as nearly anhydrous as possible with the aid of sodium, the amount of water available as an ionizing medium is very small. The six molecules of water in the ferric chloride furnish four to the ferrous chloride, and in all probability much of the remaining water is taken up by the hydrochloric acid. The slight solubility of the ferrous chloride and the removal of water by the acid formed lower to a minimum the tendency of the chlorine to oxidize the ferrous chloride, so that it is precipitated.

The electrolysis of concentrated solutions of ferric chloride, using a high current density, gives metallic iron and hydrogen at the cathode and a few bubbles of gas, probably oxygen, at the anode. Dilute solutions of ferric chloride on electrolysis with low current density yield ferrous chloride at the cathode. No chlorine or other gas is evolved. Hydrochloric acid accumulates in the solution as electrolysis continues. In general, the more rapid the electrolysis, the greater the tendency to produce hydrogen and metallic iron at the cathode. The voltage need not be greater than 4 volts.

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THE EQUILIBRIUM OF THE REACTION BETWEEN METALLIC SILVER AND FERRIC NITRATE.

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CONTENTS.—1. Introduction and Outline. 2. Preparation of the Substances and Solutions. 3. Methods of Analysis. 4. Procedure for Obtaining the Equilibrium Mixture. 5. The Experimental Data. 6. Discussion of the Results. 7. The Potential of the Ferrous-Ferric Electrode. 8. The Potential of the Silver Electrode. 9. Comparison of the Results of the Equilibrium and the Electromotive Force Measurements. 10. Summary.

1. Introduction and Outline.

When metallic silver is added to ferric nitrate solution, a partial reaction takes place as follows:

$$Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2.$$

This reaction is of interest since it is one of the few oxidation reactions in which the substances on both sides of the equation are present in comparable amounts at equilibrium. Consequently it affords an opportunity of determining the equilibrium constant by purely chemical means and of comparing it with that determined by electromotive force measurements.

The equilibrium of this reaction does not seem to have been studied chemically, but the electromotive force of the ferrous-ferric electrode has been determined by Maitland,[1] and that of the silver electrode by Lewis.[2]

In the present investigation, the equilibrium constant of the reaction has been determined chemically by approaching the equilibrium from both sides. Independent measurements of both electrode potentials were also made for comparison with those of the previous investigators.

We desire to express our great indebtedness to Prof. W. C. Bray for the great assistance he has afforded us throughout the whole course of this investigation.

2. Preparation of the Substances and Solutions.

The silver for these experiments was obtained in a very finely divided form by mixing boiling solutions of silver nitrate and ammonium formate, and washing and drying the reduced silver. As the reaction is quite violent, care must be taken to add the ammonium formate slowly. The ammonium formate itself was made by neutralizing ammonium hydroxide with formic acid. Another way of obtaining the silver was as follows: ammonium hydroxide was added to silver nitrate solution until the precipitated silver oxide redissolved, the clear solution was then heated to boiling, and formic acid added to it.

The ferric nitrate solution was made by dissolving Merck's ferric nitrate crystals in water or in dilute nitric acid. The water solution of about tenth-molal concentration was perfectly clear, but had a rather dark red color. Upon the addition of a small amount of nitric acid the color of the solution became very much lighter; and, by making the acid concentration about 0.05 normal, a light reddish yellow solution was obtained. A more dilute solution of ferric nitrate (0.03 molal) gave very nearly colorless solutions in 0.05 normal acid. That moderately concentrated ferric nitrate solutions are perfectly stable under ordinary laboratory conditions was shown by measuring the conductance of a freshly prepared, approximately tenth-molal solution, and then allowing it to stand for a couple of weeks and measuring it again. Another portion of the solution was heated to 50°–55° for about two hours, and after cooling, its conductance was remeasured. In neither case was there any appreciable change.

Ferrous nitrate solution was prepared by the interaction of a dilute nitric acid solution of ferrous sulfate and an aqueous solution of barium nitrate, the precipitated barium sulfate being removed by filtration.

