[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

OXIDATION-REDUCTION POTENTIALS. I. THE FERRIC-FERROUS ELECTRODE

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The two outstanding difficulties in the interpretation of oxidation–reduction potential half-cells are the incomplete elimination of liquid junction potentials and the lack of precise data on the activity of one electrolyte in the presence of one or more others. According to Gerke[1] the published data in this field abound with unnecessary liquid junction potential corrections which cannot be precisely computed.

In the present study of the oxidation–reduction potential of the ferric–ferrous half-cell the foregoing difficulties were reduced to a minimum. Electromotive force measurements were made of the cell

$$\mathrm{Pt, H_2 \mid HCl \mid HCl + FeCl_3 + FeCl_2 \mid Pt}$$

The liquid junction potential was kept constant by a Lamb and Larson[2] flowing junction. In each series the acid concentration was the same throughout the cell. In all cases the ratio of the concentrations of the ferric and ferrous chlorides was kept as nearly as possible equal to one.

With decreasing concentration of ferric and ferrous chlorides, within each series, both sides of the cell approach identity and the liquid junction potential approaches zero. By plotting a function of the potential against the concentration of the ferrous chloride and extrapolating to zero concentration, the liquid junction potential disappears.

To obtain the normal oxidation–reduction potential a correction must be made for the presence of the hydrochloric acid. This was accomplished by plotting the values derived from the graphs at various acidities against the acid concentration and again extrapolating to zero.

Special Equipment

1. Electrode Vessel.—An all-glass electrode vessel[3] shown in Fig. 1 was used for the potential measurements. A is the oxidation–reduction chamber in which were placed the mixtures of ferrous and ferric chlorides and hydrochloric acid. T is a platinum foil, 8 × 18 mm., sealed into a glass holder which is filled with mercury for contact. S is a stirrer with a liquid seal in which was put some of the same solution as in A. L was not used in this problem. B is the hydrogen electrode chamber. E are duplicate platinum electrodes. F is the hydrogen inlet and G the outlet. In G was placed acid of the same concentration as in B. The two chambers are connected by a Lamb and Larson flowing junction H. C contained the same solution as A and C the same as B.

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[1] Gerke, *Chem. Reviews*, **1**, 388 (1925).

[2] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920).

[3] Much credit for the design of this and other apparatus used is due to J. A. Riddick who was working on a similar problem.

The rate of flow is regulated by the overflow N. K and K' are stopcocks to prevent diffusion.

2. **Constant Temperature Bath.**—"White Rose" oil was used as the liquid in the bath. The temperature was easily kept at 25 ± 0.01°. The temperature was determined by a 0.1° thermometer which was compared with a similar thermometer calibrated by the Bureau of Standards. A Beckmann thermometer in the bath served as indicator for temperature changes.

3. **Potentiometer and Galvanometer.**—A Leeds and Northrup Type K potentiometer was used in conjunction with a Leeds and Northrup galvanometer, 2339a, and a lamp and scale reflector. A small lead storage cell was used for the working battery. The potentiometer and galvanometer were put on an equipotential base with the bath.

4. Standard Cell.—An Eppley standard cell of the unsaturated type was used. This was checked indirectly with a cell calibrated by the Bureau of Standards.

5. Oxygen Remover.—A 100-watt tungsten filament electric light bulb with sealed-in inlet and outlet tubes served to remove any possible traces of oxygen from the hydrogen used. The bulb was attached to a 110-volt circuit in series with a lamp-bank containing two 100-watt carbon bulbs in parallel.

Materials

1. All water used was redistilled from alkaline permanganate.

2. All **hydrochloric acid** was distilled twice from C. P. acid after dilution to a specific gravity of about 1.1.

3. **Ferrous Chloride.**—J. T. Baker's C. P. anhydrous salt was recrystallized twice from hydrochloric acid. Baxter and Hoover[4] found that two recrystallizations are sufficient to eliminate the predominating metallic impurities.

4. **Ferric Chloride.**—Chlorine was passed through a hot concentrated solution of the recrystallized ferrous chloride in hydrochloric acid. The ferric solution showed only a very faint and negligible test for ferrous iron. The chlorine was prepared in an all-glass vessel by adding redistilled hydrochloric acid to C. P. potassium permanganate.

