this determination exceeded 99.99 mole per cent.

The phase equilibrium diagram for the condensed system 2-methylpentane–*n*-heptane has been determined and the observed value for the eutectic point was $-160.2 \pm 0.5°$.

NORWOOD, PENNA. RECEIVED JULY 1, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, NO. 61, AND THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 390, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Measurement of the Molal Ferric–Ferrous Electrode Potential

BY WALTER C. SCHUMB, MILES S. SHERRILL AND SUMNER B. SWEETSER

In a previous paper[1] the authors calculated the molal ferric–ferrous electrode potential to be -0.782 v. from equilibrium measurements of the reaction between ferric ion and silver. This value was 10 mv. higher than that calculated by Bray and Hershey[2] from the electromotive force measurements of Popoff and Kunz[3] and the equilibrium measurements of Popoff, Fleharty and Hanson[4] for the reaction between ferric ion and mercury. The latter were made in perchloric acid solution but the former were done in hydrochloric acid solution, which necessitated a correction for complex formation. The authors' previous work was done in perchloric acid solution, but because of analytical difficulties the measurements could not be carried to low ionic strengths. Thus, although equilibrium studies of this potential have been made in perchloric acid, the only electromotive force measurements in perchloric acid which appear to have been carried out are two preliminary experiments by C. G. Clear, reported by Bray and Hershey.[2] Professor Bray has kindly furnished the results of these measurements, the average value being closely in agreement with the results obtained in this investigation.

The results of measurements of the electromotive force of the following cell are given and discussed in the present paper.

$$\mathrm{Pt,H_2(g),\ HClO_4(\mathit{c}_1),\ \begin{matrix}\mathrm{Fe(ClO_4)_3(\mathit{c}_3)}\\ \mathrm{HClO_4(\mathit{c}_1),}\\ \mathrm{Fe(ClO_4)_2(\mathit{c}_2)}\end{matrix}\quad Pt}$$

Materials and Apparatus.—Electrolytic iron with a guaranteed purity of at least 99.95% was used in the preparation of both ferrous and ferric perchlorates. The ferrous perchlorate was prepared by electrolyzing a 1:15 solution of 60% reagent grade perchloric acid, using a rod of electrolytic iron as anode and a platinum gauze as cathode. A current of 0.5 ampere was used. During the electrolysis samples of the solution were withdrawn for analysis, and more perchloric acid added when necessary to prevent hydrolysis of the iron salt. Under these conditions only a trace of chloride was formed. However, if too high a current density were used, or if the solution were heated, an appreciable reduction of perchlorate to chloride occurred.

Ferric perchlorate was prepared by oxidizing the ferrous perchlorate solution thus obtained with hot nitric acid. The solution was then evaporated three times to dense white fumes with perchloric acid to remove the excess nitric acid. No attempt was made to crystallize either the ferrous or ferric perchlorate.

Purified commercial electrolytic hydrogen was used for the hydrogen electrode. The purification train consisted of a gas washing bottle containing 10% sodium hydroxide solution, a tube containing glass wool to remove spray, and a tube containing reduced copper heated to 425°. From this the hydrogen passed through a long cooling tube, then through a bubbling tower containing perchloric acid of the same strength as that used in the cell, and finally through a 3-mm. copper tubing to the hydrogen half of the cell. There was a second saturator in the cell containing the same concentration of acid.

The cell used in this investigation was the one used by Sherrill and Haas[5] in their study of the thallic–thallous electrode potential. However, in this case only the two electrodes in the hydrogen half-cell were platinized. The two electrodes in the ferric–ferrous solution were bright platinum and were cleaned occasionally in hot chromic acid. The technique of operation was otherwise essentially the same in the two cases.

The electrical measuring apparatus consisted of a Leeds and Northrup Type K potentiometer, a Sullivan high sensitivity galvanometer, and an Eppley standard cell which was checked against a new standard cell.

Methods of Analysis.—Tenth normal potassium permanganate solution was standardized against Sörensen sodium oxalate by the method of Fowler and Bright.[6] When more dilute permanganate solutions were required, they were prepared on the day of use by diluting a standard 0.1 *N* solution with weight burets. Total iron was determined by the Zimmermann–Reinhardt method.[7] Ferrous iron was determined by diluting the sample to 400 ml., adding 25 ml. of manganous sulfate titrating

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[1] Schumb and Sweetser, THIS JOURNAL, **57**, 871 (1935).