3. Methods of Analysis.

The analyses were all made volumetrically. The total iron content of the solution was determined by reducing it to the ferrous state and titrating with potassium permanganate. In order to carry out the re-

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[1] *Z. Elektrochem.*, 12, 263 (1906).

[2] THIS JOURNAL, 28, 158 (1906).

duction successfully, it was found necessary to evaporate with 10 cc. of concentrated sulfuric acid until all the nitric acid was driven off, since the reduction products of the nitric acid interfered seriously in the titration. The ferric sulfate which separated from the strong sulfuric acid was dissolved by adding about 50 cc. of water and boiling two or three minutes; the solution was then passed through a column of pure, finely granulated zinc, and titrated with permanganate.

In the equilibrium mixture, after filtering out the precipitated silver, the ferrous iron was determined directly by titration with permanganate; and the silver nitrate was titrated with potassium thiocyanate, the ferric nitrate present serving as an indicator. The amount of ferric nitrate in the equilibrium mixture was determined by the difference between the amount of total iron at the start and the amount of ferrous iron found. All analyses were made in duplicate. They generally checked within 0.2–0.3%.

4. Procedure for Obtaining the Equilibrium Mixtures.

The experiments were carried out as follows: Three to fifteen grams of finely divided metallic silver and about 250 cc. of the ferric nitrate solution were placed in resistance-glass bottles. The stoppers were carefully sealed with melted paraffin, and the bottles were rotated in a thermostat at 25°. When equilibrium was reached, the solution was analyzed for its ferrous-iron and silver content. The time required to reach equilibrium will be discussed more fully later on; but, as a general thing, the experiments were started late in the afternoon and were allowed to run through the night.

In order to attain equilibrium from the other side, the bottles containing the ferric nitrate solution and silver were heated in a water bath to 50°–55° for about half an hour with frequent shaking. They were then placed in the thermostat at 25° as before, and allowed to remain all night. That the equilibrium must be displaced by rise of temperature in such a way as to produce silver nitrate and ferrous nitrate in excess of that required for equilibrium at 25° is shown by the heat of reaction. From the thermochemical equation[1]

$$\mathrm{Ag} + \mathrm{Fe(NO_3)_3{:}Aq} = \mathrm{AgNO_3.Aq} + \mathrm{Fe(NO_3)_2.Aq} - 172{,}300 \text{ cal}$$

it is seen that heat is absorbed by the reaction. Therefore, in accordance with the principle of Le Chatelier, the equilibrium will be displaced from left to right with increase of temperature. That the equilibrium is actually displaced by heating for half an hour was shown by analysis of one of the solutions.

Although ferrous nitrate and silver nitrate should be formed by the reaction in exactly equivalent amounts, it was found, as a matter of fact,

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[1] The thermochemical data were taken from Landolt-Börnstein-Meyerhoffer's "Tabellen."

that in every case the silver nitrate was slightly in excess, and that the difference became greater the longer the time. This was doubtless due to oxidation of the ferrous nitrate. This is borne out by the facts that upon standing for a considerable time the equilibrium mixture became very dark in color, indicating that the free acid was consumed, and that the silver in contact with the solution was found to contain a considerable amount of ferric oxide. This oxidation was observed to take place much more rapidly in acid solutions than in neutral ones. Since the concentrations in the equilibrium mixture of the silver nitrate and ferrous nitrate were separately determined, this slight oxidation could have had no effect upon the calculated value of the equilibrium constant.

5. The Experimental Data.

Values of the equilibrium constant were calculated from the concentrations of the three salts as found by analysis. This calculation was made by the equation

$$K = \frac{[Fe(NO_3)_2] \times [AgNO_3]}{[Fe(NO_3)_3]}.$$

In the following table the concentrations are all expressed as milli-formula-weights per liter, but the constant is calculated from the concentrations in formula-weights per liter. Under K_1 are given the values of the constant at 25° when the equilibrium was approached in the direction $Ag + Fe(NO_3)_3 \rightrightarrows \ldots$, and under K_2 the values when the equilibrium was approached in the opposit direction.