5. **Potassium permanganate** was recrystallized twice for making the analyzing solutions.

6. **Hydrogen** was generated electrolytically from a concentrated solution of sodium hydroxide, using nickel electrodes. The gas was passed in order through a solution of potassium permanganate, an oxygen remover and three wash bottles (the last one was in the bath) containing acid of the same concentration as that in the hydrogen electrode vessel.

7. Silver **nitrate, stannous chloride, mercuric chloride** and preventive solutions were made from the best C. P. grade chemicals obtainable.

Analytical Methods

1. **Standardization of 0.1 *N* Potassium Permanganate Solution.**—Both iron wire and sodium oxalate were used. In the former case several lengths of bright iron wire containing 99.858% of iron were dissolved in 5 cc. of concentrated hydrochloric acid and 35 cc. of water and the solution boiled for five minutes to expel carbides. A drop of stannous chloride solution was added while hot. After cooling, 10 cc. of saturated mercuric chloride and 20 cc. of preventive mixture were added. After a short in-

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[4] Baxter and Hoover, THIS JOURNAL, **34**, 1660 (1912).

terval it was titrated electrometrically with potassium permanganate. In this and all other analyses titrations were made with weight burets. Results were also obtained without adding stannous chloride. In the sodium oxalate method the conditions of McBride[5] were followed. The results are presented in Table I.

It is evident that the titer increases with the amount of iron wire used, and that the value is higher when stannous chloride is used. Since subsequent work showed that the presence of mercurous chloride is objectionable the method without stannous chloride is probably the better, especially since it compares quite favorably with the sodium oxalate method.

TABLE I

THE STANDARDIZATION OF $KMnO_4$

	With Stannous Chloride			
G. of Fe	0.22590	0.22650	0.25460	0.25700
Fe titer	0.005802	0.005800	0.005824	0.005826
	Without Stannous Chloride			
G. of Fe	0.06310	0.06400	0.12580	0.12730
Fe titer	0.005765	0.005757	0.005781	0.005796
G. of Fe	0.12830	0.22150	0.22680	
Fe titer	0.005800	0.005807	0.005808	
	Using Sodium Oxalate			
Sodium oxalate titer	0.006974	0.006984		
G. of Fe per g. of soln.	0.005815	0.005815		

The absolute value of the iron titer of the potassium permanganate was not really required in this study as it deals principally with the ratio of the concentrations of the ferrous and ferric iron. Therefore it is only necessary that the permanganate be used under identical conditions in all iron titrations, ferrous as well as total.

2. **Standardization of 0.01 *N* Potassium Permanganate.**—This was accomplished by diluting to 0.01 *N* a solution of ferrous chloride whose total iron content had been previously determined with 0.1 *N* potassium permanganate. The 0.01 *N* ferrous chloride (after reduction of the ferric iron present) was titrated electrometrically with the dilute permanganate. No satisfactory electrometric end-point could be obtained when mercurous chloride was present so it was filtered off through asbestos before titrating. To be sure that no appreciable oxidation of iron takes place in filtering and transferring the ferrous solution, three drops of stannous chloride were added to 28 cc. of one molal hydrochloric acid containing 10 cc. of mercuric chloride solution. Twelve cc. of ferrous chloride solution in one molal acid was then added, the mercurous chloride filtered off and, after adding 20 cc. of preventive mixture, the solution was titrated. Fer-

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[5] McBride, THIS JOURNAL, **34**, 393 (1912).

rous chloride solution was titrated in the usual way at the same time. The results are shown in Table II.

TABLE II

OXIDATION OF Fe^{++} BY FILTERING

	G. of Fe per g. of soln.	Average
Filtering	0.019205, 0.019213	0.019209
Not filtering	0.019209, 0.019197, 0.019213	0.019206

3. **Standardization of Silver Nitrate Solution.**—This was done electrometrically using a silver chloride electrode with hydrochloric acid as the standard.