[2] Bray and Hershey, *ibid.*, **56**, 1889 (1934).

[3] Popoff and Kunz, *ibid.*, **51**, 382 (1929).

[4] Popoff, Fleharty, and Hanson, *ibid.*, **53**, 1643 (1931).

[5] Sherrill and Haas, *ibid.*, **58**, 952 (1936).

[6] Fowler and Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

[7] See W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 305.

solution, and titrating with standard permanganate solution. In the analysis of the more dilute iron solutions one-half the above amounts of reagents were used, and the solution was diluted to only 200 ml. In all titrations for total or ferrous iron, end-points were obtained potentiometrically. Ferric iron was determined as the difference between total and ferrous iron. This introduced no serious error because the concentrations of ferric and ferrous iron were at all times approximately equal.

Sodium hydroxide solutions from 0.04 to 0.25 normal were standardized with potassium acid phthalate using phenolphthalein as indicator.

The method used previously by the authors[1] for free acid in ferric perchlorate solution was the titration of the hot solution with sodium hydroxide, whereby the ferric hydroxide precipitated and coagulated before an end-point with phenolphthalein was obtained. This method could not be used when ferrous iron was present, because the black mixture of ferric and ferrous hydroxides did not settle out rapidly enough to allow the color change at the end-point to be seen. Several potentiometric methods were also tried but were unsuccessful. The following method, using oxidation of the ferrous iron by potassium chlorate, followed by titration with sodium hydroxide, gave good results. In the oxidation of the ferrous iron by the potassium chlorate one mole of hydrogen ion is consumed for each mole of ferrous ion oxidized

$$6Fe^{++} + ClO_3^- + 6H^+ = 6Fe^{+++} + Cl^- + 3H_2O$$

However, it requires one more mole of hydroxyl ion to precipitate a mole of ferric ion as hydroxide than is required by a mole of ferrous ion, so that the amount of base required for the titration is the same whether or not the ferrous iron is oxidized by the potassium chlorate.

The procedure was as follows: one gram of potassium chlorate was dissolved in 100 ml. of water and the solution heated to boiling. This was added to the sample and the resulting solution heated again until it began to turn turbid. Standard sodium hydroxide solution was run in slowly with constant stirring until the ferric hydroxide precipitated and started to coagulate. Six drops of phenolphthalein indicator was then added. The titration was continued two drops at a time. After each addition of base the solution was stirred vigorously, and the precipitate then allowed to settle so that the color of the phenolphthalein could be seen in the supernatant liquid when the end-point was reached.

To test the method, 250 ml. of a 0.2202 normal sulfuric acid solution was measured into a 500-ml. graduated flask. Approximately 7 g. of $FeSO_4 \cdot 7H_2O$ was added and the solution diluted to the 500-ml. mark on the flask. The iron content was determined by titration with permanganate. Samples of the solution were then carried through the procedure outlined above, and the concentration of free sulfuric acid calculated. For four samples the normality was found to be 0.1102, 0.1099, 0.1100, 0.1100, which compared very favorably with the true value of 0.1101. It should be remarked that, even if a small error were made in this determination, it would not affect the final result, because it would be eliminated entirely in the extrapolation of the data.

Weight burets were used in all analytical work except the development of the method for determination of free acid in a ferric–ferrous mixture. All subsequent concentrations are expressed as formula weights of substance per kilogram of water.

Electromotive Force Measurements.—Four series of measurements were made. In preparing the solutions for each series, ferric and ferrous perchlorate solutions were mixed and adjusted to make the concentration of the ferric iron, (c_3), approximately equal to that of the ferrous iron, (c_2). Sufficient perchloric acid was added to give the desired acidity. This solution was then carefully analyzed for ferrous iron, total iron, and free acid. A solution of perchloric acid was prepared and adjusted to the same weight formality, c_1, as the free acid in the ferric–ferrous mixture. This acid solution was used in the hydrogen half-cell and in the two gas saturators throughout a series of measurements. The solutions for the ferric–ferrous half-cell were prepared by mixing weighed quantities of the iron solution and the acid solution. Thus, although the ferric and ferrous salt concentrations, c_3 and c_2, were decreased, their ratio, c_3/c_2, remained constant in each series. Likewise the concentration of perchloric acid, c_1, remained unchanged throughout each series.