No. of Expt.	Total iron at the start.	Equilibrium mixtures.			Time. Hours.	Conc. of HNO_3.	K_1.	K_2.
		$Fe(NO_3)_3$.	$Fe(NO_3)_2$.	$AgNO_3$.				
1[1]	98.5	42.0	56.5	56.9	24	0	0.076	...
	98.5	43.2	55.3	58.5	168	0	0.075	...
2[1]	88.8	40.4	48.4	47.5	1	0	0.057	...
	88.8	37.7	51.1	51.6	..	0	0.070	...
3	85.7	35.4	50.3	49.9	1	0	0.071	...
4[1]	100.0	48.2	51.8	51.5	1	0	0.055	...
	100.0	45.7	54.3	53.8	2	0	0.069	...
	100.0	42.8	57.2	56.9	30	0	0.076	...
5	98.1	42.3	55.8	55.2	30	0	0.073	...
6	103.4	45.0	58.0	57.4	24	0	0.074	...
7	103.4	44.1	58.9	58.5	24	1	0.078	...
8	103.3	45.1	57.9	57.5	24	2	0.074	...
9	103.1	44.1	58.9	58.6	24	5	0.078	...
10	102.7	42.7	60.3	59.9	24	10	0.085	...
11	99.8	37.5	62.5	62.2	24	50	0.104	...
12[1]	109.5	40.5	58.5	....	1	0	...	...
	109.5	37.0	62.0	....	2	0	...	...
	109.5	36.0	63.0	....	40	0	...	...
	109.5	36.4	62.6	62.5	60	0	0.108	...
13[1]	109.5	36.7	62.3	....	1	0	...	...
	109.5	35.0	64.0	....	2	0	...	...

No. of Expt.	Total iron at the start.	Equilibrium mixtures.			Time. Hours.	Conc. of HNO_3.	K_1.	K_2.
		$Fe(NO_3)_3$.	$Fe(NO_3)_2$.	$AgNO_3$.				
	109.5	36.1	62.9	....	40	0	...	...
	109.5	36.8	62.2	63.1	60	0	0.107	...
14[1]	109.5	36.5	62.4	....	1	0	...	...
	109.5	35.3	63.7	....	2	0	...	...
	109.5	36.1	62.9	....	40	0	...	...
	109.5	37.0	62.0	63.2	60	0	0.106	...
15[1]	108.5	46.6	61.9	62.9	2	0	0.084	...
	108.5	45.9	62.6	63.3	4	0	0.086	...
	108.5	45.7	62.8	63.1	24	0	0.087	...
	108.5	48.7	59.8	65.2	72	0	0.080	...
16	108.5	46.6	61.9	64.2	72	0	0.085	...
17[1,2]	104.3	39.2	65.1	65.9	2	50	0.109	...
	104.3	38.0	66.3	66.1	4	50	0.115	...
	104.3	39.9	64.4	66.1	24	50	0.107	...
	104.3	59.9	44.4	85.7	72	50	0.064	...
18	104.3	39.2	65.1	67.3	72	50	0.112	...
19	123.1	53.9	69.2	70.1	18	0	0.090	...
20	123.1	54.3	68.8	69.9	18	0	0.088	...
21	96.9	38.9	58.0	59.9	40	0	...	0.089
22	96.9	39.8	57.1	58.9	40	0	0.084	...
23	93.5	33.8	59.7	63.7	40	50	...	0.112
24	96.9	38.2	58.7	59.6	18	0	...	0.092
25	96.9	39.5	57.4	58.2	18	0	0.085	...
26[3]	96.9	35.6	61.3	62.7	18	0	...	0.108
27[3]	96.9	40.4	56.5	57.3	18	0	0.080	...
28	94.9	34.8	60.1	62.9	18	50	...	0.109
29	94.9	34.6	60.3	62.1	18	50	0.108	...
30	98.3	40.6	57.7	58.7	18	0	0.083	...
31	98.3	43.5	54.8	60.5	90	0	...	0.078
32	98.3	42.5	55.8	60.7	90	0	0.080	...
33	94.9	34.6	60.3	64.1	90	50	...	0.112
34	94.9	35.6	59.3	67.9	90	50	0.113	...
35	94.9	34.2	60.7	62.3	18	50	...	0.110
36	94.9	34.1	60.8	62.0	18	50	0.110	...
37	98.3	37.1	61.2	61.7	18	0	...	0.102
38	98.3	40.2	58.1	58.8	18	0	0.085	...
39	28.8	4.9	23.9	24.6	18	50	...	0.121
40	28.8	4.9	23.9	24.5	18	50	0.120	...
41	29.8	6.8	23.0	23.3	18	0	...	0.079
42	29.8	7.1	22.7	23.0	18	0	0.074	...
43	38.3	10.1	28.2	28.6	18	0	...	0.080
44	38.3	10.4	27.9	28.3	18	0	0.078	...
45	37.7	7.8	29.9	30.3	18	20	...	0.116
46	37.7	7.8	29.9	30.3	18	20	0.116	...
47[4]	36.9	8.2	28.7	29.2	18	50	...	0.102
48	36.9	7.4	29.5	29.9	18	50	0.119	...
49	36.1	7.7	28.4	30.5	18	80	...	0.113
50	36.1	7.2	28.9	29.5	18	80	0.118	...
51	109.9	39.1	70.8	71.4	1	50	...	0.129
52	109.9	43.6	66.3	66.7	1	50	0.101	...

