POTENTIOMETRIC TITRATION OF SODIUM AND POTASSIUM FERROCYANIDE.

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On the potentiometric titration of potassium and sodium ferrocyanide with metallic salts were already reported by many investigators. In 1915, Knauth[1] was studied on the potentiometric titration of potassium ferrocyanide with zinc salt by using zinc electrode as the indicator electrode and he showed that the titration might be made by the potentio-

(1) *Dissert. Dresden* (1915).

metric method. This was confirmed quite independently by Bischowsky,[1] and G. Hedrich[2] concluded that the method gave highly accurate results by the special study of this titration and also Kolthoff and Verzijl[3] was done a special study of the absolute accuracy of the method. Treadwell and Chervet[4] stated that the composition of a metal ferrocyanide depends upon the alkali metal of the ferrocyanide and they found that in titrating zinc with potassium ferrocyanide the composition of ferrocyanide was $K_2Zn_3[Fe(CN)_6]_2$, while with sodium ferrocyanide $Zn_2Fe(CN)_6$.

Hedrich also stated that the break in potential does not occur exactly at the point corresponding to the formation of $K_2CdFe(CN)_6$ in the titration of a cadmium salt with potassium ferrocyanide. Müller and Gabler[5] investigated the titration of lead with ferrocyanide and also they obtained good results when the lead concentration is larger than 0.01 molal. Hedrich studied the titration of potassium ferrocyanide with cupric salt and Niemz[6] with silver salt at 70°C. But Müller showed that the ferrocyanide titration is not suitable for the determination of silver and copper.

In this investigation the potentiometric titration of potassium and sodium ferrocyanide with mercuric chloride, nickel sulphate and cobalt sulphate by using platinum electrode as the indicator electrode at 25°C. were employed.

In the titration of potassium and sodium ferrocyanide with metallic salts, the reactions take place as follows.

$$2Hg^{++} + Fe(CN)_6^{----} = Hg_2Fe(CN)_6 \qquad (1)$$

$$2Ni^{++} + Fe(CN)_6^{----} = Ni_2Fe(CN)_6 \qquad (2)$$

$$2Co^{++} + Fe(CN)_6^{----} = Co_2Fe(CN)_6 \qquad (3)$$

In the above reactions the potential is governed by the following equation by adding a little ferricyanide to the solution and taking bright platinum as the indicator electrode.

$$E = e + 0.0591 \log \frac{[Fe(CN)_6^{---}]}{[Fe(CN)_6^{----}]} \qquad (4)$$

(1) *J. Ind. Eng. Chem.*, **9** (1917), 668.
(2) *Dissert. Dresden* (1915).
(3) *Rec. Trav. Chim.*, **43** (1924), 380; *Z. anorg. Chem.*, **132** (1923), 318.
(4) *Helv. Chim. Acta.*, **5** (1922), 633.
(5) *Z. analyt. Chem.*, **62** (1923), 29.
(6) *Dissert. Dresden* (1920).

From the reactions (1), (2) and (3), we have next equation,

$$[Fe(CN)_6^{----}] = \frac{S_{Me_2Fe(CN)_6}}{[Me^{++}]^2}$$

By substituting this value in equation (4) and taking $[Fe(CN)_6^{---}]$ as a constant, we have

$$E_{Fe(CN)_6} = e' - 0.0591 \times 2P_{Me}$$

Therefore we knew that the ferrocyanide electrode responds to the concentration of metal ions (Ni^{++}, Co^{++}, Hg^{++}).

Experimental Part.

Potassium and sodium ferrocyanide, potassium and sodium ferricyanide, mercuric chloride, nickel suphate and cobaltous sulphate used were of Kahlbaum's. These salts were purified by recrystallization. One-tenth molal solutions of these salts were prepared very carefully.

(1) Titration by Sodium Ferrocyanide with Mercuric Chloride. 10 C.c. of one-tenth molal solution of sodium ferrocyanide and 1 c.c. of one-tenth molal sodium ferricyanide were taken in the half cell and this solution diluted to 100 c.c. with conductance water, and then the half cell was connected with decinormal calomel electrode with decinormal salt bridge. After the cell was kept in a thermostat at 25±0.05°C. for one hour, the electromotive forces of the cell were measured. Then a c.c. of mercuric chloride solution was added from the burette into the half cell and stirred, and then the electromotive force of the cell was measured. The results are summarized in Table 1.