The results of the four series of measurements are shown in Table I. The values in the columns give the concentrations of ferric perchlorate as determined by analysis and the observed electromotive force of the cell corrected to a pressure of one atmosphere of hydrogen. The vapor pressures of the various perchloric acid solutions necessary for this correction were taken from the data

TABLE I

EXPERIMENTAL DATA

Series 1		Series 2	
$c_1 = 0.2726$		$c_1 = 0.1046$	
$c_3/c_2 = 1.010$		$c_3/c_2 = 1.008$	
$Fe(ClO_4)_3$	$E_{obsd.}$	$Fe(ClO_4)_3$	$E_{obsd.}$
0.05728	0.77589	0.02524	0.80488
.02539	.77598	.009714	.80538
.01007	.77652	.003949	.80594
.007727	.77667	.003216	.80599
.005181	.77683	.002078	.80609
.002543	.77694	.0009910	.80620
0	.77710	0	.80629
Series 3		Series 4	
$c_1 = 0.05212$		$c_1 = 0.02586$	
$c_3/c_2 = 1.020$		$c_3/c_2 = .9790$	
0.02565	0.82568	0.01021	0.84516
.01022	.82552	.007571	.84480
.007681	.82562	.005072	.84480
.005093	.82598	.002555	.84519
.002526	.82647	.001009	.84577
.001073	.82688	.0005060	.84591
.0005235	.82705	0	.84618
0	.82720		

of Pearce and Nelson.[8] At the top of the columns is given c_1, the concentration of perchloric acid in each of the half-cells, and the ratio of ferric to ferrous perchlorate, c_3/c_2.

As indicated previously, this ratio remains constant but the concentrations change. Therefore, the variation in potential within any series must be caused by three factors, a change in the liquid junction potential, a change in the activity coefficients of the ions with decreasing ionic strength, or a change in the fraction of the ferric ion lost by hydrolysis. Since the concentration of the acid is the same on both sides of the cell, each of these effects is reduced to zero by plotting $E_{\text{obsd.}}$ against either c_3 or c_2 and extrapolating to zero concentration. This was done for each series, and the curves obtained were extrapolated graphically as shown in Fig. 1. In Table I the last value of $E_{\text{obsd.}}$ in each series is the extrapolated value.