No. of expt.	Total iron at the start.	Equilibrium mixtures.			Time. Hours.	Conc. of HNO_3.	K_1.	K_2.
		$Fe(NO_3)_3$.	$Fe(NO_3)_2$.	$AgNO_3$.				
53	109.9	40.5	69.4	70.0	2	50	...	0.120
54	109.9	42.6	67.3	67.7	2	50	0.107	...
55	109.9	41.3	68.6	69.4	4	50	...	0.115
56	109.9	42.4	67.5	68.0	4	50	0.108	...
57[5]	95.4	47.6	47.8	108.2	18	50	0.108	...
58[5]	95.4	46.8	48.6	105.9	18	50	...	0.110
59[5]	92.6	44.3	48.3	99.7	18	100	0.109	...
60[5]	92.6	43.0	49.6	100.0	18	100	...	0.115
61[6]	95.4	56.8	38.6	157.2	18	50	0.107	...
62[6]	95.4	58.1	37.3	167.0	18	50	...	0.107
63[7]	142.6	41.3	101.3	42.8	18	50	0.105	...
64[7]	142.6	42.3	100.3	44.0	18	50	...	0.104
65[8]	165.2	42.4	122.8	35.4	18	50	0.103	...
66[8]	165.2	43.9	121.3	36.5	18	50	...	0.101
67[9]	232.5	39.4	193.1	19.9	18	50	0.098	...
68[9]	232.5	41.4	191.1	20.7	18	50	...	0.096

Notes.—In Expts. 1–11, 3 grams of silver were used per 250 cc. of solution. In Expt. 12, 5 grams of silver were used. In Expt. 13, 10 grams of silver were used. In Expt. 14, 15 grams of silver were used. In Expt. 15–68, 10 grams of silver were used.

[1] The bottles were opened and samples were withdrawn for analysis, after which the bottles were put back in the thermostat.

[2] The solution was nearly colorless at the start but at the end of 72 hours it was very dark in color, much darker than in Expt. 15 where no nitric acid was used.

[3] Coarse silver made from silver oxide was used.

[4] The stopper blew out during heating.

[5] About 2 grams of solid silver nitrate were added to each bottle at the start, in order to obtain an excess of silver nitrate in the equilibrium mixture.

[6] About 5 grams of silver nitrate were added.

[7] About 25 cc. of approximately 0.5 molal ferrous nitrate solution were added to each bottle at the start, in order to obtain an excess of ferrous nitrate in the equilibrium mixture.

[8] About 50 cc. of the ferrous nitrate were added.

[9] About 100 cc. of the ferrous nitrate were added.

In Expts. 63–68, the ferrous and ferric nitrate solutions were mixed and analyzed for total iron before the silver was added.

