes were constructed by sealing a platinum wire in the bottom of a small tube connected by an inner seal to the ground glass cap. Electrical contact between the lead wire to the potentiometer and this platinum wire was made by pouring mercury into the small tube. The side arm on the larger half-cell was sealed to the delivery tube of the deoxygenating apparatus when filling the cell.

B. **Materials. Massive Iron Electrodes.**—Liquid iron carbonyl was decomposed and the iron powder recovered. This powder was vacuum melted in alundum crucibles. The melt was made by the Non-Ferrous Division of the Naval Research Laboratory, Washington, D. C., by E. J. Chapin.

The result of the melt was a silvery ingot which was stored in a desiccator, and electrodes cut from it when needed.

Carbonyl Iron Powder (Hydrogen Reduced).—The powder used was the SF grade prepared by the Antara Division of the General Aniline and Film Corporation. Also used were the following: mercury, triply distilled; lead, finely divided, reagent grade; mercurous sulfate; mercurous chloride; ferrous sulfate and ferrous chloride. These last four chemicals were especially purified and furnished by the Mallinckrodt Chemical Works.

C. **Methods. Cleaning of Cells.**—Before each use the cells were washed with Alconox and hot water, steamed with concentrated nitric acid, rinsed ten to twenty times with distilled water and dried in the oven.

Introduction of Anode Materials.—The loading of a mercury–mercurous sulfate half cell will illustrate the procedure. The same method was used in loading mercury–mercurous chloride and lead–lead sulfate half-cells. Enough mercury was poured into the bottom of the cell to completely cover the platinum lead. On top of this was placed a layer of mercury-mercury sulfate paste. And on top of this was placed a small layer of pure mercury sulfate. Finally, clean glass wool was placed in the arm in such a manner as to cover the bridge arm and the chemicals. The male joint

---

[1] T. W. Richards and G. E. Behr, Jr., Carnegie Inst. Pub. No. 61 (1906).

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

[3] M. Randall and M. Frandsen, THIS JOURNAL, **54**, 47 (1932).

[4] W. A. Patrick and H. B. Wagner, *Anal. Chem.*, **21**, 752 (1949).

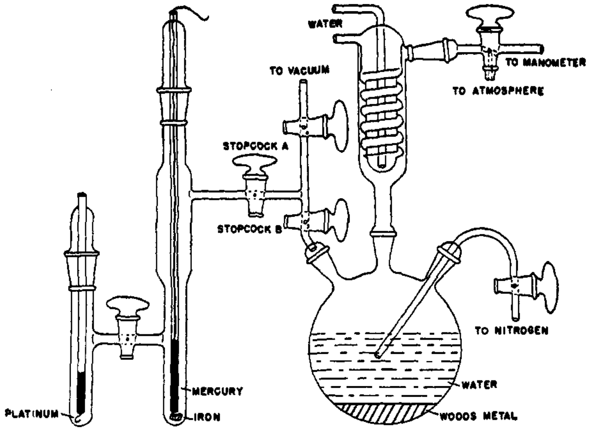

Fig. 1.

was greased with silicone and rotated until the joint was smooth.

Introduction of Cathode Materials. 1. **Carbonyl Powder Half-cells.**—The powder was poured into the right arm to such a depth as to completely cover the platinum lead. On top of the powder was placed a 1 inch layer of glass wool. The ferrous sulfate (or ferrous chloride) was poured on top of the glass wool and the male joint was carefully brought into position.

2. **Massive Electrode.**—A square piece of metal was freshly cut from the large block. The platinum lead was tightly wound about the electrode and all of the platinum joint was covered by a layer of nitro-seal. The salt was poured into the bottom of the tube and the male joint greased and inserted so that the electrode hung in about the center of the smaller half of the right-hand arm.

