Summary

1. The heat capacities of zinc and cadmium oxide from 70 to 300° Kelvin have been determined.

2. The entropy of zinc oxide at 298°K. is 10.28 ± 0.05 cal./mole/degree, and of cadmium oxide is 13.17 ± 0.1 cal./mole/degree.

3. For zinc oxide we find from an accurate value of the free energy and the entropy of formation $\Delta H = -83{,}130 \pm 100$, and for cadmium oxide we find from the entropy of formation and a somewhat uncertain value of the heat of formation, $\Delta F^\circ_{298} = -54{,}200$.

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THE EQUILIBRIUM $2K_3Fe(CN)_6 + 2KI \rightleftarrows 2K_4Fe(CN)_6 + I_2$ IN AQUEOUS POTASSIUM CHLORIDE SOLUTIONS

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I. Introduction

This paper comprises one phase of a study of the kinetics of ionic reactions which proceed to a measurable equilibrium state, the purpose of the study being to investigate the velocity of the reaction not only in its initial stages but also in the neighborhood of equilibrium.

The reaction between ferricyanide and iodide ions yielding ferrocyanide and iodine, as follows

$$2Fe(CN)_6^{---} + 2I^- \rightleftharpoons 2Fe(CN)_6^{----} + I_2 \qquad (1)$$

possesses certain advantages for such a study since

1. The reaction reaches an equilibrium state after 2–13% conversion, depending upon the composition and the amount and character of added neutral salts. The equilibrium state is therefore accessible to experimental measurement and is well adapted for a study of salt effects.

2. The velocity of the reaction is also highly sensitive to neutral salt catalysis, a subject of considerable theoretical interest at the present time.[1]

3. Previous studies[2,3,4] have shown that the velocity of the reaction, unlike most reversible ionic reactions, is of a magnitude that can be followed.

In the investigations of Donnan and Le Rossignol,[2] Just[3] and Wagner,[4] the reaction was followed by adding measured amounts of thiosulfate and

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[1] For a critical discussion see J. N. Brönsted, "Acid and Basic Catalysis," Copenhagen, **1926**, translated from the Danish by the authors for *Chemical Reviews*, September, 1928, particularly Chapters 4 and 5 and appendix.

[2] Donnan and Le Rossignol, *J. Chem. Soc.*, **83**, 703 (1903).

[3] Just, *Z. phys. Chem.*, **63**, 513 (1908).

[4] Wagner, *ibid.*, **113**, 261 (1924).

starch and noting the time of appearance of the blue color. Although this very simple technique, known as the compensation method of Harcourt and Esson,[5] has the advantage of continuously regenerating the iodide ion as fast as it is converted to iodine by ferricyanide, so that the concentration of iodide is constant throughout the course of the reaction, it is impossible to study the equilibrium state by this method since the reaction is forced to completion by the addition of thiosulfate.

We have accordingly adopted the method of titrating the liberated iodine in aliquots removed at definite time intervals. The kinetic measurements will be reported later and only data on the equilibrium state and its relation to the component potentials of the ferro–ferricyanide and iodine–iodide systems will be considered in the present paper.

II. The Equilibrium Constant in Salt Solutions

The thermodynamic mass action function for Reaction (1) may be written as follows

$$\frac{c^2_{\mathrm{Fe(CN)_6^{----}}} \cdot c_{\mathrm{I_2}}}{c^2_{\mathrm{Fe(CN)_6^{---}}} \cdot c^2_{\mathrm{I^-}}} \times \frac{f^2_{\mathrm{Fe(CN)_6^{----}}} \cdot f_{\mathrm{I_2}}}{f^2_{\mathrm{Fe(CN)_6^{---}}} \cdot f^2_{\mathrm{I^-}}} = K_a \tag{2}$$

$$K_c \times K_f = K_a \tag{3}$$

where c refers to the stoichiometric concentration and f to the stoichiometric activity coefficient of the participating components. K_a is a true constant for any given temperature and pressure and is independent of changes in concentration. The value of K_a is calculated in Section (V). To avoid the cumbersome quotients the abbreviated symbols given in (3) corresponding to (2) are introduced.

