TABLE II

The results of our experiments are given in this table. $\Delta\zeta$ is defined as the change in ζ caused by the presence of deuterium. The last column gives the time necessary for the HI to come within one part in 2000 of equilibrium calculated from M. Bodenstein's data. The values for experiment 5 differ slightly from those previously reported[2] because of a more exact calibration of the interferometer readings used in the analysis for deuterium.

Expt.	T, °C.	Concn. D	ζ Expt.	ζ Calcd.	$\Delta\zeta$ Expt.	$\Delta\zeta$ Calcd.	Time of run	Time for HI to come to equilibrium
1	398	0.0%	0.20719[a]	....	....	....	70 hours	26 hours
2	398	14.3[d]	.20838	0.20894	0.00119	0.00175	144	36
3	468	0.0	.22724[b]	....	....	....	30	0.9
4	468	41.7[d]	.23287	.23326	.00563	.00602	14[e]	0.8
5	468	75.5[c]	.23877	.23904	.01153	.01222	41	0.9

[a] Bodenstein's value for ζ at this temperature is 0.20703.   [b] Bodenstein's value for ζ at this temperature is 0.22772. [c] Concentration of deuterium in the hydrogen iodide.   [d] Concentration of deuterium in the hydrogen produced by the decomposition.   [e] The reaction vessel was kept at 500° for two hours at the beginning of the run.

Precision of Results.—We estimate that the errors in the temperature at which the equilibria were measured to be 1° for the lower temperature and 3° for the higher. No attempt was made to determine the temperature more precisely since the rate of change of $\Delta\zeta$ with temperature is small. For run 5, $d(\Delta\zeta)/dT = 0.000017$.

We estimate the accuracy of ζ to be 0.00050 for runs 1 and 2 and to be 0.00040 for the remainder. Our experimental results agree with the calculated ones to this precision. It is to be noted that all our experimental results are lower than the calculated ones. Our results do not have a sufficient precision to warrant any conclusion in regard to the reality of this deviation between experiment and theory. If, however, instead of using our formula (II), we had used formula (I) for the energy states of HD and D_2[(1)]

it would lower our calculated values of ζ by about 0.00050 for the 75.5% sample, by 0.00030 for the 41.7% sample and by 0.00007 for the 14.3% sample. This would bring our experimental values into slightly better agreement with the calculated ones.

Summary

The percentage of thermal dissociation of mixtures of protium and deuterium iodide has been determined at 398 and 468°, and compared with the theoretical predictions. They are found to be in agreement within the limits of experimental error. A determination of the equilibrium constant for the protium iodide decomposition at these two temperatures agreed within our limits of experimental error with the values given by Bodenstein.

NEW YORK CITY   RECEIVED JUNE 9, 1934

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

The Hydrolysis of Ferric Ion. The Standard Potential of the Ferric–Ferrous Electrode at 25°. The Equilibrium $Fe^{+++} + Cl^- = FeCl^{++}$

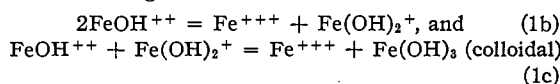BY WILLIAM C. BRAY AND ALLEN V. HERSHEY

Dilute aqueous solutions of ferric salts are known to contain considerable amounts of colloidal ferric hydroxide and hydrogen ion, but the possibility of isolating the first step in the hydrolysis

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \qquad (1)$$
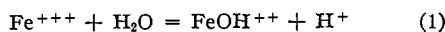
has received little attention. Thus, although in 1907 Bjerrum,[1] from a study of the conductivity of 0.025 to 0.0003 molal ferric chloride solutions, calculated the equilibrium constant of this reaction to be $K_1 = 25 \times 10^{-4}$ at 25°, chemists seem to

(1) Bjerrum, Z. physik. Chem., **59**, 350 (1907).

prefer the theory that $FeOH^{++}$ is unstable with respect to ferric ion and the colloid. In other words, it is usually assumed that equilibrium lies far to the right in the reactions

$$2FeOH^{++} = Fe^{+++} + Fe(OH)_2^+, \text{ and} \qquad (1b)$$
$$FeOH^{++} + Fe(OH)_2^+ = Fe^{+++} + Fe(OH)_3 \text{ (colloidal)} \qquad (1c)$$

Our approach to this problem is based upon the following ideas. When the hydrolysis of a ferric salt is gradually decreased by the addition of acid, the quantities of colloid and $Fe(OH)_2^+$ must decrease more rapidly than that of $FeOH^{++}$;

and in sufficiently acid solution the hydrolysis will be represented nearly quantitatively by Equation 1. Also, when another equilibrium involving ferric ion is studied at high acid concentration, the error due to hydrolysis will gradually increase as the concentration of hydrogen ion is lowered. A study of the magnitude of this error should therefore lead to a determination of the equilibrium constant K_1, unless $FeOH^{++}$ is too unstable (Reactions 1b and 1c). On account of the great tendency of ferric ion to form addition compounds, the presence of chloride, sulfate and acetate ions is to be avoided; but complex ion formation may be neglected in dilute perchlorate or nitrate solutions.