6. Discussion of the Results.

The time required for the reaction to reach equilibrium is dependent to a large extent upon the surface of the silver exposed, and, therefore, upon the fineness of its state of division. For example, by comparing Expts. 26 and 27, in which a rather coarse form of silver was used, with the two preceding experiments, it will be seen that the reaction did not proceed so rapidly in either direction as it did when the finely divided silver was used. In order to determin the most advantageous amount of silver to use, Expts. 12, 13 and 14 were made, using 5, 10 and 15 grams of silver respectively. The formation of ferrous nitrate was taken as a measure of the rate. From the results, it was evident that 10 grams of silver is the best amount to use, since the smaller amount gave a decidedly slower reaction, while the reaction rate with 15 grams was practically the same as that with 10. The small decrease of ferrous concentration found at the end of forty hours was undoubtedly due to oxidation of the ferrous salt, since the bottles had been opened several times, and during the last period of the reaction were only partially filled with the solutions.

As stated earlier, the experiments were generally started in the afternoon and allowed to run all night, giving about 18 hours for the reaction. A series of experiments (51–56) was carried out to determin more exactly the time actually required for reaching equilibrium. The results, taken from the preceding table, are as follows:

		Equilibrium constant at 25°.	
No. of Expt.	Time.	K_1.	K_2.
51 and 52	1 hour.	0.101	0.129
53 and 54	2 hours	0.107	0.120
55 and 56	4 hours	0.108	0.115

From the above results it is seen that the reaction in the direction Ag + $Fe(NO_3)_3 \rightrightarrows$... is much more rapid than that in the opposit direction. In the first direction the equilibrium was very nearly reached in two hours, while in the second, the solution was still a considerable distance from equilibrium at the end of four hours. From this it is seen that the eighteen hours generally given is much more than sufficient for the reaction in the first direction, and it must have been enough also for the reaction in the other direction, since both constants obtained at the end of that time were practically the same.

As previously stated, when the ferric nitrate crystals were dissolved in pure water, the solution was rather dark red in color, and this color became much lighter on the addition of a small amount of nitric acid. With the dark red solutions it was more difficult to obtain reproducible results than with the nearly colorless ones containing free acid. The series of experiments 43 to 50 were made to determin the effect of nitric acid on the equilibrium. The results show that the effect on the equilibrium constant of increasing the concentration of nitric acid is quite marked up to 0.02 *N*, but that the concentration of the acid can then be further increased considerably without appreciable effect. The conclusion was reached, therefore, that the difficulty in obtaining reproducible results from the solutions of ferric nitrate in pure water was due, in part at least, to the small, varying amount of acid in the crystals—an amount too small to prevent appreciable hydrolysis of the ferric salt. The effect was eliminated as far as possible in the later work by dissolving the solid ferric nitrate in 0.05 *N* nitric acid. At this acid concentration the equilibrium mixture was very nearly colorless, showing that in this solution the hydrolysis was very small.

It will be noticed that the value of the constant varies considerably with the salt concentration, being considerably larger in the dilute solutions than in the more concentrated ones. The values of the equilibrium constant are plotted in Figure 1 against the total nitrate concentration.