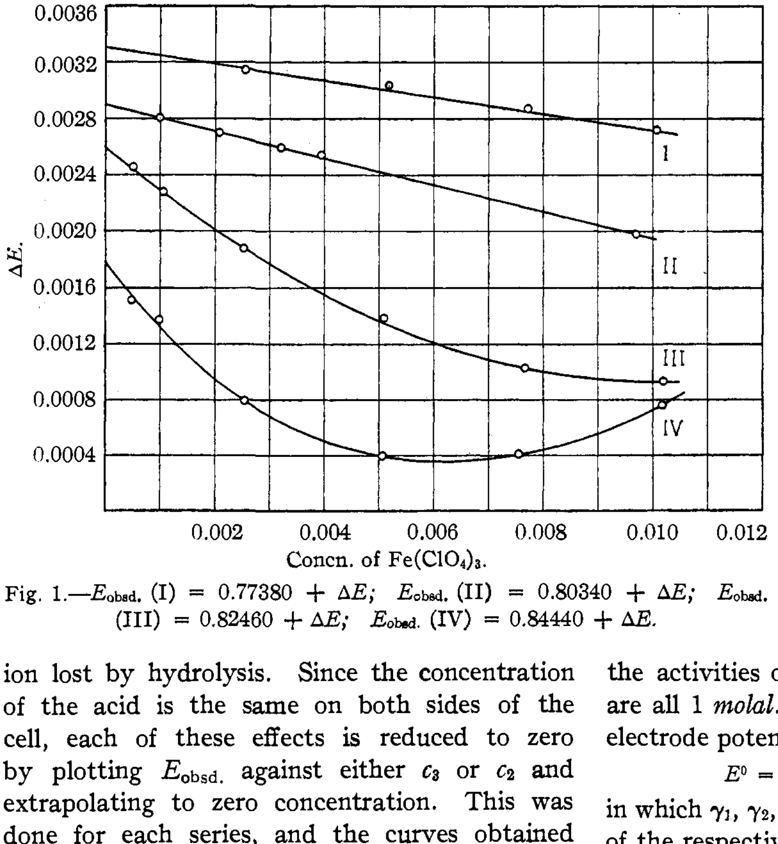

Fig. 1.—$E_{\text{obsd.}}$ (I) = 0.77380 + ΔE; $E_{\text{obsd.}}$ (II) = 0.80340 + ΔE; $E_{\text{obsd.}}$ (III) = 0.82460 + ΔE; $E_{\text{obsd.}}$ (IV) = 0.84440 + ΔE.

These values of $E_{\text{obsd.}}$ have to be corrected for certain factors before a value of the molal electrode potential E^0 can be obtained. A summary of these corrections is given in Table II. The fraction of the ferric iron which was hydrolyzed was calculated by the method of Bray and Hershey.[2] These authors consider $Fe^{+++} + H_2O = Fe(OH)^{++} + H^+$ to be the hydrolysis reaction, and have determined how the hydrolysis constant, K_H, expressed in terms of molal concentrations, varies with the ionic strength of the solution.

In each series of measurements, as the salt concentrations c_3 and c_2 were made to approach zero, the ratio c_3/c_2 and the acid concentration, c_1, remained constant; the ionic strength approached the acid concentration, c_1; the hydrolysis constant, K_H, approached the value recorded in the table corresponding to this ionic strength; the fractional hydrolysis, h, of the ferric salt approached a definite value equal to $K_H/(c_1 + K_H)$ and $E_{\text{obsd.}}$ approached the definite value, E, as discussed below.

$\Delta E_{\text{hydr.}}$ is the correction to be added in order to bring the electromotive force of the cell to the value it would have if there were no hydrolysis. $E^{0\prime}$ is the value of the molal ferric–ferrous electrode potential calculated, as shown by Eq. 2, from E under the assumption that $HClO_4$, $Fe(ClO_4)_3$, and $Fe(ClO_4)_2$ are completely dissociated into ions which behave as perfect solutes. It will be called the *formal* ferric–ferrous electrode potential, since $-E^{0\prime}$ is the electromotive force of the cell (plus the small hydrolysis correction $\Delta E_{\text{hydr.}}$) when c_1, c_2, and c_3 are all 1 *formal*. Similarly $-E^0$ corresponds to the electromotive force of the cell when the activities of the H^+, Fe^{++}, and Fe^{+++} ions are all 1 *molal*. The relation between these two electrode potentials is shown by the equation

$$E^0 = E^{0\prime} + 0.05915 \log (\gamma_3/\gamma_1\gamma_2)$$

in which γ_1, γ_2, and γ_3 are the activity coefficients of the respective ions, H^+, Fe^{++}, and Fe^{+++}, in the solution of ionic strength, c_1. An approximate value, $E^{0\prime\prime}$, for the molal electrode potential was calculated for each series by the third equation in Table II. This equation employs a modified form of the limiting Debye–Hückel equation suggested by Guggenheim and Schindler.[9] It assumes that the activity coefficient γ_A of any ion A of valence Z_A in a solution of ionic strength μ is given by the equation

$$\log \gamma_A = -0.505 Z_A^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}$$

An alternate method of handling the data is to correct each value of $E_{\text{obsd.}}$ for hydrolysis, activity

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[8] Pearce and Nelson, This Journal, **55**, 3075 (1933).

[9] Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 543 (1934).

TABLE II

CORRECTIONS FOR OBTAINING THE MOLAL ELECTRODE POTENTIAL

Series	1	2	3	4
c_1	0.2726	0.1046	0.05212	0.02586
c_3/c_2	1.010	1.008	1.020	.9790
K_H	0.00196	0.00239	0.00279	.00330
h	.0071	.0223	.0508	.1132
$\Delta E_{\text{hydr.}}$	.00018	.00058	.00134	.00309
E	.77710	.80629	.82720	.84618
$-E^{0\prime}$	.74362	.74868	.75216	.75592
$-E^{0\prime\prime}$	.78463	.77788	.77438	.77247