In evaluating K_1 we have used the equilibrium data of Popoff, Fleharty and Hanson[2a] at 25° and of Fleharty[2b] at 35° in perchlorate solutions at low acid concentration and low ionic strength for the reaction

$$2Fe^{+++} + 2Hg = 2Fe^{++} + Hg_2^{++} \qquad (2)$$
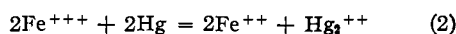
and those of Noyes and Brann[3] at 25° in nitrate solutions at high ionic strength and high acid concentration for the reaction

$$Fe^{+++} + Ag = Fe^{++} + Ag^+ \qquad (3)$$
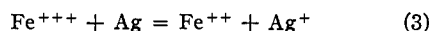
The equilibrium quotient, K, for each of the ferric reactions decreases rapidly with increasing ionic strength, μ. According to the Debye–Hückel theory, in a log K vs. $\mu^{1/2}$ plot, the limiting slope at $\mu^{1/2} = 0$ is proportional to ΔZ^2, where Z is the charge on each ion. For Reactions 1 and 3, $\Delta Z^2 = 2^2 + 1^2 - 3^2 = -4$; and for Reaction 2, $\Delta Z^2 = -6$. For any equilibrium, the relation may be expressed in the form

$$-\left(\frac{1}{\Delta Z^2}\right)\log_{10} K = -\left(\frac{1}{\Delta Z^2}\right)\log_{10} K^\circ + f(\gamma) \qquad (4)$$

where $f(\gamma)$ is a function of the activity coefficients of the ions in each reaction, and at 25° approaches the limit $-0.5\ \mu^{1/2}$ as $\mu^{1/2}$ approaches zero.

Randall[4] has made effective use of $-(1/\Delta Z^2)$ log K_m vs. $\mu^{1/2}$ plots in interpreting equilibrium and electromotive force data, and has shown that values of $f(\gamma)$ for any equilibrium may be represented by some one of the family of log γ curves for single electrolytes. On the basis of his results we have concluded that values of $f(\gamma)$ for the three analogous equilibria, Nos. 1, 2 and 3, are identical at low ionic strength, and will not differ greatly up to $\mu^{1/2} = 1$.

(2) (a) Popoff, Fleharty and Hanson, THIS JOURNAL, **53**, 1643 (1931); (b) Fleharty, *ibid.*, **55**, 2646 (1933).

(3) Noyes and Brann, *ibid.*, **34**, 1016 (1912).

(4) (a) Randall and Vietti, *ibid.*, **50**, 1526 (1928); (b) Randall, *J. Chem. Ed.*, **8**, 1062 (1931); (c) unpublished results.

The values of $f(\gamma)$ which we have chosen are listed in the second column of Table I. As the results of Noyes and Brann in the range $\mu^{1/2} = 0.4$ to 1 lie on a rather flat curve in the $\mu^{1/2}$ diagram (Fig. 3 below), the $f(\gamma)$ curve characteristic of ferric equilibria has been assumed to be one of the highest of the log γ curves, and therefore approaches log γ_{HCl} at low ionic strength. Accordingly, Randall and Young's measurements[5] of log γ were used when $\mu^{1/2}$ is less than 0.4.

TABLE I

$Fe^{+++} + H_2O = FeOH^{++} + H^+$

EQUILIBRIUM QUOTIENTS

$\mu^{1/2}$	$f(\gamma)$	K_1/K_1^0	$(10^4)K_1$ at 25°	$(10^4)K_1$ at 35°
0.00	0.00	1.000	60 ± 5	120 ± 15
.05	− .023	0.809	48.6	99
.1	− .0438	.668	40.1	80
.2	− .0760	.496	29.8	60
.3	− .097	.409	24.6	49
.4	− .111	.360	21.6	
.5	− .120	.331	19.9	
.6	− .125	.316	19.0	
.7	− .128	.308	18.5	
.8	− .131	.299	18.0	
.9	− .133	.294	17.6	
1.0	− .135	.288	17.3	

Our conclusions with respect to the hydrolysis of ferric ion are summarized in Table I. The values of K_1/K_1^0 in the third column were calculated by means of the relation log $K_1/K_1^0 = 4f(\gamma)$, which corresponds to Equation 4. The fourth and fifth columns contain the results of our study of the equilibrium data[2] for Reaction 2. Since no measurements were made at high acid concentration, it was necessary to determine by successive approximations K_1 and K_2, the equilibrium quotients of the two reactions.