4. **Standardization of Hydrochloric Acid Solution.**—A carbonate-free solution of sodium hydroxide was prepared by adding a slight excess of barium hydroxide to an approximately 0.4 *N* solution of sodium hydroxide. This was filtered through asbestos out of contact with carbon dioxide and then standardized with benzoic acid and by hydrochloric acid diluted from constant boiling acid prepared by the method of Foulk and Hollingsworth.[6] The two methods agreed to within 0.05%. An error of 0.1% in the standardization of one molal acid will make an error of 0.06 mv. in the potential of the hydrogen electrode. The solution was kept in a paraffined bottle. After two months it showed no change. The acid solutions were standardized with this base, using phenolphthalein as the indicator.

5. **The Determination of Ferrous Iron.**—As the iron titer of a solution varies with the amount of acid present, enough acid was added in every titration to make a total of approximately 40 cc. of one molal hydrochloric acid. Twenty cc. of preventive mixture and enough water were added to make the volume at the close of the titration 200 cc. The titration was performed electrometrically.

That no appreciable oxidation of ferrous iron takes place during the time of titration is shown in Table III by comparing values obtained by titrating a solution containing ferrous iron (and about the same concentration of ferric iron) in one molal hydrochloric acid with 0.01 *N* potassium permanganate. As all titrations were made under these conditions, the air was not excluded.

TABLE III

COMPARISON OF Fe TITRATION IN AIR AND CO_2

G. of Fe per g. of soln.	In air	0.00052061	0.00052062
	In CO_2	0.00052061	0.00052074

When the ratio of ferrous and ferric iron is nearly one and the concentration of acid is about one molal, there is very little oxidation when left standing in a bottle half full of air. In one case there was no appreciable

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[6] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

decrease in ferrous iron concentration overnight and less than 1% decrease in a week.

When the ratio of ferrous to ferric iron is greater than one, oxidation is slightly more rapid in one molal acid and considerably more rapid in solutions of lower acid concentration.

6. **The Determination of Total Iron.**—This was done in a similar fashion after reduction with stannous chloride and filtering off the mercurous chloride. The total iron content for the solutions employed (Tables II and IV) was about the same. That the filtering of the mercurous chloride is necessary is shown by the results in Table IV.

TABLE IV

INFLUENCE OF Hg_2Cl_2 ON TITRATION OF IRON

G. of Fe per g. of soln.	Filtered	0.016303	0.016298
	Not filtered	0.016320	0.016324

The difference of 0.15% between the filtered and non-filtered will cause a difference of 0.3% in the ratio of the concentration of ferrous to ferric iron. An error of 0.4% in the ratio will make an error of 0.1 mv. in the potential of the cell.

7. **Determination of Total Chlorides.**—This was done electrometrically with a silver chloride electrode as in the standardization of the silver nitrate solution. Table V shows a comparison between the chloride content of one solution determined by the electrometric method and by the Volhard method.

TABLE V

COMPARISON BETWEEN ELECTROMETRIC AND VOLHARDT METHODS FOR THE DETERMINATION OF CHLORIDES

Method	Volhard	Electrometric
G. of Cl per g. of soln.	0.05697, 0.05688	0.05704, 0.05706

The better agreement of duplicates and the rapidity of the electrometric method are strong arguments in its favor. Here again the exact value for the chloride content is not so important, for any error is minimized by dilution with accurately standardized acid.

Experimental Methods and Calculations

1. **Hydrochloric Acid Solution.**—The stock solution of acid was analyzed and the value recorded as grams of vacuum weight hydrogen chloride per gram of air weight of solution. This was diluted to the required molality by weighing out a definite quantity and adding the calculated weight of water, using the proper buoyancy correction factors. After dilution the solution was checked by another analysis and readjusted if not within 0.1% of the desired molality.

2. **Ferrous Chloride Solutions.**—The stock solution of ferrous chloride in hydrochloric acid was analyzed for ferrous iron, total iron and total chlorides. The ferric iron content was taken as the difference between the total and ferrous iron. The

amount of water required to dilute the solution to the proper molality of acid was calculated and then added.

3. **Ferric Chloride Solutions.**—These were diluted to the same molality as the ferrous chloride solution and in the same manner.