In the above titration, when 5 c.c. of mercuric chloride solution were added to sodium ferrocyanide solution, the solution took green colour. As it can be seen in Table 1 and Fig. 1, we obtained 20.05 c.c. as the end point.

(2) Titration by Mercuric Chloride with Sodium Ferrocyanide. 40 C.c. of one-tenth molal solution of mercuric chloride was taken and this solution was diluted to 100 c.c. with conductivity water, and then the titration was done by the one-tenth molal solution of sodium ferrocyanide. The results are summarized in Table 2.

In Table 2 and Fig. 1, we obtained 20.02 c.c. as the maximum point. During the titration, the solution changed yellow to blueish green. We had very good agreement with each other.

Table 1.

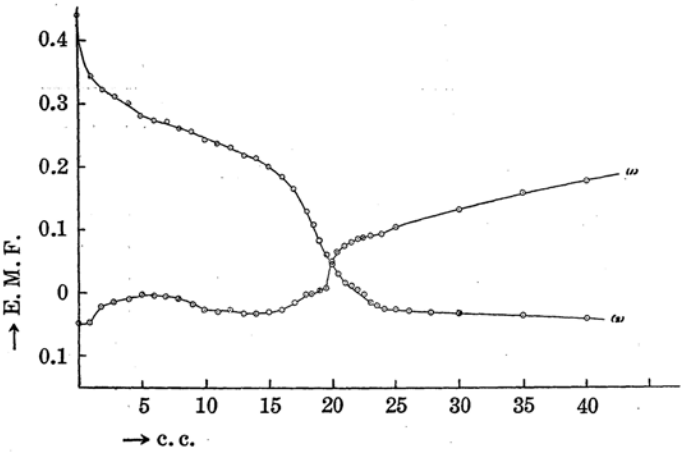
C.c. of $HgCl_2$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.04616	
		1150
2	.02316	
		997
3	.01319	
		519
4	.00800	
		172
5†	.00628	
		158
6	.00470	
		162
7	.00632	
		104
8	.00736	
		917
9	.01653	
		939
10	.02592	
		333
11	.02925	
		185
12	.02740	
		744
13	.03484	
		484
14	.03000	
		150
15	.02850	
		225
16	.02625	
		1000
17	.01625	
		763
18	.00862	
		1535
19	+.00125	
		3699
20	.04920	
		3918*
20.5	.06605	
		1850
21	.07530	
		1020
21.5	.08040	
		860
22	.08470	
		610
22.5	.08775	
		450
23	.09000	
		384
24	.09384	
		316
25	.09700	
		808
30	.13742	
		400
35	.15742	
		250
38	.16745	
		327
40	.17400	

† Green colour.
* Maximum point.
Experimental value 20.05 c.c.

Table 2.

C.c. of $Na_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.43690	
		9645
1	.34045	
		2045
2	.32000	
		1150
3	.30850	
		850
4	.30000	
		800
5	.29200	
		680
6	.28520	
		425
7	.28095	
		829
8	.27266	
		726
9	.26540	
		1394
10	.25146	
		497
11	.24649	
		729
12	.23920	
		955
13	.22965	
		1190
14	.21775	
		1425
15	.20350	
		1990
16	.18360	
		2000
17	.16360	
		2730
18	.13630	
		3660
18.5	.11800	
		4470
19	.09395	
		4690
19.5	.07050	
		4732
20	.04574	
		5038*
20.5	.02055	
		1250
21	.01430	
		954
21.5	.00953	
		808
22	.00549	
		549
23	.00000	
		1520
24	−.01520	
		345
25	.01865	
		541
26	.02406	
		228
30	.03320	
		69
35	.03665	
		41
40	.03870	

* Maximum point.
Experimental value 20.02 c.c.



(1) with mercuric chloride titrated
(2) with $Na_4Fe(CN)_6$ titrated

Fig. 1.

(3) Titration by Nickel Sulphate with Potassium Ferrocyanide. 20 C.c. of one-tenth molal solution of nickel sulphate was taken in the half cell and diluted to 100 c.c. with conductivity water and then titrated with 0.1 molal solution of potassium ferrocyanide after the cell was kept in a thermostat at 25±0.05°C. for one hour. The results are summarized in Table 3. In this case we obtained 10.06 c.c. at the maximum point. The ratio of Ni to ferrocyanide is 1.98:1.