$$\Delta E_{\text{hydr.}} = 0.05915 \log \frac{1}{1 - h} \qquad (1)$$

$$-E^{0\prime} = E - 0.05915 \log \frac{c_3}{c_1 c_2} + \Delta E_{\text{hydr.}} \qquad (2)$$

$$E^{0\prime\prime} = E^{0\prime} - 0.05915 \times 0.505 \times 4 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (3)$$

coefficients, etc. These corrected values, instead of $E_{\text{obsd.}}$ can then be plotted against c_2 or c_3 and extrapolated to zero concentration. The range of electromotive force covered by one of these curves for any series is about ten times greater than when $E_{\text{obsd.}}$ is used, so that only four figures were obtained by graphical extrapolation. There were no maxima or minima in these curves, unlike the previous set. The values of $-E^{0\prime\prime}$ found by this method for series 1 to 4, respectively, are 0.7846, 0.7778, 0.7744, and 0.7724 v. A comparison of the values obtained by the two methods shows that in all cases they differ by less than 0.1 mv.

An exact value for the molal electrode potential, E^0, was obtained from the values of $E^{0\prime\prime}$ in Table II by graphical extrapolation. As shown in Fig. 2, the values of $E^{0\prime\prime}$ were plotted against the corresponding values for the ionic strength, c_1, of the solution, and E^0 taken equal to the value approached by $E^{0\prime\prime}$ as the ionic strength approached zero. Extrapolated values were also obtained by the analytical procedure described below.

The following equation was fitted to the data

$$E^{0\prime\prime} = E^0 - A\mu - B\mu^{3/2}$$

The values of $E^{0\prime\prime}$ and μ in series 1, 2, and 4 were used to calculate the constants. The result obtained was

$$E^{0\prime\prime} = -0.7701_0 - 0.1087_6\,\mu + 0.1062_0\,\mu^{3/2} \qquad (4)$$

This equation was used to calculate $E^{0\prime\prime}$ for series 3 and gave -0.77451 compared to the experimental result of -0.77438 v. From another equation[10] used for the extrapolation E^0 was found to be -0.77013 v. These figures have been rounded off to -0.7701 v. The authors believe that this value is in error by less than 0.2 mv. It is 12 mv. lower than the value of -0.782 v. obtained by the authors from equilibrium measurements[1] and 2 mv. lower than the value reported by Bray and Hershey.[2]

The most dilute solution used in this work had an ionic strength of 0.03, which is considerably lower than that reached in the authors' equilibrium measurements[1] (μ = 0.1) and somewhat lower than that used by Popoff and Kunz[3] in their electromotive force measurements (μ = 0.05). However, it is much higher than the ionic strength of 0.002 which Popoff, Fleharty, and Hanson[4] reached in their equilibrium measurements.

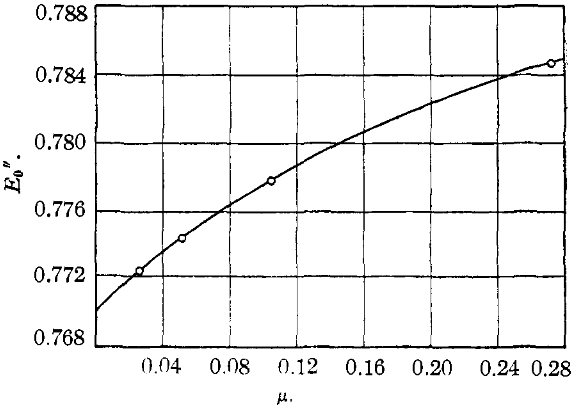

Fig. 2.

The experiments in this investigation were not carried to more dilute solutions, because the hydrolysis correction would have been too great. In series 4 more than 11% of the ferric iron has hydrolyzed, and this necessitates a correction of 3 mv. in the electrode potential. Lower concentrations would have involved still larger corrections, which did not seem justified, in view of the fact that Bray and Hershey do not claim great accuracy for their method of calculating hydrolysis at low ionic strengths. It should be mentioned that had it been desirable to use more dilute solutions, a new type of cell would have been necessary because in the one used the electrical connection between the two half-cells depended on the leakage of the solution around a ground glass stopper. As the solution became more dilute, the resistance of this connection increased so greatly that in the last series it was felt that the limit of sensitivity of the galvanometer had been reached.

