

THE EQUILIBRIUM CONSTANT IN THE SYSTEM:



AT LOW CONCENTRATIONS

A THESIS

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By

Fred M. Roberts

Georgia School of Technology
Atlanta, Georgia
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I

INTRODUCTION

The value for the equilibrium constant at 25° C in the system:



was first determined by Noyes and Brann¹. They determined the value for the equilibrium constant by allowing silver to react with ferric nitrate at various concentrations. When equilibrium had been established, the mixtures were analyzed for the amounts of ferrous ions and silver ions present. The amounts of ferric ions present in the mixtures were determined by the difference between the concentration of the ferrous iron in the equilibrium mixtures and the total concentration of iron present at the beginning of the experiments. The equilibrium constants at the different concentrations were calculated from the

¹Noyes and Brann, J. Am. Chem. Soc., 34, 1016 (1912)

expression:

$$K_c = C_{Fe^{2+}} \times C_{Ag^+} / C_{Fe^{3+}} \quad (2)$$

Noyes and Brann plotted their values for K_c against total nitrate concentration, and extrapolated the curve to zero concentration. The curve obtained was a straight line, which, when extrapolated to zero concentration, gave a value of 0.128 for K_a^2 .

The determination of the equilibrium constant for the reaction between metallic silver and ferric nitrate has been worked out as a laboratory experiment for physical chemistry by Shaw and Hyde³. The procedure for the determination of the constants at various concentrations was the same as that used by Noyes and Brann. The values for the equilibrium constant were to be plotted against μ , the ionic strength, and the curve extrapolated to zero concentration. A typical value for the equilibrium constant to be obtained by this experiment was 0.130.

Schumb and Sweetser⁴ determined the value for the equilibrium constant for the same reaction, using the per-

²The expression K_c represents the equilibrium constant calculated from concentrations, while K_a represents the true equilibrium constant, or K_c extrapolated to zero concentration.

³Shaw and Hyde, J. Chem. Ed., 8, 2065, (1931)

⁴Schumb and Sweetser, J. Am. Chem. Soc., 57, 871, (1935)

chlorates instead of the nitrates. The method used was essentially the same as that used by Noyes and Brann. Schumb and Sweetser allowed ferric perchlorate to be reduced by metallic silver. When the mixtures had reached equilibrium, they were analyzed for concentrations of ferrous ions and silver ions. The ferric ion concentrations were determined by the difference between the ferrous iron in the equilibrium mixtures and the total iron present at the beginning of the experiments. The results were not plotted as K_c against μ , since the slope of the curve changes rapidly at low concentrations. In order to obtain a curve which could be more accurately extrapolated, the data were plotted as μ , against $\log K_c + 2.02 \mu^{1/2}$ as derived from the Debye-Hückel theory⁵. The equilibrium constants were calculated from Equation (2), while the true constant, or K_c extrapolated to zero ionic strength, is given by the equation:

$$K_a = C_{Fe^{2+}} \times C_{Ag^+} / C_{Fe^{3+}} \times \left(\frac{\gamma_{Ag^+} \times \gamma_{Fe^{3+}}}{\gamma_{Fe^{2+}}} \right) = K_c \times \frac{\gamma_{Fe^{2+}} \cdot \gamma_{Ag^+}}{\gamma_{Fe^{3+}}} \quad (3)$$

where γ is the activity coefficient of the corresponding ions. Taking the logarithm of both sides of the equation, we have:

$$\log K_a = \log K_c + \log \left(\frac{\gamma_{Fe^{2+}} \cdot \gamma_{Ag^+}}{\gamma_{Fe^{3+}}} \right) \quad (4)$$

⁵Debye and Hückel, Physik Z., 24, 185, (1923)

Introducing the limiting law of Debye and Hückel

$$- \log \gamma = 0.0504 z^2 \mu^{\frac{1}{2}} \quad (5)$$

where z is the valence of the ion in question, and substituting in Equation (4) for $\log \gamma$ we obtain the equation:

$$\log K_a = \log K_c - 0.504 z^2 \mu^{\frac{1}{2}} \quad (6)$$

By substituting the values for z we obtain:

$$\log K_a = \log K_c + 2.02 \mu^{\frac{1}{2}} \quad (7)$$

When the data of Schumb and Sweetser were plotted as μ against $\log K_c + 2.02 \mu^{\frac{1}{2}}$, and the curve extrapolated to zero concentration, a value of 0.531 was obtained for the equilibrium constant.