(4) Titration by Potassium Ferrocyanide with Nickel Sulphate. 5 C.c. of one-tenth molal potassium ferrocyanide solution and 0.5 c.c. of one-tenth molal solution of potassium ferricyanide were taken in the half cell and the solution diluted to 100 c.c. and then this solution titrated with nickel sulphate solution. The results are shown in Table 4. As it can be seen in the Table 4 and Fig. 2, we obtained 9.95 c.c. as the maximum point. This value is very good agreement with other.

(5) Titration by Potassium Ferrocyanide with Cobaltous Sulphate. 5 C.c. of one-tenth molal solution of potassium ferrocyanide and 0.5 c.c. of one-tenth molal solution of potassium ferricyanide were taken and the mixed solution was diluted to 100 c.c. with conductivity water, and then titrated with one-tenth molal solution of cobaltous sulphate. The results are summarized in Table 5. As it can be seen in the Table 5 and Fig. 3, we obtained 10.02 as the maximum point. Therefore the ratio of Co to ferrocyanide is 1: 2.004.

Table 3.

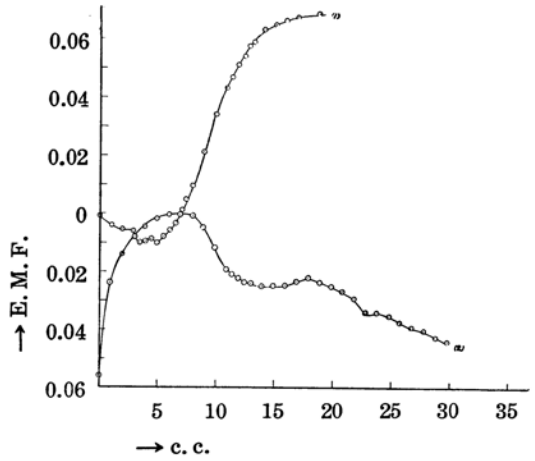
C.c. of $K_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.05585	
		3190
1	.02395	
		1009
2	.01386	
		706
3	.00680	
		182
4	.00498	
		300
5	.00198	
		136
6	.00062	
		37
7	.00025	
		—
8	.00025	
		255
8.5	.00280	
		368
9	.00464	
		600
9.5	.00764	
		800
10	.01164	
		884*
10.5	.01606	
		700
11	.01956	
		344
11.5	.02128	
		268
12	.02262	
		45
13	.02307	
		93
14	.02400	
		50
15	.02450	
		125
16	.02420	
		100
17	.02320	
		32
18	.02288	
		179
19	.02467	
		80
20	.02547	
		222
21	.02767	
		200
22	.02967	
		513
23	.03480	
		—
24	.03480	
		100
25	.03580	
		315
26	.03895	
		177
27	.04072	
		200
28	.04272	
		106
29	.04378	
		99
30	.04477	

* Maximum point.
Experimental value 10.06 c.c.

Table 4.

C.c. of $NiSO_4$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.000225	
		3375
1	.003600	
		2220
2	.005820	
		285
3	.005535	
		8310
3.5	.009690	
		2000
4	.008690	
		360
4.5	.008370	
		1368
5	.009554	
		4278
5.5	.007415	
		4652
6	.005089	
		2178
6.5	.004000	
		8000
7	.000000	
		9000
7.5	+0.004500	
		9000
8	.009000	
		10000
8.5	.014000	
		11100
9	.019550	
		11150
9.5	.025125	
		13750*
10	.032000	
		13020
10.5	.038510	
		10980
11	.044000	
		6000
11.5	.047000	
		8000
12	.051000	
		6000
13	.057000	
		6111
14	.063111	
		2689
15	.065800	
		—
16	.065800	
		2000
17	.067800	
		3800
18	.068184	
		1331
19	.069525	
		—
20	.069525	

* Maximum point.
Experimental value 9.95 c.c.



(1) with $NiSO_4$ titrated
(2) with $K_4Fe(CN)_6$ titrated

Fig. 2.