In Figs. 1 and 2 values of $(1/6)$ log K_2 for the original results at 25 and 35° are plotted against $\mu^{1/2}$. By applying hydrolysis corrections, calculated on the basis of different values of K_1, it was found that the wide divergence of the results at different concentrations of acid was removed if K_1^0 did not exceed the limits 55 to 65 × 10^{-4} at 25°, and 105 to 135 × 10^{-4} at 35°. The corresponding ranges of K_2^0 are listed below the figures. The corrected results, based on $K_1^0 = 60 \times 10^{-4}$ and 120×10^{-4}, are in satisfactory agreement with the smooth curves except for the most dilute solutions, where the experimental error is relatively great. This deviation in the dilute solutions is in the wrong direction to be

(5) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

attributed to additional hydrolysis according to Reactions 1b, c, which supports our assumption that the second and third steps in the hydrolysis of ferric ion are negligible in these experiments. Were this assumption in error, our values of K_1^0 and K_2^0 would be too high.

Fig. 1.—2Fe^{+++} + 2Hg = 2Fe^{++} + Hg$_2^{++}$: equilibrium data at 25°; concentrations in moles per 1000 g. of water; O, original results of Popoff, Fleharty and Hanson in 0.02 to 0.002 molal HClO$_4$ solutions; □, original extrapolation corresponding to K_2^0 = 0.0188 and E_2^0 = −0.0510 volt; ●, corrected for hydrolysis; (1/6) log K_2^0 = $\bar{1}.856$ ± 0.005, K_2^0 = 0.137 ± 0.010, E_2^0 = −0.0262 ± 0.0010/volt.

In Table II are listed values of (1/6) log K_2 and K_2 which correspond to the smooth curves in Figs. 1 and 2. It may be noted that the difference, (1/6) log K_2 − (1/6) log K_2^0, is equal to the corresponding value of $f(\gamma)$ in Table I; and that probable values of K_2 at higher ionic strength may be calculated. With increasing ionic

TABLE II

VARIATION OF K_2 WITH IONIC STRENGTH

$\mu^{1/2}$	At 25°; see Fig. 1 (1/6) log K_2	K_2	At 35°; see Fig. 2 (1/6) log K_2	K_2
0.00	$\bar{1}.856$	0.137	$\bar{1}.957$	0.55
.05	$\bar{1}.833$	.100	$\bar{1}.934$	.40
.10	$\bar{1}.812$	.075	$\bar{1}.913$	.30
.20	$\bar{1}.780$	.048	$\bar{1}.881$	.19
.30	$\bar{1}.758$	.035	$\bar{1}.859$	

strength K_2 decreases more rapidly, and $K_2^{1/2}$ less rapidly, than K_1.

Inspection of the summaries below Figs. 1 and 2 shows that at 25° K_2^0 has been increased sevenfold, ΔH_2 by five thousand calories, and E_2^0 by 25 millivolts.