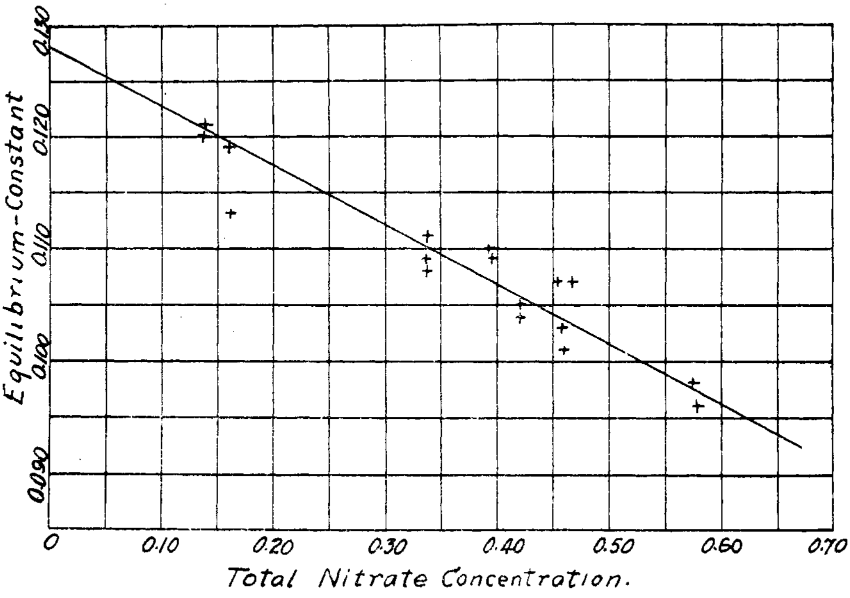

Figure 1.

The best representative graph is seen to be nearly a straight line, and the prolongation of it to zero concentration gives as the value of the ordinate 0.128. This may be considered to be the equilibrium constant at 25° of the ion reaction $Fe^{+++} + Ag = Fe^{++} + Ag^{+}$.

7. The Potential of the Ferrous-Ferric Electrode at 25°.

Maitland[1] has determined the electromotive force of the ferrous-ferric electrode, using ferrous and ferric nitrates for that purpose. The present work was carried out to confirm his results.

The solutions of ferrous and ferric nitrates were prepared as described above. The desired concentrations for the electrode potential measurements were obtained by mixing the calculated amounts of these solutions, each mixture being usually made 0.05 *N* in nitric acid, but in a few cases somewhat less. Three half-cells were charged with each mixture. The check measurements with these agreed with each other within 0.2–0.3 millivolt. The half-cells used were of ordinary form and contained

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[1] *Z. Elektrochem.*, 12, 263 (1906).

electrodes of platinum foil which had a surface of about 7 sq. cm. The cells measured were of the type:

$$\begin{array}{l|l|l|l|l|l} \mathrm{Pt} & \mathrm{Fe(NO_3)_3 + Fe(NO_3)_2} & \text{Saturated or } \tfrac{1}{2} & \text{Normal KCl} & \mathrm{HgCl} & \mathrm{Hg} \\ & + 0.05\ N\ \mathrm{HNO_3} & \text{satur. KCl sol.} & \text{sol.} & & \end{array}$$

The calomel electrode used was compared with a standard calomel electrode which had been carefully prepared for another purpose in this laboratory. For the intermediate liquid a saturated or half-saturated potassium chloride solution was used, in order to eliminate as far as possible the liquid potential.[1]

The values obtained for the electromotive force of the above cell (in the direction in which it is written) are shown in the following table. The results of Maitland are also included in the next to last column. The E_0 values given in the last column were calculated by the equation

$$E = E_0 - 0.059 \log \frac{(\mathrm{Fe^{+++}})}{(\mathrm{Fe^{++}})}$$

the ion concentrations being taken as equal to the salt concentrations, which involves the assumption that the two salts are equally ionized. These E_0 values represent the electromotive force of the electrode when the concentrations of ferrous-ion and ferric-ion are equal.

	Milliformula weights per liter.			Observed e. m. f.			
No.	$\mathrm{Fe(NO_3)_2}$.	$\mathrm{Fe(ON_3)_3}$.	$\mathrm{HNO_3}$.	Sat. KCl (3.50 N).	$\frac{1}{2}$ sat. KCl (1.75 N).	Maitland normal KCl.	Calculated e. m. f. (E_0).
1	50.0	50.0	50.0	—0.4494	—0.4479	—0.4476	—0.4494
2	25.0	25.0	50.0	0.4510	0.4498	0.4480	0.4510
3	12.5	12.5	50.0	0.4531	0.4525	0.4513	0.4531
3*a*	1.0	1.0	50.0	....	....	0.4510	....
4	65.0	40.6	50.0	0.4352	0.4340	....	0.4472
5	25.7	6.4	50.0	0.4131	0.4121	....	0.4487
6	29.3	73.9	50.0	0.4729	0.4723	....	0.4492
7	20.0	20.0	25.0	0.4483	0.4482	0.4515[2]	0.4483
8	10.0	10.0	12.5	0.4519	0.4517	....	0.4519
9	5.0	5.0	6.3	0.4507	0.4506	....	0.4507
10	2.5	2.5	3.2	0.4448	0.4448	....	0.4448
11	17.8	22.3	50.0	0.4619	0.4616	....	0.4561
12	8.9	11.2	50.0	0.4644	0.4642	....	0.4586
13	4.5	5.6	50.0	0.4649	0.4649	....	0.4591
14	2.3	2.8	50.0	0.4634	0.4634	....	0.4576