(6) Titration by Cobaltous Sulphate with Potassium Ferrocyanide. 20 C.c. of one-tenth molal cobaltous sulphate solution were taken and diluted to 100 c.c. with conductance water and then titrated one-tenth molal potassium ferrocyanide at 25±0.05°C. We obtained the results shown in Table 6. We obtained 9.98 c.c. as the maximum point from the Table 6 and Fig. 3. Hence we knew that the ratio of Co to ferrocyanide is corresponding to 1 : 1.996.

(7) Titration by Potassium and Sodium Ferrocyanide with Ferric Chloride and Silver Nitrate. As already mentioned above, we studied the potentiometric titration by potassium and sodium ferrocyanide with metallic salts. In the following experiments, the potentiometric titration compared with potassium and sodium ferrocyanide by the solutions of ferric chloride and silver nitrate at the same condition or different condition.

Ferric chloride and silver nitrate used were of Kahlbaum's. These salts were purified by washing with conductance water and then each 0.1 molal solution was prepared very carefully.

At first the potentiometric titration was carried out with 0.1 molal solution of potassium and sodium ferrocyanide by 0.1 molal solution of ferric chloride and at the second by 0.1 molal solution of silver nitrate. Each 10 c.c. of 0.1 molal solution of potassium and sodium

Table 5.

C.c. of $CoSO_4$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	−0.00108	
		49
1	.00157	
		27
2	.00185	
		185
3	.00000	
		—
4	.00000	
		102
5	+0.00102	
		274
6	.00376	
		124
7	.00500	
		300
8	.00800	
		200
8.5	.00900	
		210
9	.01010	
		380
9.5	.01200	
		390
10	.01395	
		510*
10.5	.01750	
		300
11	.01900	
		200
11.5	.02000	
		150
12	.02150	
		120
13	.02270	
		243
14	.02513	
		282
15	.02795	
		165
16	.02950	
		304
17	.03254	
		200
18	.03454	
		117
19	.03571	
		168
20	.03739	
		201
25	.03940	
		60
30	.04000	

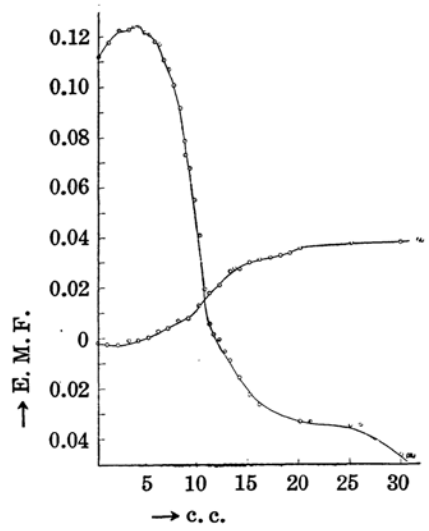
* Maximum point.
Experimental value 10.02 c.c.

Table 6.

C.c. of $K_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.11565	
		535
1	0.12100	
		560
2	0.12660	
		—
3	.12660	
		130
3.5	.12790	
		—
4	.12790	
		550
4.5	.12515	
		180
5	.12425	
		540
5.5	.12155	
		310
6	.12000	
		1280
6.5	.11360	
		580
7	.11070	
		1410
7.5	.10365	
		1900
8	.09415	
		2850
8.5	.08090	
		2180
9	.07000	
		2590
9.5	.05705	
		4902*
10	.03254	
		2508
10.5	.02000	
		2800
11	.00600	
		800
11.5	.00200	
		400
12	.00000	
		1000
12.5	−0.00500	
		800
13	.00900	
		700
14	.01600	
		750
15	.02350	
		430
16	.02780	
		163
20	.03434	
		53
25	.03550	
		253
30	.04765	

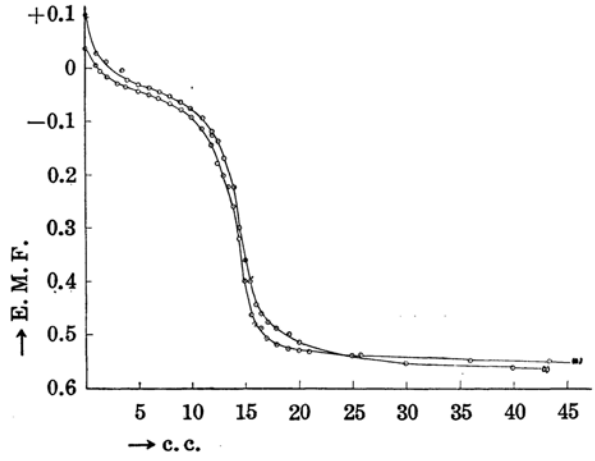
* Maximum point.
Experimental value 9.98 c.c.

ferrocyanide and 1 c.c. of 0.1 molal solution of potassium and sodium ferricyanide were taken and these solutions diluted to 100 c.c. with conductance water and then each solution was titrated by 0.1 molal solution of ferric chloride. The platinum electrode was used as the indicator electrode. The results are summarized as Tables 7 and 8.