4. **Mixing Solutions to 1 : 1 Ratio of Ferric and Ferrous Iron.**—The total iron content of the ferrous and ferric chloride solutions was calculated from dilution data. The ferrous content of the ferrous chloride solution was determined by titration just before mixing.

The ferrous-ferric mixture was made in the ratio of 0.998:1 in order to take care of a small amount of oxidation which takes place in the mixing and standing before use.

In Series V the 1:1 mixture was made up for each run and then diluted to the desired concentration of ferrous iron with one molal hydrochloric acid. After completing the potential measurements of the cells the ferrous iron of the solution of the cell was determined and the ratio of ferrous to ferric iron calculated. In all cases the ratio was within a few tenths of one per cent. of the value calculated for dilution.

In the other series a larger quantity of the 1:1 mixture was made up, analyzed and kept in an atmosphere of carbon dioxide. The solution was analyzed before using for dilution and again the following day. Typical results are given in Table VI.

TABLE VI

THE STABILITY OF MIXTURES OF FERROUS AND FERRIC CHLORIDE IN AN ATMOSPHERE OF CO_2

G. of Fe per g. of soln.	Before use	0.011096	0.011095
	After use (one day)	0.011085	0.011093

That there is no appreciable oxidation of ferrous iron during the process of dilution is shown in Table VII.

TABLE VII

COMPARISON OF ANALYZED AND CALCULATED AMOUNTS OF Fe^{++}

G. of Fe per g. of soln.	Calculated	0.00023872
	Analyzed	0.00023870, 0.00023850

5. **Calculation of Potentials.**—There are three sources of potential in the cell

$$\mathrm{Pt,\ H_2} \mid \mathrm{HCl} \mid \mathrm{HCl + FeCl_2 + FeCl_3} \mid \mathrm{Pt}$$

$$E_1 \qquad E_2 \qquad\qquad\qquad E_3$$

E_1 is the potential of the hydrogen electrode, which is given by the equation

$$E_1 = -0.05915 \log a_{H^+}/a_{H_2} \qquad (1)$$

or

$$E_1 = 0.05915 \left(\tfrac{1}{2} \log p_{H_2} - \tfrac{1}{2} \log 760 - \log a_{H^+}\right) \qquad (2)$$

in which p is the partial pressure of the hydrogen of a solution of hydrochloric acid whose hydrogen-ion activity is a.

The values of Randall and Young[7] for the activities of hydrochloric acid were used. The partial pressure of the hydrogen was taken as the barometric pressure (corrected for temperature of barometer) minus the vapor pressure of the acid used. Values for the vapor pressures were calculated from data in "International Critical Tables."[8]

[7] Randall and Young, THIS JOURNAL, **50**, 995 (1928).

[8] "International Critical Tables," **1928**, Vol. III, p. 293.

E_2 is a liquid junction potential which cannot be computed at finite concentrations of ferrous and ferric chlorides. In the method of extrapolation used it disappears; hence it is included with E_3. E_3 is the potential of the ferric–ferrous electrode given by equation

$$E_3 = E_1 - E_{\text{cell}} \tag{3}$$

6. Experimental Details.—The hydrogen electrode vessels (Fig. 1) were filled to a level so that half of the platinized platinum electrode was immersed in the acid and the other half exposed to the hydrogen gas. The electrodes were platinized by the method of Popoff, Kunz and Snow[9] except that the treatment with nitric acid was omitted. Electrodes prepared with and without treatment with nitric acid agreed to within 0.01 mv. All duplicate electrodes prepared were within this agreement.

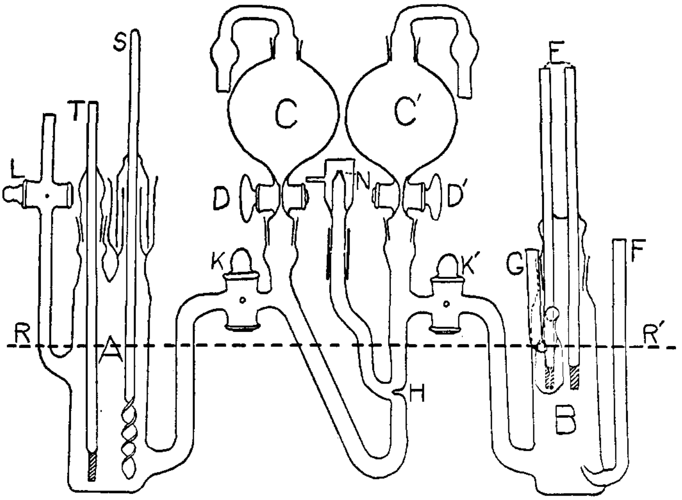

Fig. 1.—Electrode vessel.