King⁶ has pointed out that the extrapolation to zero concentration of the data of Noyes and Brann is in error. The values of the equilibrium constants were determined at concentrations too high to allow an accurate extrapolation to be made.

Bray and Hershey⁷ have plotted the results of

⁶King, J. Chem. Ed., 9, 150, (1912)

⁷Bray and Hershey, J. Am. Chem Soc., 56, 1889, (1934)

Noyes and Brann as $\frac{1}{4} \log K_c$ against $\mu^{\frac{1}{2}}$, and upon extrapolation, obtained a value for the equilibrium constant of 0.350. However, the curve which they obtained has its greatest curvature in the range below the values experimentally determined by Noyes and Brann.

It was the purpose of this investigation to extend the measurements of the equilibrium constant to lower concentrations than any other investigators have done.

II

PREPARATION OF MATERIALS

Silver

Silver was prepared by the reduction of silver nitrate with ammonium formate. Merck eighty-five per cent formic acid solution was diluted with one-third water, and neutralized with concentrated ammonium hydroxide. The solution of ammonium formate was heated to boiling, and added slowly to a boiling solution of silver nitrate. The reaction was violent, and care had to be taken not to add the ammonium formate too rapidly. The precipitated silver was filtered, thoroughly washed with distilled water, and dried by suction. The silver was kept in a desiccator over sulfuric acid until used.

Potassium Permanganate

Potassium permanganate solution was made up by dissolving C. P. potassium permanganate in hot water, allowing the solution to stand for twenty-four hours, then filtering through an asbestos filter. The permanganate was standardized against Bureau of Standards sodium oxalate, and kept in a dark bottle, the top of which was kept covered with a beaker to exclude dust. The solution was restandardized the next day, and if there was no change, it was kept. The potassium permanganate prepared and kept in this

manner maintained its strength over a period of several weeks.

Ferric Nitrate

Ferric nitrate solutions were made up by dissolving Coleman and Bell C. P. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 0.0352 molar nitric acid. The solutions were standardized by boiling with sulfuric acid to convert to the sulfate, reducing with zinc, and titrating with standard potassium permanganate. The reduction of the iron was carried out in flasks fitted with Bunsen valves so that a reducing atmosphere was maintained over the solutions at all times.

Potassium Thiocyanate

Potassium thiocyanate solution was made up by dissolving Baker and Adamson reagent grade potassium thiocyanate in recently boiled distilled water. The solution was standardized against pure silver. The silver used was that prepared by the reduction of silver nitrate. The silver was dissolved in six normal nitric acid, and titrated with the potassium thiocyanate, using ferric nitrate as the indicator.

Nitric Acid

The nitric acid for the preparation of the ferric nitrate solutions was prepared by diluting 15 normal C. P. nitric acid with distilled water. The solution was standardized against sodium carbonate.

Sodium Carbonate

Sodium carbonate was prepared by heating sodium bicarbonate. The sodium bicarbonate was first recrystallized. A saturated solution was prepared by warming with distilled water at a temperature just below that required for the evolution of gas. The solution was decanted from the undissolved bicarbonate, and evaporated in a large porcelain dish at a temperature under 40° C until crystals began to separate. This process was repeated, and the crystals were dried at 100° C. To convert to the carbonate, the bicarbonate was heated in a platinum crucible until the mass just fused.

Carbon Dioxide

Carbon dioxide was obtained by heating sodium bicarbonate in a pyrex tube. The carbon dioxide was dried with sulfuric acid.

Water

All water used in the experiments was recently boiled distilled water.

All other chemicals were of C. P. grade.

III

EXPERIMENTAL PROCEDURE

Approximately one and one-half grams of silver were placed in a 250-cc volumetric flask, and the flask was filled to the mark with ferric nitrate solution of the desired concentration. Concentrations varied from 0.1025 molar to 0.005028 molar as shown in Table I. To prevent oxidation of the ferrous ions formed in the reaction, the air in the flasks was swept out with a slow stream of carbon dioxide. The stoppers were coated lightly with stopcock grease, pressed firmly into place, sealed with paraffin, and taped down. The flasks were placed in a shaker, and shaken moderately for about six hours. The flasks were then transferred to a thermostat at $25.0 \pm 0.01^\circ \text{C}$. After twenty-four hours a sample was taken and analyzed for concentrations of ferrous ions and silver ions.

Analyses were made volumetrically. All titrations were made with weight burettes. Ferrous iron in the equilibrium mixtures was determined by titrating with standard potassium permanganate. A small amount of 18 normal sulfuric acid was added to the solution to prevent obscuring of the end point by ferric hydroxide from the hydrolysis of ferric nitrate.