(1) with $CoSO_4$ titrated
(2) with $K_4Fe(CN)_6$ titrated

Fig. 3.



(1) with $Na_4Fe(CN)_6$ titrated
(2) with $K_4Fe(CN)_6$ titrated

Fig. 4.

Table 7.

Titration by $K_4Fe(CN)_6$ with Ferric Chloride

C.c. of $FeCl_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.04566	
		3460
1	.01106	
		31
2	−0.01075	
		1274
3	.02349	
		783
4	.03132	
		694
5	.03826	
		714
6	.04540	
		866
7	.05406	
		818
8	.06224	
		1096
9	.07320	
		1560
10	.08880	
		1906
11	.10786	
		3486
12	.14272	
		3286
12.5	.17555	
		4070
13	.19590	
		4564
13.5	.21872	
		7816
14	.25780	
		12004
14.5	.31782	
		16000*
15	.39782	
		13216
15.5	.46390	
		3220
16	.48000	
		1900
16.5	.48950	
		3644
17	.50772	
		1038
18	.51810	
		850
19	.52660	
		175
21	.53010	
		261
26	.54132	
		69
36	.54825	
		27
46	.55000	

* Maximum point
Experimental value 14.62 c.c.

Table 8.

Titration by $Na_4Fe(CN)_6$ with Ferric Chloride

C.c. of $FeCl_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.10500	
		6977
1	.03523	
		1736
2	.01787	
		1577
3	.00210	
		1985
4	−0.01775	
		896
5	.02671	
		659
6	.03330	
		670
7	.04000	
		972
8	.04972	
		973
9	.05945	
		1435
10	.07380	
		1620
11	.09000	
		2570
12	.11570	
		3450
12.5	.13295	
		6520
13	.16555	
		5474
13.5	.19292	
		5196
14	.21890	
		16000*
14.5	.29890	
		12302
15	.36041	
		8658
15.5	.40370	
		8000
16	.44370	
		4600
16.5	.46670	
		2340
17	.47840	
		1610
18	.48645	
		1355
19	.50000	
		1514
20	.51514	
		1266
21	.52780	
		412
25	.54450	
		200
30	.55450	
		111
40	.56566	

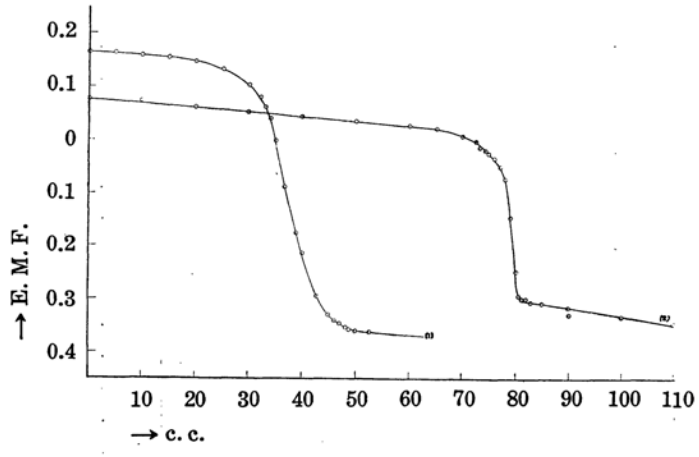
* Maximum point
Experimental value 14.60 c.c.