Filling of Cell.—The side arm of the loaded cell was sealed to the delivery arm of the deoxygenating apparatus. The stopcock in the bridge was opened, stopcock A leading to the vacuum pump was opened and stopcock B was closed. The vacuum pump was turned on, and the cell was pumped down for a period of approximately 48 hours. Then stopcock A and the bridge stopcock were closed and stopcock B was opened to pump out the water. After the evolution of air had stopped, stopcock B was closed, and the system was brought to atmospheric pressure with Airco nitrogen. Then this procedure was repeated, with the nitrogen being pumped out of the water and fresh nitrogen added. The water was then boiled with the Woods metal for four to five hours. The bridge stopcock was then closed and an ice-bath was placed around the cell. A pinch clamp was closed on the vacuum line and stopcocks A and B were opened. The oxygen-free water was distilled into the large arm of the cell. When this arm was approximately three-quarters filled, stopcock B was closed. The glass in the center of the side arm was collapsed with the flame of a torch, and the end of the side arm was sealed as the cell was carefully removed from the deoxygenating apparatus. The cell was agitated to ensure thorough mixing of the solution. The bridge stopcock was then opened to allow the solution to flow into the left-hand arm. The cell was placed in the oil-bath for measurement. Copper lead wires were inserted in the mercury tubes and connected to the potentiometer. The cells were disturbed as little as possible, although occasionally a cell would have to be removed and shaken when a vapor bubble would form in the bridge. The e.m.f. of each cell was checked at regular intervals until a constant value was reached and measurements were continued for from five to ten days thereafter to ensure constancy. The cells were then removed from the bath and analyzed for ferrous ion, using ceric sulfate as oxidizing agent and orthophenanthroline as indicator, as given by Kolthoff and Sandell.[5] (Note: Where any deviation from the procedure given above occurs, it will be noted in the discussion of the particular cell.)

Results

The standard electrode potential for the iron–ferrous ion couple has been calculated from the appropriate equation:

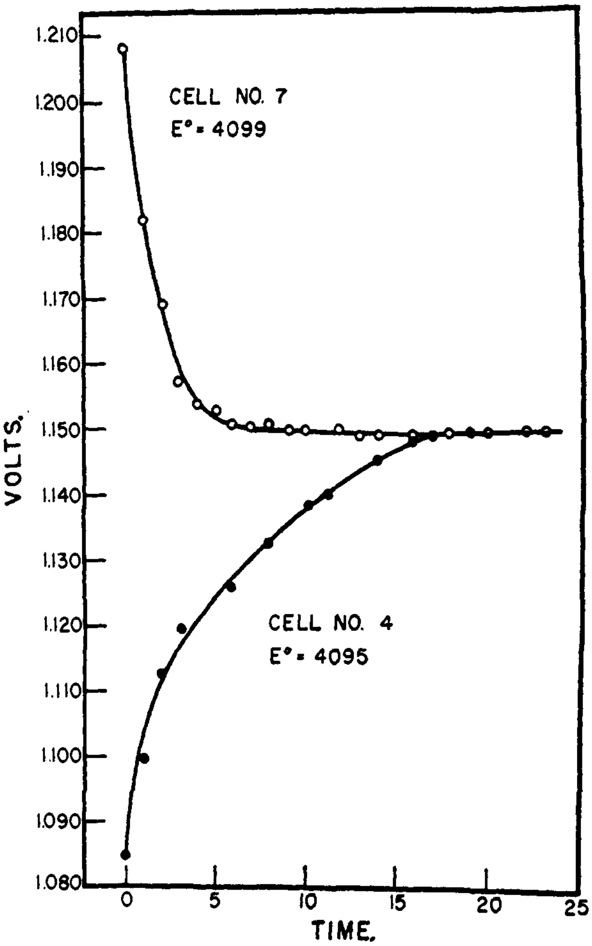

Fig. 2.

$$E^0 = E + 0.05914 \log a_{\mathrm{Fe}^{++}} - 0.6151 \text{ for } \mathrm{FeSO_4{-}Hg_2SO_4} \text{ systems} \quad (1)$$

$$E^0 = E + 0.05914 \log a_{\mathrm{Fe}^{++}} + 0.355 \text{ for } \mathrm{FeSO_4{-}PbSO_4} \text{ systems} \quad (2)$$

$$E^0 = E + 0.02957 \log \gamma^3(m_{\mathrm{Fe}^{++}})(m_{\mathrm{Cl}^-})^2 - 0.2676 \text{ for } \mathrm{FeCl_2{-}Hg_2Cl_2} \text{ systems} \quad (3)$$

The activity coefficients used for ferrous sulfate were taken from the work of De Massieuz and Fedoroff.[6]

Activity coefficients for ferrous chloride and the standard potentials for the reference half-cells are from Latimer.[7]

In calculating the half-cell potential of iron we made use of independently determined values of the activity coefficients of the ferrous ion at the particular concentration that prevailed in the cell. The activity coefficient, of course, will change with changes of pH; that is to say, the hydrolysis of the ferrous ion will modify its thermodynamic state. But all such changes are included in the value of the activity coefficient.