Similar increases in K_3^0 and E_3^0 have resulted from our study of the equilibrium data[3] for Reaction 3 (cf. the summary below Fig. 3), but these are due almost wholly to the change in the method of extrapolation and not to the correction for hydrolysis. Noyes and Brann demonstrated that the error due to hydrolysis was large at low concentrations of acid, and therefore accepted only those measurements in which the concentration of nitric acid was 0.05 molal or greater. The result of their linear extrapolation (K_3 vs.
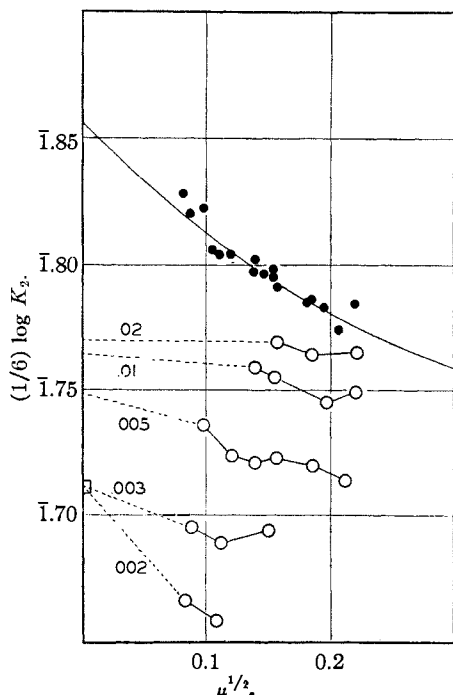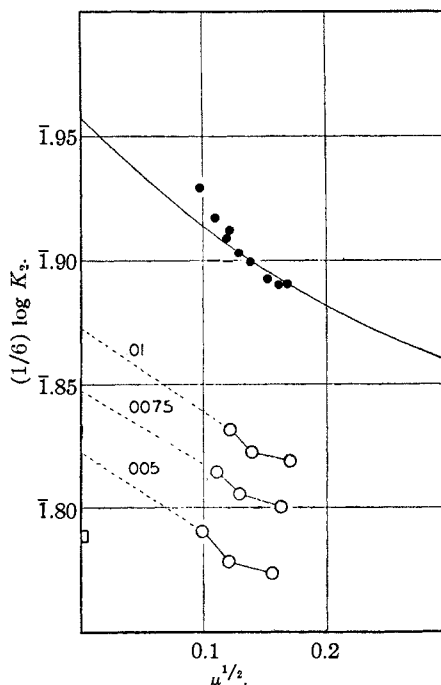

Fig. 2.—2Fe^{+++} + 2Hg = 2Fe^{++} + Hg$_2^{++}$; equilibrium data at 35°: O, original results of Fleharty in 0.01 to 0.005 molal HClO$_4$; □, original extrapolation corresponding to K_2 = 0.0539 and ΔH_2 = 20,000 cal.; ●, corrected for hydrolysis; (1/6) log K_2^0 = $\bar{1}.957$ ± 0.008, K_2^0 = 0.55 ± 0.05, ΔH_2 = 25,000 ± 2000 cal.

nitrate concentration) was adopted by Lewis and Randall,[6] apparently without examination of the method. Extrapolation of the same data in the

(6) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 397, 411.

(1/4) log K_3 vs. $\mu^{1/2}$ diagram gave $K_3^0 = 0.350$, which is almost the same as that obtained after applying the small corrections for hydrolysis: $K_3^0 = 0.363 \pm 0.015$.

per 1000 grams of water. We have estimated that this change would increase K_3 by two or three per cent. at $\mu^{1/2} = 1$.

The identity of the standard potentials, $E_2^0 =$

TABLE III

CORRECTIONS FOR HYDROLYSIS: *cf.* FIGURE 3

		Original Data				Results of Calculations			
No.	HNO₃ mole/liter	Fe⁺⁺⁺ mole/liter at equil.	$\mu^{1/2}$	K_3	$10^4 K_1$	FeOH⁺⁺ mole/liter	H⁺ mole/liter	$\mu^{1/2}$	K_3 corrected
40	0.05	0.0049	0.420	0.120	21.2	0.00020	0.0508	0.420	0.125
45 46	.02	.0078	.432	.116	21.0	.00071	.0211	.430	.127
48	.05	.0074	.461	.119	20.4	.00029	.0507	.461	.124
50	.08	.0072	.489	.118	20.0	.00017	.0807	.493	.121
21	.0	.0389	.684	.089	18.7	.00855	.00665	.669	.114
29	.05	.0346	.708	.108	18.5	.00117	.0530	.707	.111
19	.0	.0539	.775	.090	18.2	.00945	.0086	.763	.108
20	.0	.0543	.776	.088	18.2	.0096	.0085	.763	.107
59	.10	.0443	.781	.109	18.1	.00079	.1008	.781	.111
63	.05	.0413	.803	.105	18.0	.00140	.0514	.801	.108
67	.05	.0394	.941	.098	17.5	.0013	.0513	.940	.101

Details of the calculations are given in Table III (1) for typical experiments in 0.05 to 0.10 M HNO₃ and (2) for those experiments at lower acid concentration for which there is definite evidence that equilibrium was reached. K_3