As will be seen, the difference of the electromotive forces in the case of the saturated and of the half-saturated potassium chloride solutions is less than 1.5 millivolts in every case. It is, therefore, reasonable to assume that in the case of the saturated potassium chloride diffusion-potentials have been practically eliminated. The E_0 values have therefore been calculated from these measurements.

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[1] *Z. physik. Chem.*, 53, 428 (1905).

[2] $\mathrm{HNO_3}$, 10 milli-normal.

It is also to be observed that when allowance is made for the difference in concentration of the potassium chloride solutions, the agreement of the above values with those of Maitland is satisfactory.

As can be seen from the first three measurements, the E_0 value steadily increases with increasing dilution. This is probably due to the fact that at moderate concentrations ferric nitrate is less ionized than ferrous nitrate, while the two ionizations approach equality as the solution becomes more dilute.

In order to determin the effect of concentration, all the E_0 values obtained in the presence of 0.05 N HNO_3 both by Maitland and ourselves were plotted against the total NO_3 concentration; and best values were derived from the plot at certain concentrations or for certain concentration intervals. These values are:

Milli-formula wts. NO_3 per liter.	E. m. f. (N. & B.).	E. m. f. (Maitland).
300	—0.448	—0.448
175	—0.455	—0.448
150	—0.456	...
100–120	—0.454	—0.451
60–75	—0.458	—0.451

It will be seen that there is no indication of a progressive change with the dilution—at any rate below 0.175 N. Taking into account the fact that Maitland's values should probably be increased by at least 2 millivolts to allow for the diffusion-potential, we may adopt —0.456 as the potential of the normal ferrous-ferric electrode.

8. The Potential of the Silver Electrode.

Lewis[1] has determined the potential of the silver electrode. At his suggestion, a slight modification of his method was employed in making the present determination. The side arm of the cell used for the measurements was provided with a three-way stopcock so that the arm which connected the cell with the intermediate liquid could be filled without disturbing the contents of the main cell. The cell was provided with an electrode of sheet platinum which was completely covered with finely divided silver. The cell was then rinsed several times with 0.1 N silver nitrate solution, and was finally completely filled with this solution. It was then placed in the thermostat at 25° and allowed to remain for several hours with frequent shaking, in order to come to equilibrium.

The cell measured was:

$$\text{Ag} \mid 0.10\,N\ \text{AgNO}_3 \mid 0.10\,N\ \text{KNO}_3 \mid 0.10\,N\ \text{KCl} + \text{HgCl} \mid \text{Hg}.$$

The electromotive force, in the direction from left to right, was found to be —0.3992 volt at 25°. Lewis found for the same combination —0.399 volt. The 0.1 N calomel electrode used was measured against

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[1] This Journal, 28, 166 (1906).

a standard normal electrode, the electromotive force being found to be —0.0531.

Diffusion-potentials were calculated by the method of Lewis and Sargent.[1] They found that in the case of two uni-univalent salts having a common ion at the same concentration, the diffusion-potential is equal to 0.059 log (Λ_1/Λ_2), where Λ_1 and Λ_2 are the equivalent conductances of the two salts at the given concentration. In this case at 25°, Λ_{AgNO_3} is 109, Λ_{KNO_3} is 120, and Λ_{KCl} is 129. Hence, the diffusion-potential between $AgNO_3$ and KNO_3 is —0.0025, and that between KNO_3 and KCl is +0.0018, or the sum of the diffusion-potentials for the whole cell is —0.0007. From these data the calculation of the E_0 value is made as follows:

For the cell Ag | 0.10 N $AgNO_3$ | 0.10 N KNO_3 | normal electrode,

$$E = -0.3992 - 0.0531 = -0.4523.$$

Eliminating the diffusion-potentials, we get

$$E = -0.4523 + 0.0007 = -0.4516.$$

Assuming silver nitrate to be 81% ionized in 0.1 N solution, we get

$$E_0 = -0.4516 - 0.059 \log (1/0.081) = \mathbf{-0.5160}$$

as the potential of the silver electrode against normal silver ion.