Experimental.—Pertinent data on the following cells are given in Table I and shown graphically in Fig. 3.

---

[5] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1941.

[6] N. De Massieuz and B. Fedoroff, *Ann. chim.*, **16**, 225 (1941).

[7] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1936.

TABLE I

Cell	Reference cell	Condition (air)	Molality	Activity coefficient	E	E^0
		Massive iron from carbonyl				
8	$PbSO_4$–Pb	Deoxygntd.	0.0677	0.198	0.1654	0.409^6
3	Hg_2Cl_2–Hg	Deoxygntd.	.0760	.60	.7770	.0482
		Carbonyl iron powder				
1	Hg_2SO_4–Hg	Deoxygntd.	0.0718	0.193	1.1335	0.4085
2	$PbSO_4$–Pb	Deoxygntd.	.0300	.281	0.1771	.4094
4	Hg_2SO_4–Hg	Deoxygntd.	.0274	.290	1.1488	.4095
5	Hg_2SO_4–Hg	Deoxygntd.	.0220	.330	1.1522	.4115
7	Hg_2SO_4–Hg	Air	.029	.281	1.1485	.4099
6	Hg_2SO_4–Hg	Deoxygntd.	.0160	.72	0.8298	.4080
		Iron reduced from oxide				
9	Hg_2Cl_2–Hg	Air	0.0864	0.60	0.8065	0.443
10	Hg_2Cl_2–Hg	Deoxygntd.	.0675	.60	.8520	.477

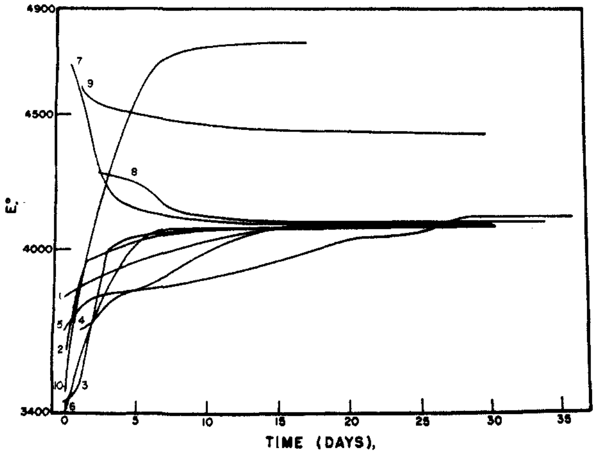

Fig. 3.

A. Group I

Each cell of this group contained either a pentacarbonyl iron powder electrode or a massive electrode cut from our vacuum-melted ingot. No sign of corrosion could be detected on the massive electrodes even after weeks in the cell. Also, electrodes which were lying unprotected about the laboratory showed no traces of rust after many months exposure.

Cells 1, 2, 3, 4, 5 and 6.—These cells followed the same general pattern, *i.e.*, a sharp initial rise in potential followed by a gradual approach to a steady value within a period of 12 to 30 days. The agreement among the cells is excellent; and since three different reference half-cells have been used, there seems to be little doubt as to the accuracy of the value. The potential value of 0.4090 v. is constantly reproducible to 1 mv. Cell 5, which was identical with 4, except for a slight difference in molal concentration, gave the greatest potential of all our so-called "good" cells, namely, 1.1522 v, with an $E°$ value of 0.4115 v. After 20 days of slowly increasing voltage, there was an unusual increase for a period of 4 to 5 days, after which the potential leveled off to the above constant value. It may be that the peculiar behavior of this cell was caused by a slight leak, which eventually closed.

Cell 7.—Air was intentionally admitted to this cell by momentarily opening the iron half-cell at the joint and immediately resealing it. The graph shows the radically different behavior of this cell from that of cells 1, 4 and 5 which had been prepared in exactly the same manner and with the same materials, but which had been completely deoxygenated. However, the calculated standard potential is in good agreement, indicating that the presence of small amounts of oxygen does not materially affect the potential of this type of iron, but that it does greatly alter the manner in which the steady value is approached. The potential, instead of rising, as is the case with the completely deoxygenated cells, falls regularly to a constant value.