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(10) $E^{0\prime\prime} = -0.77013 - \dfrac{0.09783_4\,\mu}{1 + 3.0789\,\mu}$

Although most of the authors' work on equilibrium measurements[1] was done at higher ionic strengths than were used in the present investigation, the three lowest points on the curve for the previous work fell within the range covered by the electromotive force measurements. In order to determine whether the two sets of measurements checked with each other in the regions where the concentrations overlapped, values of $E^{0\prime}$ corresponding to the ionic strength of the most dilute solutions in the equilibrium measurements were calculated from both sets of data. $E^{0\prime}$ was calculated from the electromotive force measurements by combining Equations 3 and 4.

$$E^{0\prime} = -0.7701 - 0.1088\mu + 0.1062\,\mu^{3/2} + 2.02\,(0.05915)\,\frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (5)$$

The equation used to calculate $E^{0\prime}$ from K_c was

$$(E^0_{\mathrm{Ag}} - E^{0\prime})F = RT \ln K_c + RT \ln \frac{\gamma_{\mathrm{H}^+}}{\gamma_{\mathrm{Ag}^+}}$$

The value of the last term in this equation is unknown. However, it should be small because γ_{H^+} and γ_{Ag^+} in the same solution should be nearly equal. Therefore it was neglected in the calculation of $E^{0\prime}$. The value used for the molal silver–silver ion electrode potential was −0.7985 v.[2] A comparison of the values obtained is given in Table III. Whereas the values of E^0 obtained by the two methods differ by 12 mv., the maximum difference in the overlapping values of $E^{0\prime}$ is only 4.1 mv. and in one case is only 0.2 mv.

TABLE III

COMPARISON OF VALUES OF THE FORMAL FERRIC–FERROUS ELECTRODE POTENTIAL CALCULATED FROM EQUILIBRIUM AND ELECTROMOTIVE FORCE MEASUREMENTS

μ	K_c	$-E^{0\prime}$ calcd. from K	$-E^{0\prime}$ calcd. from e. m. f.	Difference
0.1083	0.1672	0.7526	0.7485	0.0041
.1657	.1393	.7479	.7464	.0015
.2742	.1181	.7437	.7435	.0002

These values of $E^{0\prime}$ are not strictly comparable because the values of μ in the equilibrium measurements were based on volume formalities while in the electromotive force measurements weight formalities were used. For the comparisons that have been made here, however, this difference is not appreciable. For example, from the density data of Pearce and Nelson[8] a perchloric acid solution having a weight formality of 0.2742, the highest at which any comparison is made, is found to have a volume formality of 0.2702. The corresponding values of $E^{0\prime}$ are −0.7435 and −0.7436 v., the change being in the direction to make a smaller rather than a larger difference in the values obtained by the two methods.

Expressions involving molal electrode potentials are useful for theoretical considerations, but are of little value for calculating the oxidizing or reducing power of solutions of finite concentrations because they involve the activities of the constituent ions, and these are generally not known. If in these exact equations the formal electrode potentials are substituted for the molal electrode potentials, and the formal concentrations of the substances for their activities, the equations have been shown to hold fairly closely in many cases even in solutions of higher ionic strengths. For this reason a knowledge of the formal electrode potentials is often of more practical importance than the more fundamental molal values.

It should be pointed out that a formal electrode potential varies not only with the ionic strength of the solution but also with the nature of both ion constituents of the substance involved in the electrode reaction. For example, the formal ferric–ferrous electrode potential is appreciably smaller in hydrochloric acid solution than in perchloric acid solution of the same concentration because of the tendency of ferric iron to form complexes in the former medium.

For these reasons the formal electrode potentials shown in Table IV were calculated for the complete range of ionic strength covered by this investigation and the previous equilibrium studies.[1]

TABLE IV

VARIATION OF FORMAL ELECTRODE POTENTIAL WITH IONIC STRENGTH

μ	$-E^{0\prime}$	μ	$-E^{0\prime}$
0	0.7701	0.4	0.743
0.1	.749	.5	.742
.2	.746	.7	.741
.3	.744	1.0	.741

The values above an ionic strength of 0.25 were obtained from the equilibrium measurements by calculating $E^{0\prime}$ and plotting it against μ. Values at the desired ionic strength were then read from the graph. The values below 0.25 were calculated from Equation 5. Additional values of $E^{0\prime}$ from an ionic strength of 0 to 0.25 may also be calculated from that equation.