As it was shown in Tables 7 and 8 and Fig. 4, the electromotive force in the case of sodium ferrocyanide was very little greater than that of potassium ferrocyanide before 25 c.c. of ferric chloride solution were added to potassium and sodium ferroyanide solution, but after 25 c.c. of ferric chloride solution were added to each solution, the former electromotive force was a little lower. However the maximum value of each case was nearly same. That is, the value for sodium ferrocyanide was 14.60 c.c. and for potassium ferrocyanide 14.62 c.c. Therefore each reaction will take place as follows.

$$3Na_4Fe(CN)_6+4FeCl_3 = Fe_4[Fe(CN)_6]_3+12NaCl$$

$$3K_4Fe(CN)_6+4FeCl_3 = Fe_4[Fe(CN)_6]_3+12KCl$$

The following potentiometric titrations were carried out by the different conditions. That is, 20 c.c. of 0.1 molal solution of sodium ferrocyanide and 10 c.c. of 0.1 molal solution of potassium ferrocyanide were taken and then 1 c.c. of 0.1 molal solution of sodium ferricyanide and potassium ferricyanide were added to each solution. These solutions were titrated with 0.1 molal solution of silver nitrate. The results are summarized in Tables 9 and 10. As it is shown in Fig. 5, each curve was of the same type and we obtained 39.35 c.c. and 78.80 c.c. at the above titration. Therefore the difference of c.c. at the maximum



(1) with $K_4Fe(CN)_6$ titrated
(2) with $Na_4Fe(CN)_6$ titrated

Fig. 5.

Table 9.

Titration by $Na_4Fe(CN)_6$ with Silver Nitrate

C.c. of $AgNO_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.07441	
		4
10	.07397	
		147
20	.05925	
		82
30	.05104	
		10
40	.04000	
		47
50	.03525	
		78
60	.02740	
		133
65	.02074	
		214
70	.01000	
		500
72	.00000	
		1580
73	−0.01580	
		698
74	.02278	
		367
75	.02645	
		1020
76	.03665	
		1171
77	.04836	
		1039
77.5	.05875	
		2770
78	.07260	
		6774
78.5	.10647	
		10878*
79	.16086	
		9698
79.5	.20935	
		8000
80	.24935	
		7890
80.5	.28880	
		2280
81	.30020	
		198
81.5	.30119	
		—
82	.30119	
		475
83	.30594	
		—
84	.30594	
		—
85	.30594	
		210
90	.31745	
		170
100	.33445	
		131
110	.34760	

* Maximum point
Experimental value 78.80 c.c.

Table 10.

Titration by $K_4Fe(CN)_6$ with Silver Nitrate

C.c. of $AgNO_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.16385	
		90
5	.15934	
		80
10	.15530	
		53
15	.15265	
		78
20	.14875	
		450
25	.12846	
		465
30	.10520	
		1090
32	.08340	
		2128
33	.06212	
		3132
34	.03080	
		3080
35	.00000	
		3730
36	−0.03730	
		5045
37	.08775	
		5191
38	.13966	
		5468
38.5	.16700	
		5632
39	.19516	
		6778*
39.5	.22905	
		4000
40	.24905	
		2164
43	.31399	
		1147
45	.33694	
		901
46	.34595	
		215
47	.34810	
		760
48	.35655	
		789
49	.36444	
		—
50	.36444	

* Maximum point
Experimental value 39.35 c.c.

point was 0.1 c.c. and also the ratio of silver to ferrocyanide is corresponding to 1 : 3.935 or 1 : 3.940. Hence we knew that the reaction takes place in each case as follows.

$$4Ag^{+} + Fe(CN)_6^{----} = Ag_4Fe(CN)_6$$

Summary.

(1) The potentiometric titrations of potassium and sodium ferrocyanide with mercuric chloride, nickel sulphate and cobaltous sulphate by using platinum electrode as an indicator electrode were studied at 25°C.

(2) From the above titration we found that the reactions take place as follows.

$$2Hg^{++} + Fe(CN)_6^{----} = Hg_2Fe(CN)_6$$

$$2Ni^{++} + Fe(CN)_6^{----} = Ni_2Fe(CN)_6$$

$$2Co^{++} + Fe(CN)_6^{----} = Co_2Fe(CN)_6$$

(3) Also the potentiometric titrations were compared with potassium and sodium ferrocyanides by ferric chloride and silver nitrate solution at the same condition or different conditions, and a very good agreement was found with each other.

(4) In this titration we found that the reaction takes place as reported already by Niemz[1] at the case of silver and in other case as follows:

$$4Ag^{+} + Fe(CN)_6^{----} = Ag_4Fe(CN)_6$$

$$4Fe^{+++} + 3Fe(CN)_6^{----} = Fe_4[Fe(CN)_6]_3.$$

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(1) Niemz, Dissert. Dresden (1920).