Cell 8.—This cell was intended to be a completely deoxygenated one. However, since the potential value of the cell decreased to a steady value, as was the case with cell 7, the authors are of the opinion that there must have been a small quantity of oxygen present.

B. Group II

Cell 9.—In order to check our apparatus and chemicals, it was decided to repeat, in essence, the experiment of Randall and Frandsen. Accordingly, the cell was loaded with iron powder prepared by reduction of the oxide with hydrogen, the water was boiled, nitrogen was passed through it, and the cell was filled in the usual manner. After the cell was sealed, one of the joints was opened momentarily to admit a small quantity of air. As may be seen from the graph, the cell behaved exactly as did those of Randall and Frandsen. An initial large fall of potential occurred followed by a gradual approach to constancy (to 0.5 mv.) in a period of about 20 days.

The calculated result of 0.443 v. for the iron potential is in fair agreement with the results of Randall and Frandsen, although slightly higher.

Cell 10.—After checking the accepted value with cell 9, it was decided to investigate the hydrogen-reduced powder electrode in our completely deoxygenated system. The potential increased over 0.1 v. in the first 7 days and then rapidly became constant. The cell was analyzed after 17 days as we did not wish to establish the potential with any great accuracy, but rather to ascertain the effect of deoxygenation. The surprising potential of 0.477 v. was obtained. It seems likely that an oxide layer inhibits the true potential value of a hydrogen reduced powder electrode. It is to be especially noted that the potential of this completely deoxygenated cell increased, in contradistinction to all other experiments with this type of electrode, when air was present. A summary of the results obtained from the cells of these two groups is presented in Table I and Fig. 3. The calculated standard electrode potential ($E°$) is plotted *vs.* time.

C. Group III

Cell 11.—As a final conclusive test of the difference between a hydrogen reduced powder electrode and a pentacarbonyl iron powder electrode, it was decided to measure the potential directly, using ferrous sulfate as the electrolyte. The value $E = 0.054$ v. is an average value of the readings taken during the course of a week. This measured value is in fair agreement with the difference we have found indirectly ($0.477 - 0.409 = 0.068$).

D. Discussion of Groups I, II, III

An average value for the standard electrode potential of the iron–ferrous ion couple calculated from the result obtained from the cells of Group I is $E^0 = 0.4090$ v.

It seems clear from these results that a reproducible standard potential value for iron has been measured which is much lower than any measured heretofore. Of prime importance is the agreement between the massive and powder forms of this iron and the agreement between completely deoxygenated systems and those containing small amounts of oxygen. It is believed that this is the first time such agreement has been obtained. It also seems apparent that the manner in which the steady state was approached was in all cases dependent upon whether or not oxygen was present in the system.

Since the potential of hydrogen-reduced iron powder electrodes was greater in a completely deoxygenated system than in one containing oxygen, and since hydrogen reduced iron gives a much higher potential value than our pentacarbonyl iron electrodes, it appears certain that the value of the standard potential for iron is dependent on whether or not atomic hydrogen is present in the metal.

Thus we conclude that the presence of hydrogen in some active form raises the measured potential of the system and that the direction of the approach to the steady state is determined by the presence or absence of oxygen gas in the system.

The increase of potential to a steady state in cells 1, 2, 3, 4, 5, 6 and 10 is explained by the slow removal of the initial layer of iron oxide from the iron electrode. Our method of deoxygenating the solution does not remove the oxide film from the iron; this takes place slowly by means of electrochemical changes within the cell. The decrease of potential in cells 7, 8 and 9 is caused by the disappearance of the small amount of oxygen, which is acting as an electron sink and at a lower potential than the Hg_2SO_4–Hg electrode. The amount of oxygen involved was too small to effectively change the activity of the ferrous salt, or the final equilibrium potential. Large quantities of oxygen would greatly change the activity of the electrolyte by the introduction of OH ions

$$2e^- + {}^1/_2O_2 + H_2O \longrightarrow 2OH^-$$

These two opposing effects are strikingly illustrated in Fig. 2.