Silver was determined in the equilibrium mixtures

by titrating with standard potassium thiocyanate. The silver determination was carried out in the same solution used previously for the iron determination. The ferric iron present acted as an indicator for the determination.

In order to make sure that the system had reached equilibrium, each flask was again swept out with carbon dioxide, sealed as above, and after being shaken for three to four hours, was placed in the thermostat. After a total time of forty-eight hours had elapsed, another sample was taken and analyzed. If there was a change in the concentrations of ferrous ions and silver ions, the flasks were again swept out with carbon dioxide, sealed, shaken, and allowed to remain in the thermostat for another twenty-four hours. At the end of this time the mixtures were again analyzed. It was found that in all mixtures the concentrations of ferrous ions and silver ions did not change to any appreciable extent after a period of forty-eight hours. In later experiments, the mixtures were analyzed after this length of time. The procedure was finally as follows: The flasks were prepared as above, and after shaking for about six hours, were placed in the thermostat for twenty-four hours. At the end of this time, they were taken from the bath and placed in the shaker for three to four hours. The flasks were replaced in the thermostat, and after a total time of forty-eight hours had elapsed, the mixtures

were analyzed for content of ferrous ions and silver ions. The concentrations of ferric ions were determined by taking the difference between the ferrous iron and the total iron at the beginning of the experiments. All analyses were run in duplicate, and a duplicate of each mixture was run.

IV

DATA AND CALCULATIONS

The equilibrium constants at the different concentrations were calculated from Equation (2). The observed data and the calculated results are shown in Table I.

Table I

All solutions made up in 0.0352 molar nitric acid. Concentrations are expressed in moles per liter.

Total iron	Equilibrium Mixtures			K_c (Eq. 2)	μ	Log $K_c + 2.02 \mu^2$
	Ferrous	Silver	Ferric			
*0.1043	0.0651	0.0673	0.0392	0.112	0.5398	
.1025	.0650	.0655	.0375	.113	.5294	0.513
.1025	.0647	.0654	.0378	.112		
.06371	.04561	.04611	.01810	.116	.3263	.230
.06371	.04560	.04600	.01811	.115		
.03740	.03019	.03019	.00721	.128	.1892	-.006
.03740	.03021	.03026	.00719	.127		
*.0369	.0295	.0299	.0074	.119	.2126	
*.0288	.0239	.0246	.0049	.121	.1754	
.01979	.01772	.01769	.00207	.151	.1181	-.119
.01979	.01771	.01788	.00209	.153		

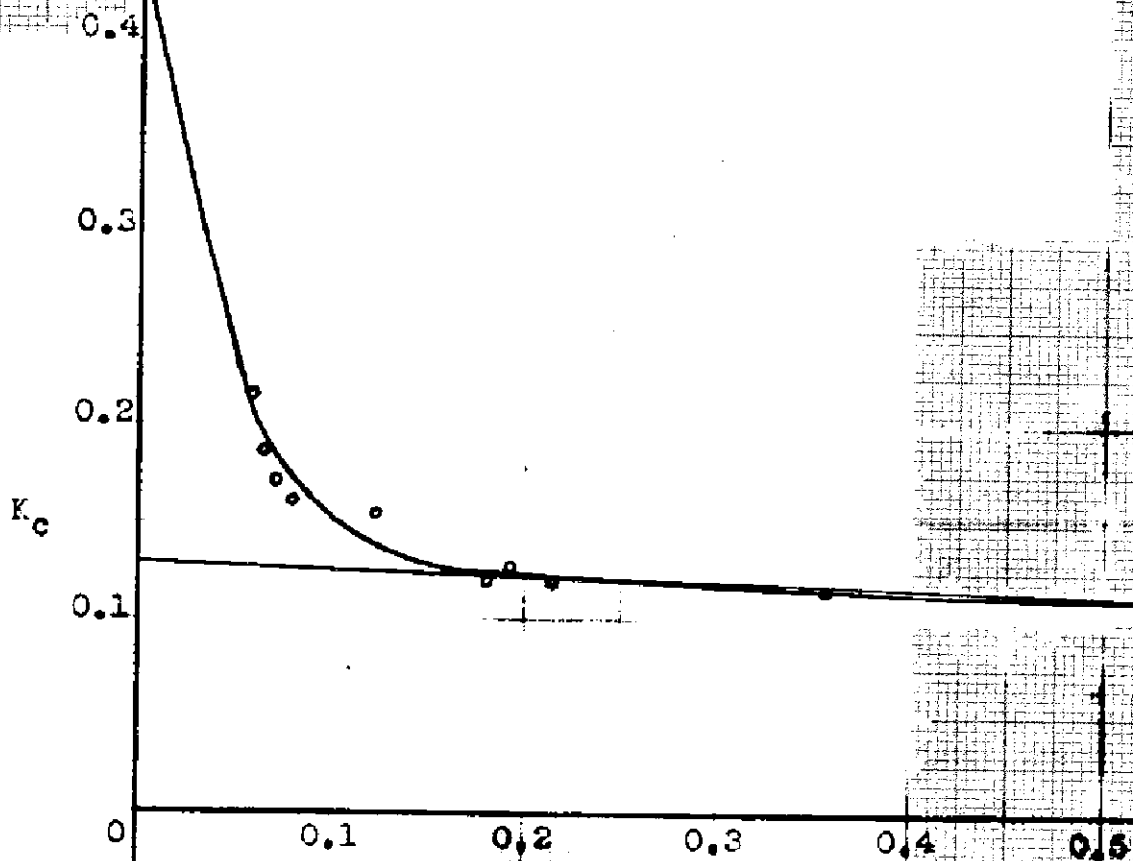
*These data are taken from the results of Noyes and Brann.