In the previous investigation thinly and thickly plated electrodes were found to give the same potential to within 0.1 mv. The present study showed that the agreement is within 0.01 mv. However, the thickly coated electrode requires a longer time to attain equilibrium.

The oxidation–reduction half-cells were completely filled with the mixture of ferrous and ferric chlorides in hydrochloric acid. That no oxidation of the ferrous iron takes place in the cells was proved by analyzing the solution from duplicate cells, one at the end of one day and the other the following day. The variations of the results were within the limits of the experimental precision.

The cells were immersed in the oil of the bath up to line RR′. The rate of overflow from the flowing junction was about 300 cc. per hour.

Measurements of the electromotive forces of the cells were made about two hours after the hydrogen was admitted. Readings were then made about every half hour. After the cell readings did not differ for two hours the cells were assumed to be at equilibrium as cells left in overnight did not change their potential. In the fifth series potential measurements were recorded to 0.01 mv. At the lower (0.2 to 0.05) concentration of acid the readings could only be obtained definitely to 0.05 mv. All observa-

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[9] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

tions were made with stopcocks K and K′ closed. These were greaseless. No change in potential was caused by stirring the solution in the oxidation-reduction chambers.

Experimental Data and Discussion

1. The Oxidation–Reduction Potential at Various Acid Concentrations.—In Table VIII are presented the potentials of the ferric–ferrous electrode at various acid concentrations and with the ratio of the concentrations of the ferric and ferrous ion nearly equal to one. The data from which the potentials were calculated are also given. In every case there is a liquid junction potential (E_l) which decreases with dilution. The potential of the electrode, then, is expressed by the equation

$$E = E_0 - 0.05915 \log (a_{\text{Fe}^{+++}}/a_{\text{Fe}^{++}}) \pm E_l \qquad (4)$$

or

$$E_0 = [E + 0.05915 \log (C_{\text{Fe}^{+++}}/C_{\text{Fe}^{++}})] + 0.05915 \log (\gamma_{\text{Fe}^{+++}}/\gamma_{\text{Fe}^{++}}) \pm E_l \qquad (5)$$

Table VIII

The Oxidation–Reduction Potentials

Cell	Fe, mml. per 1000 g. of soln.	Obs. e.m.f. of cell	E_a	Cell	Fe, mml. per 1000 g. of soln.	Obs. e.m.f. of cell	E_a
Series I (0.05 *M* Hydrochloric Acid)				Series IV (0.5 *M* Hydrochloric Acid)			
A	73.336	0.80550	−0.72449	A	71.963	0.72790	−0.70359
B	37.550	.80860	− .72759	B	36.301	.73065	− .70634
C	19.067	.81235	− .73137	C	18.291	.73255	− .70817
D	9.4312	.81470	− .73372	D	9.2493	.73340	− .70902
E	5.3184	.81695	− .73597	E	4.5286	.73375	− .70937
F	2.5539	.81815	− .73719	F	2.4826	.73395	− .70957
Series II (0.1 *M* Hydrochloric Acid)				Series V (1 *M* Hydrochloric Acid)			
A	19.191	.79020	− .72593	A	56.939	0.70042	−0.69642
B	9.3974	.79240	− .72821	B	29.001	.70209	− .69801
C	4.7993	.79370	− .72949	C	12.412	.70313	− .69891
D	2.5977	.79440	− .73023	D	6.0924	.70353	− .69931
Series III (0.2 *M* Hydrochloric Acid)				E	3.4839	.70366	− .69967
A	17.847	.76665	− .71903				
B	8.8552	.76835	− .72073				
C	4.5451	.76900	− .72138				
D	2.2022	.76945	− .72183				

The values of the terms in the parentheses ([ ]) are called E_a in the tables. The factor 0.05915 log $(C_{\text{Fe}^{+++}}/C_{\text{Fe}^{++}})$ corrects for the small departure from a one to one ratio between the ferric and ferrous iron concentrations. Since the difference is very small it will not appreciably affect the ratio of the activity coefficients.