BALTIMORE 18, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY]

The Oxidation–Reduction Potential of the Sexa- and Quinquevalent Molybdenum System

BY H. K. EL-SHAMY AND A. M. EL-AGGAN

RECEIVED APRIL 16, 1952

Spectrophotometric measurements have shown that in hydrochloric acid solutions of normality less than 3, molybdenum-(V) produces a brown color, while at acid normalities above 5.75, the color is emerald green. These colors correspond to two different series of ionic species which show strong absorption at wave lengths of 395 and 450 mμ, respectively. Other ionic species exist at intermediate acidities. The oxidation–reduction potentials of the Mo(VI)–Mo(V) system have been determined against a hydrogen electrode over a range of hydrochloric acid concentrations from 8 *N* to less than 0.01 *N*. The E_0 value obtained by graphical extrapolation was 0.4826 v. at 30 ± 0.02°. Measurements against a calomel electrode at the same temperature gave 0.4825 v.

The work so far done on molybdenum solutions does not completely solve the problem of the constitution of sexa- and quinquevalent molybdenum ions, especially in acid solutions. Foerster, Fricke and Hausswald[1] in their determinations of the oxidation–reduction potentials of the sexa- and quinquevalent molybdenum ions in 2, 4 and 8 *N* hydrochloric acid, suggested a single formula for the molybdenum ion in each state of oxidation, irrespective of the acidity. The observed potentials were found, however, to differ considerably from those calculated, especially in 2 and 4 *N* acid. This was attributed to a profound effect of the acid on quinquevalent molybdenum ions in solution, which manifested itself in the color change from green to brown as the solutions passed from 8 to 2 *N* acid.

Tourky and El-Shamy[2] tried to elucidate the change in constitution of the molybdenum ions accompanying the color change. They established the most probable formulas for the sexa- and quinquevalent molybdenum ions in 8–6 and 4–2 *N* hydrochloric acid, and postulated the existence of two different forms within these two acid ranges.

In the present article measurements are reported of the oxidation–reduction potentials of the sexa- and quinquevalent molybdenum system against both hydrogen and calomel electrodes over a wide range of acid concentration. This study necessitated the carrying out of spectrophotometric measurements for the purpose of obtaining information on the effect of hydrochloric acid on molybdenum ions in solution, especially in connection with changes in the chemical nature of quinquevalent molybdenum ions corresponding to the change in color on passing through the range of acidity from 8 *N* to less than 0.01 *N* hydrochloric acid.

Experimental

The preparations and analyses of the solutions used were carried out as described in an earlier publication.[2] A Unicam quartz spectrophotometer (model 3p500), covering a range from 200–1000 mμ, was used in the light transmission measurements, which were accurate to about 0.2% under the conditions used. Glass cells of 1.00 cm. optical length were used. The results are expressed in terms of optical density, *D*, defined by the relationship $D = \log_{10} (I_0/I)$, where I_0 and I are the incident and transmitted light intensities, respectively.

In making measurements, three glass cells were used; one containing a blank solution of hydrochloric acid and the other two containing test solutions. The cells, which were not thermostated, were allowed to stand in the instrument to attain the temperature of the cell compartment prior to measurement. Since small temperature variations may occur within the instrument, check measurements were made with a fresh series of solutions. The effect of ordinary fluctuations in room temperature (25 ± 1°) was not usually serious. Measurements were made at wave lengths between 350–600 mμ, in which region there was selective absorption for the systems investigated. A hydrogen lamp was used as a light source. The cells were always cleaned, washed and dried with specially prepared and spectroscopically pure reagents. The filled cells were carefully wiped with lint-less cloth.

The measurements were made on hydrochloric acid solutions containing equimolecular amounts of sexa- and quinquevalent molybdenum. The acidity varied from 8–0.01 *N*, while the molybdenum content was kept in the range 0.01–0.004 *M*. Similar investigations were done on solutions containing only sexavalent molybdenum. These were found to have no absorption bands in the spectral region investigated. The shape of the curves obtained and the position of the maximum could, therefore, be considered to

---

(1) F. Foerster, E. Fricke and R. Hausswald, *Z. physik. Chem.*, **146**, 177 (1930).

(2) A. R. Tourky and H. K. El-Shamy, *J. Chem. Soc.*, No. 1, 140 (1949).