9. Comparison of the Results of the Equilibrium and the Electromotive Force Measurements.

The chemical reaction, $Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2$, takes place in a cell of the form

$$Pt \mid Fe(NO_3)_3, Fe(NO_3)_2 \mid AgNO_3 \mid Ag.$$

The electromotive force of this cell is, however, the difference of the two single potentials; and these may be expressed by the equations:

$$E^{Fe^{+++}}_{Fe^{++}} = E_0{}^{Fe^{+++}}_{Fe^{++}} - 0.059 \log (Fe^{+++}/Fe^{++}),$$

and

$$E^{Ag} = E_0{}^{Ag} - 0.059 \log (Ag^+).$$

But at equilibrium the electromotive force of the cell, will be zero; that is, $E^{Fe^{+++}}_{Fe^{++}} - E^{Ag} = 0$, and, therefore,

$$0.059 \log \frac{(Ag^+)(Fe^{++})}{(Fe^{+++})} = 0.059 \log K = E_0{}^{Ag} - E_0{}^{Fe^{+++}}_{Fe^{++}} = -0.516 + 0.456.$$

From this equation the equilibrium constant K of the ion reaction $Ag + Fe^{+++} = Ag^+ + Fe^{++}$, is found to be 0.100. This value is in tolerable agreement with the value 0.128, obtained by the analytical method.

Making the calculation in the reverse way (namely, by substituting in the last equation for K the value 0.128 and for $E_0{}^{Ag}$ the value —0.516),

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[1] THIS JOURNAL, 31, 363 (1909).

we find for $E_{0\,\mathrm{Fe}^{++}}^{\mathrm{Fe}^{+++}}$ the value —0.463, instead of the value —0.456 derived from the direct measurements.

10. Summary.

The equilibrium constant at 25° of the reaction

$$Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2$$

has been determined by analysis of the equilibrium mixture. The values of the constant are found to vary considerably with the concentration of the solution. By plotting the values of this constant against the total nitrate concentration and extrapolating to zero concentration, it is found that 0.128 is the value for the expression $\frac{(Fe^{++})(Ag^{+})}{(Fe^{+++})}$, at equilibrium.

The potential of the ferrous-ferric electrode and of the silver electrode at 25° have also been determined. The value —0.456 was found for the former and —0.516 for the latter, these being in good agreement with those previously obtained by Maitland and by Lewis, respectively.

From the equilibrium constant and the potential of the silver electrode, the potential of the ferrous-ferric electrode was calculated to be —0.463, in fair agreement with that derived from the direct electromotive force measurements.

BOSTON, June, 1912.

BENZOIC ACID AS AN ACIDIMETRIC STANDARD.[1]

BY GEORGE W. MOREY.

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The study of the suitability of benzoic acid as a primary standard in acidimetry and alkalimetry was suggested by experience gained in the purification of benzoic acid to be used as a calorimetric standard. During that work it was found that benzoic acid could be titrated with standard alkali to a high degree of accuracy, and that this titration afforded the most rapid and accurate method of comparing the purity of various samples. Since pure benzoic acid has been furnished for some time by the Bureau of Standards as a calorimetric standard, it would, of course, be advantageous to use it also for a standard in acidimetry, if found suitable.

A search of the literature showed that Wagner,[2] in a report presented to the Fifth International Congress of Applied Chemistry, in 1903, had mentioned benzoic acid among a number of other possibilities for the purpose named; and that Phelps and Weed[3] had later included it in a short study of the availability of several organic acids and acid anhydrides.

The method used in studying this problem was that of standardizing

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Proc. Fifth Internat. Cong. Appl. Chem., Berlin, 1, 323 (1903).

[3] *Am. J. Sci.*, 26, 141 (1908).