Table I (continued)

Total iron	Equilibrium Mixtures			K_c (Eq. 2)	μ	Log $K_c \mu^{\frac{1}{2}}$ +2.02
	Ferrous	Silver	Ferric			
0.01029	0.00970	0.00970	0.00059	0.159	0.0774	-.231
.01029	.00970	.00965	.00059	.158		
.008109	.007748	.007767	.000361	.167	.0684	-.244
.008109	.007750	.007765	.000359	.169		
.007118	.006861	.006860	.000257	.183	.0641	-.221
.007118	.006860	.006860	.000258	.183		
.005028	.004915	.004913	.000113	.215	.0555	-.186
.005028	.004914	.004913	.000112	.217		

FIGURE I

Data of Table I Plotted as K_c against μ



○ Results of the Present Work

□ Data of Noyes and Brann

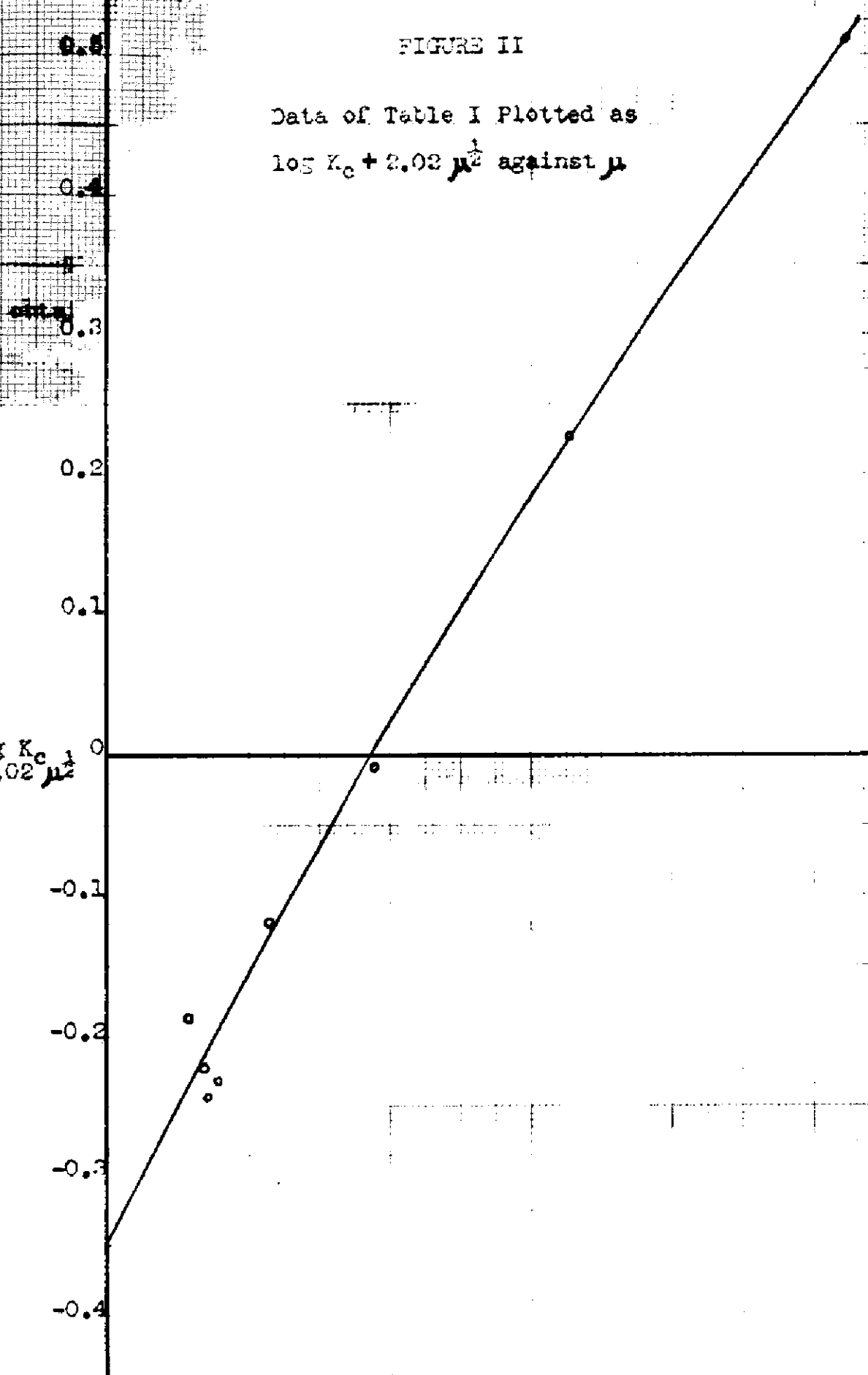
FIGURE II

Data of Table I Plotted as
 $\log K_c + 2.02 \mu^{\frac{1}{2}}$ against μ

$\log K_c + 2.02 \mu^{\frac{1}{2}}$

0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4

0.1 0.2 0.3 0.4 0.5
 μ



V

DISCUSSION OF RESULTS

When the values for K_c are plotted against μ , a curve is obtained which, in the same range of ionic strengths, coincides with the curve obtained from the data of Noyes and Brann (see Figure I). However, at lower concentrations, the curve obtained from the data in Table I deviates considerably from the straight line obtained by the extrapolation of the data of Noyes and Brann. When the data in Table I are plotted as K_c against μ , and the curve extrapolated to zero ionic strength, the value obtained for the equilibrium constant is 0.445.

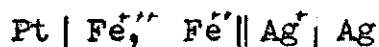
As can be seen from Figure I, the slope of the curve obtained by plotting K_c against μ is changing rapidly, and for that reason a determination of the equilibrium constant by extrapolation cannot be as accurately made as if the curve were plotted as $\log K_c + 2.02 \mu^{\frac{1}{2}}$ against μ . By plotting the data in this manner, a curve was obtained which had its intercept at -0.350 (Figure II). This is $\log K_a$, and corresponds to a value of 0.4467 for the equilibrium constant.