Fig. 3.—Fe⁺⁺⁺ + Ag = Fe⁺⁺ + Ag⁺; equilibrium data of Noyes and Brann at 25°; concentrations in moles per liter; □, original extrapolation, linear in a K_3-μ diagram; $K_3^0 = 0.128$, $E_3^0 = -0.0528$ volt; ●, corrected for hydrolysis; ○, original results in which the hydrolysis exceeds 3.2%; (1/4) log $K_3^0 = 1.890 \pm 0.004$, $K_3^0 = 0.363 \pm 0.015$, $E_3^0 = -0.0260 \pm 0.0010$ volt.

corrected/K_3 *original* is equal to the concentration ratio Fe⁺⁺⁺ *original*/(Fe⁺⁺⁺ *original* − FeOH⁺⁺ *calculated*). The correction of the measurements in low acid brings them into agreement with those in high acid, thus proving that the hydrolysis quotients listed in Table I are approximately correct even at higher ionic strengths. However, no great accuracy can be claimed for the values of K_1 in this region, since the $f(\gamma)$ curves for Reactions 1 and 3 may differ, and the curve in Fig. 3 would be somewhat higher at the right (and therefore flatter) if the concentration units were changed from moles per liter to moles

$E_3^0 = -0.026$ volt at 25°, for Reactions 2 and 3 signifies that the E^0 values for the electrode reactions

$$2Hg_2^{++} + 2E^- = 2Hg, \text{ and} \quad (5)$$
$$Ag^+ + E^- = Ag \quad (6)$$
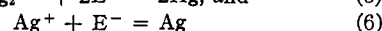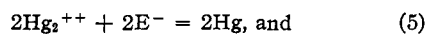
differ by not more than one millivolt. In the first case the value of Linhart,[7] $E_5^0 = 0.7926$, was raised by Lewis and Randall[8] to 0.7986 by a change in the method of extrapolation. After plotting the original data in a $\mu^{1/2}$ diagram, we adopted the value

$$E_5^0 = 0.7975 \pm 0.0010 \text{ volt at } 25°$$

For the silver ion–silver electrode we have accepted the conclusion of Randall, based on the experimental results of Randall and Young,[5] that the value of Lewis and Randall[9] 0.7995, should be lowered by 1 millivolt.

$$E_6^0 = 0.7985 \pm 0.0010 \text{ volt at } 25°$$

Combination of these values with $E_2^0 = E_3^0 = -0.026$ volt gives the standard potential of the ferric–ferrous electrode

$$Fe^{+++} + E^- = Fe^{++}: E_{298}^0 = 0.772 \pm 0.001 \text{ volt}$$
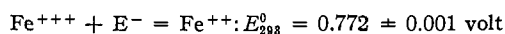
This value of E^0 for the ferric–ferrous electrode exceeds the generally accepted value by 25 millivolts. We selected for study the precise electromotive force measurements of Popoff and Kunz[10] for the reaction

$$Fe^{+++} + \tfrac{1}{2}H_2 = Fe^{++} + H^+ \ (\Delta Z^2 = -4)$$
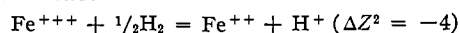
in hydrochloric acid solutions. By plotting their results against $\mu^{1/2}$, their value, $E^0 = 0.7477$, is

(7) Linhart, THIS JOURNAL, **38**, 2356 (1916).
(8) Lewis and Randall, Ref. 6, p. 417.
(9) Lewis and Randall, Ref. 6, p. 414.
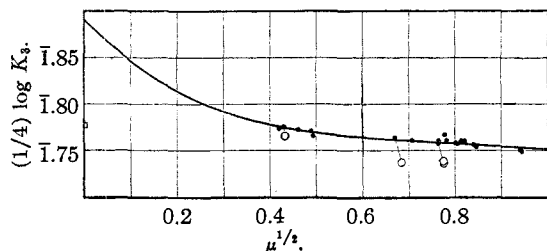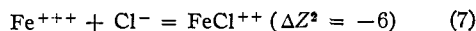(10) Popoff and Kunz, THIS JOURNAL, **51**, 382 (1929).

raised to 0.765. Correction for hydrolysis raises the value to 0.767. There remains a discrepancy of 5 millivolts, which we have attributed to the presence of the complex ion $FeCl^{++}$ formed in the reaction

$$Fe^{+++} + Cl^- = FeCl^{++} \ (\Delta Z^2 = -6) \quad (7)$$

Popoff and Kunz made five series of measurements, at 0.05, 0.1, 0.2, 0.5 and 1.0 molal hydrochloric acid. The concentrations of ferric and ferrous chlorides were varied in each series, but their ratio was nearly unity in each experiment. They corrected their measurements to 1 atmosphere hydrogen pressure, to unit hydrogen-ion activity by using the γ_{HCl} values of Randall and Young,[5] and to equal concentrations of ferric and ferrous ions. Their results, E_a in their Table VIII, are therefore electrode potentials for the half reaction $Fe^{+++} + E^- = Fe^{++}$, for which $\Delta Z^2 = -5$.