Fig. 2 shows the results of plotting the values of E_a at each acidity against the concentration of the ferrous iron and extrapolating to zero concentration at which E_l is eliminated. The extrapolated values (E_0') read from the graph are presented in Table IX.

TABLE IX

THE OXIDATION–REDUCTION POTENTIAL AT VARIOUS ACID CONCENTRATIONS

Series	I	II	III	IV	V
Molality of HCl	0.05	0.1	0.2	0.5	1.0
E_0'	−0.7386	−0.7311	−0.7222	−0.7098	−0.7000

It is suggested that these values of E_0' are of greater practical importance than the theoretical value of E_0 since in actual practice oxidation–reduction reactions involving iron are usually carried out in acid solution. Therefore in making predictions based on Equation 4 these values should be used.

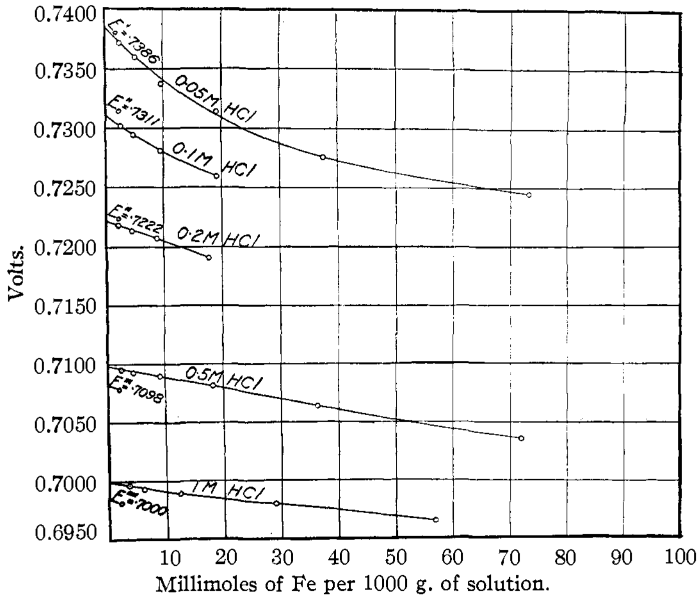

Fig. 2.—The oxidation–reduction potentials at various acid concentrations and with decreasing iron concentrations.

2. **The Normal Oxidation–Reduction Potential.**—In Fig. 3 the values of E_0' are plotted against the concentration of acid and the curve extrapolated to zero concentration. This corrects for the effect of the hydrochloric acid upon the activities of the ferrous and ferric ions and the normal oxidation–reduction potential of the ferric–ferrous electrode is found to be −0.7476 volt.

In Fig. 4 the logarithms of the values of E_0' are plotted against the acid concentration and extrapolated in the same way. This gives a somewhat better curve for extrapolation. The extrapolated value is 8.8737-10, whose antilogarithm is 0.7477.

3. **Comparison between Results from Equilibrium and Electromotive**

Force Methods.—Noyes and Brann[10] determined equilibrium constants at 25° for the reaction

$$Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2 \qquad (6)$$

at an acid concentration of 0.05 *M* nitric. By plotting the values obtained against the total nitrate concentration and extrapolating to zero concentration, they obtained 0.128 for the true equilibrium constant of the above reaction.