If the equilibrium constant for the reaction is known, ΔF° may be calculated. When the system is in equilibrium, ΔF° is found from the equation:

$$\Delta F^\circ = - RT \ln K \quad (8)$$

Substituting in this equation the value 0.4467 for the equilibrium constant, ΔF_{298}^0 was calculated to be 446.66 calories.

If the potential of the molal silver electrode is known, it is possible to calculate the potential of the molal ferrous-ferric electrode. Using the equilibrium constant determined here and the value 0.7985 volts for the potential of the molal silver electrode as determined by Randall and Young⁸, the potential of the molal ferrous-ferric electrode has been calculated. The reaction between metallic silver and ferric nitrate takes place in the cell:



The standard electromotive force for this cell may be determined by the difference between the standard electromotive forces of the two single cells as follows:

$$E_0 = RT \ln K_a = E_{\text{Ox}}^{\text{Fe}^{3+}} - E_{\text{Ox}}^{\text{Ag}^+} \quad (9)$$

From this equation the potential of the molal ferrous-ferric electrode is found to be 0.7778 volts.

⁸Randall and Young, J. Am. Chem. Soc., 50, 989, (1931)

VI

SUMMARY

The equilibrium constant at 25.01° C for the reaction between metallic silver and ferric nitrate has been determined at ionic strengths of less than one-tenth. The values obtained for K_c were plotted as K_c against μ , and as $\log K_c + 2.02 \mu^{\frac{1}{2}}$ against μ , and the curves extrapolated to zero ionic strength. A value of 0.4467 was obtained for the equilibrium constant.

The results bear out King's suggestion that the extrapolation of the data of Noyes and Brann is in error.

The value for ΔF_{298}° has been calculated to be 446.66 calories.

Using the constant determined here, the potential of the molal ferrous-ferric electrode has been found to be 0.7778 volts.

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