In Fig. 4, $E_a/5(0.05915)$ is plotted against $\mu^{1/2}$. Our extrapolation of the original results is represented by the lower curve, and the effect of the hydrolysis correction is indicated. In correcting for complex chloride formation, values of K_7/K_1^0 were calculated by the relation log $K_7/K_1^0 = 4f(\gamma)$, $f(\gamma)$ being taken from Table I. If K_1^0 does not lie outside the limits 15 to 25, the correction for $FeCl^{++}$ formation removes the discrepancy in E^0, raises the $f(\gamma)$ curve into agreement with the curves for Reactions 1, 2 and 3, and brings the results at low hydrochloric acid concentration into better agreement with the $f(\gamma)$ curve.

After the completion of these calculations we decided to check the conclusions by making, in perchlorate solutions, electromotive force measurements similar to those of Popoff and Kunz in chloride solutions. Preliminary results have just been obtained by Mr. C. G. Clear. At $\mu^{1/2} = 0.45$ and 0.50, the potentials are 15 and 18 millivolts higher than those of Popoff and Kunz; and correspond to points on or above the upper curve in Figure 4.
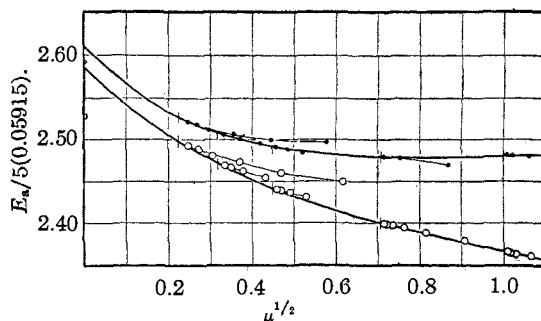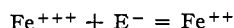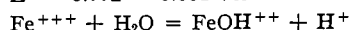

Fig. 4.—$Fe^{+++} + 1/2H_2 = Fe^{++} + H^+$; electromotive force data of Popoff and Kunz at 25°; concentration in moles per 1000 g. of solution; $\square$, original extrapolation by an E-HCl concentration diagram, $E^0 = 0.7477$ volt; $\bigcirc$, original results, E^0 uncorrected $= 0.765$; $\triangleright$, corrected for hydrolysis, $E^0 = 0.767$ volt; $\bullet$, corrected for hydrolysis and complex chloride formation ($K_7^0 = 20$); $E^0/5(0.05915) = 2.610 \pm 0.003$, $E^0 = 0.772 \pm 0.001$ volt.
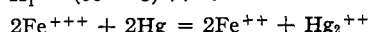
Summary

By using a graphical application of the Debye-Hückel theory, already developed by Randall, the following constants were calculated at 25° from measurements available in the literature.
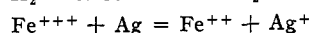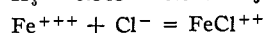
$Fe^{+++} + E^- = Fe^{++}$
$E^0 = 0.772 \pm 0.001$ volt
$Fe^{+++} + H_2O = FeOH^{++} + H^+$
$K_1^0 = (60 \pm 5) \times 10^{-4}$
$2Fe^{+++} + 2Hg = 2Fe^{++} + Hg_2^{++}$
$K_2^0 = 0.137 \pm 0.010 \quad E_2^0 = -0.026 \pm 0.001$
$Fe^{+++} + Ag = Fe^{++} + Ag^+$
$K_3^0 = 0.363 \pm 0.015 \quad E_3^0 = -0.026 \pm 0.001$
$Fe^{+++} + Cl^- = FeCl^{++}$
$K_7^0 = 20 \pm 5$

At 35° $K_1^0 = (120 \pm 15) \times 10^{-4} \quad K_2^0 = 0.55 \pm 0.05$

The electrode potentials are 25 millivolts higher than the previously accepted values.

The equilibrium quotient of reactions involving ferric ion, which decrease rapidly in low ionic strength, are nearly constant when $\mu^{1/2} = 0.6$ to 1.0. Approximate values in this range are $K_1 = 18 \times 10^{-4}$, $K_2 = 0.022$, $K_3 = 0.11$, $K_7 = 3$, at 25°.