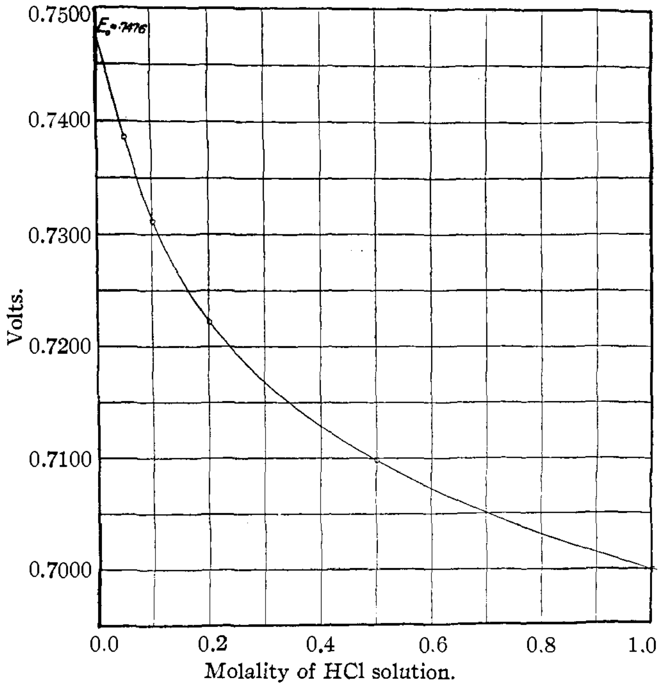

Fig. 3.—The oxidation-reduction potentials plotted against the acid concentrations.

Using −0.7995 for the potential of the silver electrode and the foregoing equilibrium constant, the normal oxidation-reduction potential of the ferric-ferrous electrode was calculated as −0.7467.

At the same time they determined the potential of the ferric-ferrous electrode to be −0.738 volt by direct e.m.f. measurements and a similar plotting of results. In the latter case, however, a salt bridge of saturated potassium chloride solution was used to eliminate liquid junction potentials. According to Lewis and Randall,[11] it is now certain that this method by no means eliminates and sometimes may even increase the

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[10] Noyes and Brann, This Journal, **34**, 1016 (1912).

[11] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 399.

liquid potential. In view of this Lewis and Randall accept their equilibrium data as the more precise determination of the normal electrode potential. This value (−0.7467) compares quite favorably with the value determined in this study (−0.7477). Being cognizant of the errors of extrapolation we are inclined to believe that the final value of −0.7477 is uncertain by 0.5 mv.

4. **The Normal Oxidation-Reduction Potential Calculated from the Principle of Total Ionic Strength.**—The total ionic strengths (one-half of the sum of the molalities of each ion times the square of its valence) of the solutions used in cells of Series I were calculated. Cells E and F have a total ionic strength of less than one-tenth at which the principle of ionic strength might be expected to hold. Therefore E_0 was calculated from these cells by Equation 4. The activity coefficients of the ferrous iron were interpolated from the values given by Lewis and Randall[12] for any bivalent ion. The ferric ion activity coefficients are similarly obtained from the values given for lanthanum. The values of E_0 calculated in this manner are given in Table X.

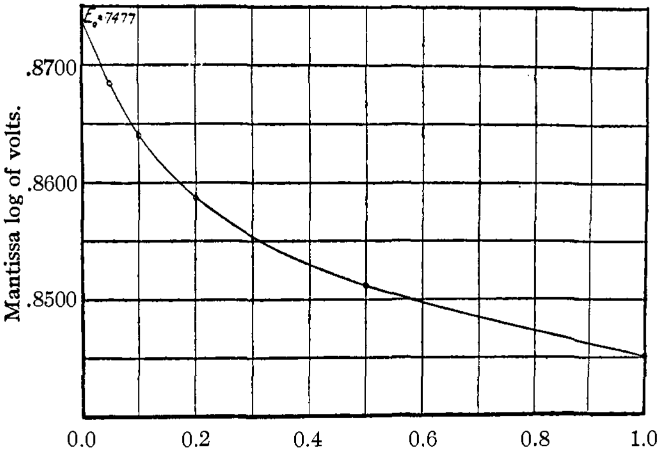

Fig. 4.—The mantissa of log of oxidation-reduction potentials plotted against the acid concentrations.

TABLE X

E_0 CALCULATED FROM IONIC STRENGTH

Cell	E	F
Total ionic strength	0.097956	0.073998
E_0	−0.7487	−0.7497

In view of the admitted uncertainties in the values for the activity

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[12] See ref. 11, p. 382.

coefficients used the agreement with the value obtained by extrapolation in this study (-0.7477) is as good as may be expected.