It will be seen from the table that above μ = 0.1 the formal electrode potential changes very little with the ionic strength of the solution. Its value between $\mu = 0.5$ and 1.0 may be considered to be -0.741 v.

Acknowledgment.—For various helpful suggestions and for assistance in the interpretation of the experimental data we are glad to acknowledge our indebtedness to Professor George Scatchard of this Institute.

Summary

The molal ferric–ferrous electrode potential has been obtained from electromotive force measurements in perchloric acid solution of cells of the type described in the introduction. The value found is -0.7701 v. The electromotive force data have been corrected for hydrolysis of ferric iron and plotted in such a way that errors from liquid junction potentials and changing activity coefficients are removed by extrapolation.

A table of values of the formal ferric–ferrous electrode potential of $Fe(ClO_4)_3$–$Fe(ClO_4)_2$ mixtures in $HClO_4$ solution from an ionic strength of 0.1 to 1.0 has been prepared. For the ionic strength range 0.5 to 1.0, the value is -0.741 v.

A new method for the determination of free acid in the presence of ferrous and ferric iron is described.

CAMBRIDGE, MASS. RECEIVED JULY 28, 1937

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

The Heats of Ionization of Water, Ammonium Hydroxide, Carbonic, Phosphoric, and Sulfuric Acids. The Variation of Ionization Constants with Temperature and the Entropy Change with Ionization

BY KENNETH S. PITZER[1]

In addition to their value as thermochemical data, these heats of ionization make possible the calculation of the changes of entropy with ionization, and the entropies of some of the ions involved. The latter calculations will be presented in another paper. Also it is found that certain approximate generalizations can be made concerning the change in entropy and heat capacity with ionization, and that these results lead to equations for the variation of ionization constants with temperature.

Throughout this paper a defined calorie equal to 4.1833 international joules will be used, and extrapolations to infinite dilution will be made consistent with the Debye–Hückel theory. The uncertainties given for the various results are from two to three times the probable errors and should, therefore, outline a region within which the true value almost certainly lies. An attempt has been made to include all possible sources of error, including questionable assumptions and estimates made as part of the calculations.

Apparatus.—The chief aim in the design of this calorimeter was the attainment of high sensitivity in temperature determination. This makes possible heat of reaction measurements at sufficiently low concentration so that heats of dilution may be estimated without too great uncertainty. Another feature is the economy in electrical equipment.

The calorimeter itself consists of a Pyrex vacuum flask with a ground glass joint in the neck. Into this fits a stopper which is also evacuated, and which carries the electrical leads and stirrer through a central tube of small diameter. Thus, when the flask is so filled that the water surface is just up in the small central tube, there is little opportunity for evaporation. The flask is 25 cm. long and has a volume of 885 ml. The entire unit is completely submerged in a water thermostat controlled to within 0.003° during a single run. For heat of solution measurements the sample is placed in a very thin glass bulb sealed with paraffin on to a glass rod which in turn slides through the hollow stirrer shaft. An additional propeller is placed just above the sample where it will be most effective after the bulb has been broken against the bottom of the flask. When two solutions are to be mixed one is used at relatively high concentration and placed in a glass tube with silver disks sealed into its ends by means of paraffin. This is supported just below the stirrer through which a rod may be thrust, breaking the seals.

A resistance thermometer consisting of 96 ohms of no. 38 silk insulated copper wire and a heater composed of 100 ohms of no. 30 manganin are wound on a silver tube 5.2 cm. in diameter and 16 cm. long. The leads are of no. 24 manganin and no. 24 copper, respectively, and single in each case. The windings are afforded protection by a cover of thin silver welded in place. This thermometer serves also as a stirrer tube which with its large surface gives excellent heat exchange.

The electrical circuits are shown in Fig. 1. The three constant arms of the thermometer bridge are of manganin, wound in a manner similar to the thermometer itself and submerged in a three-liter oil-bath. The heat exchange is such that a current of 0.01 amp. may be used if desired. The connections to the thermometer have so low

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[1] Shell Research Fellow, Academic Year, 1936-1937.