In the calculation of E_0 from ionic strength the liquid junction potential was not considered. The latter was not considered because an uncertainty of one in the second decimal place of the activity coefficient of iron causes a variation of 1.3 mv. in the value of E_0.

Influence of Variation of Concentration of Iron and Acid.—The effect of decreasing the concentration of iron and acid is to increase the oxidation–reduction potentials. This is to be expected when one considers that ferric chloride forms complex salts with hydrochloric acid while ferrous chloride does not, and that the activity coefficients of a trivalent ion must increase much faster with dilution than those of a divalent ion since both become equal to one at infinite dilution. It is not safe therefore to assume, as some[13] have, that the activity coefficients of ferric and ferrous chlorides are the same.

The decrease of the oxidation–reduction potential (not the normal) with increase of the concentration of acid is in agreement with Carter and Clews[14] findings and tends to throw light (at least on half of the story) on the fact that ferrous chloride is oxidized by sulfur dioxide in strong acid solution but that ferric chloride is reduced by sulfur dioxide in dilute acid solution.

Use of Salts without Recrystallization.—It is reasonable to suppose that in the present study the salts employed need not necessarily be of "atomic weight" purity since in the extrapolations the effect of impurities will also be extrapolated to zero. J. T. Baker's best grades of ferrous and ferric chlorides were employed in one molal hydrochloric acid. The potentials coincided very closely with those obtained with the recrystallized salts. In the dilute solution the values practically coincided.

Summary and Conclusions

1. A method has been devised for the precise determination of oxidation–reduction potentials, consisting of the use of a special electrode vessel, suitable procedure, and mathematical and graphical treatment which eliminate uncertainties in former methods regarding liquid junction potentials and the activity of one electrolyte in the presence of others.

2. Methods of analysis which lead to greater precision in the determination of iron are given. A method was chosen for each analysis which gave results within 0.1% of those obtained by a widely different method. The errors of analysis were smaller than the corresponding errors in the electromotive force measurements.

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[13] Peters, *Z. physik. Chem.*, **26**, 193 (1895). Getman, "Outlines of Theoretical Chemistry," John Wiley and Sons, New York, **1927**, p. 581.

[14] Carter and Clews, *J. Chem. Soc.*, **125**, 1880 (1924).

3. The treatment with nitric acid of hydrogen electrodes which had been plated in solutions containing lead was found to be unnecessary. Thinly platinized electrodes give practically the same potentials as thickly coated ones.

4. The oxidation–reduction potentials of the ferric–ferrous electrode have been determined at various acid concentrations. It is to be emphasized that these values are of practical importance in attempting to make predictions.

5. The normal oxidation–reduction potential determined in this study compares favorably with the potential calculated from equilibrium measurements by Noyes and Brann.

6. The principle of ionic strength was applied to the calculation of the normal potential employing data obtained in 0.05 molal hydrochloric acid. The values thus calculated are in fair agreement (considering the uncertainty of activity coefficients now available) with that derived by extrapolation.

7. The value for the normal oxidation–reduction potential of the ferric–ferrous electrode determined in this study is -0.7477. The uncertainty is probably of the order of ± 0.5 mv.

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[CONTRIBUTION FROM THE PHYSIOLOGICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF MINNESOTA AND THE SOUTH CAROLINA FOOD RESEARCH COMMISSION LABORATORY IN AFFILIATION WITH THE MEDICAL COLLEGE OF THE STATE OF SOUTH CAROLINA]

THE DETERMINATION OF TRACES OF IODINE. II. IODINE IN VEGETABLES[1]

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In the first paper of this series[3] the general principles of a method for the determination of traces of iodine were outlined. The statement was made that an apparatus for feeding in milk powder was used. This apparatus is also useful for vegetables and consists of a steel tube with water-cooled open end and piston in the other end which is advanced by means of a screw similar to the piston of an "Alemite gun." Vegetables are made into a stick, placed in the steel tube, and advanced slowly by means of the screw and thus fed into a silica tube furnace and burned in oxygen.

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[2] With the technical assistance of F. B. Culp.

[3] McClendon, THIS JOURNAL, **50**, 1093 (1928).