From what is known of the behavior of the activity coefficient as a function of valence and the total electrolyte concentration in dilute solution,[6] it is evident that the ratio

$$K_f = f^2_{\mathrm{IV}} \cdot f_0 / f^2_{\mathrm{III}} \cdot f^2_{\mathrm{I}} \tag{4}$$

where the roman subscripts refer to the valences of the ions involved in (1) and (2), should presumably decrease with increasing salt concentration, which means that the equilibrium state will be displaced to the right. Constant values for the stoichiometric equilibrium "constant" K_c therefore can only be expected when the ratio of the coefficients in (4) is constant, that is, when a constant thermodynamic environment[7] is maintained.

Although measurements exist for computing an estimate of the change of the component activity coefficients in K_f as a function of salt concen-

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[5] Harcourt and Esson, *Phil. Trans.*, **157**, 117 (1867).

[6] For a review of this subject and for references to previous literature see La Mer, *Trans. Am. Electrochem. Soc.*, **51**, 507–556 (1927).

[7] See Washburn, "Principles of Physical Chemistry," 2d ed., McGraw-Hill Book Company, **1921**, pp. 268, 321, for a clear presentation of the meaning and influence of this factor in both equilibrium and kinetic measurements; also Washburn and Strachan, THIS JOURNAL, **35**, 710 (1913).

tration, in no case do the measurements correspond to the exact environment which is produced by the simultaneous presence of both systems, and particularly for concentrated solutions.

In their studies on the equilibrium

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2^- \qquad (5)$$

Brönsted and Kai Pedersen[8] showed that a constant environment could be obtained by the addition of an excess of neutral salt. They found 1.65 *M* KCl + 0.1 *M* HCl to be sufficient for the conditions under which they studied their reaction.

In view of its importance for our further studies, it seemed desirable to determine whether or not the general principle enunciated by Brönsted,[9] namely, "That the simple gas laws hold good for ions or salts when other salt solutions are employed as solvents, the concentration being large in comparison with the concentration of the dissolved ion or ions," would also hold good for the present reaction where tri- and tetravalent ions were involved and at considerably higher concentrations than those employed in the experiments of Brönsted and Pedersen.[8] The highly specific behavior[10,11] of ferro- and ferricyanides in dilute solutions makes it especially desirable to test the principle with these ions.

III. Experimental Procedure

Weighed amounts of potassium ferricyanide corresponding to the concentrations given in Col. 2 of the tables were dissolved in boiled distilled water in a volumetric flask, calibrated to deliver 50 cc., and immersed in a thermostat at 25°. The potassium iodide and potassium chloride (also potassium ferrocyanide in Expts. 21 and 22) were weighed out, dissolved in 250 cc. of distilled water and brought to 25° in a 500cc. Erlenmeyer flask. When both solutions had acquired the temperature of the bath, the reaction was started by adding the 50 cc. of ferricyanide solution to the potassium iodide. A series of Erlenmeyer flasks containing definite amounts of $N/100$ $Na_2S_2O_3$, weighed out from a weight buret and diluted to 125 cc. with boiled water containing 0.08 g. of dissolved starch, were in readiness before the start of the reaction. Samples were withdrawn at 2.5-minute intervals in a 10cc. measuring pipet calibrated to a 0.1cc. graduation and allowed to flow rapidly into these flasks until the color change due to iodine was retained on stirring.

From four to six titrations were made on the system after equilibrium was reached and the average was recorded in Col. 8 of the tables in terms of the concentration of potassium ferrocyanide formed. The maximum deviation from the average was about 0.3%. It required about forty to sixty minutes to reach equilibrium in the presence of excess potassium chloride and a somewhat longer time in its absence.

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[8] Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

[9] Brönsted, *Medd. Vetenskapsakad. Nobelinst.*, **5**, No. 25 (1919), (in English). See also *Kgl. Danske Videnskab. Selsk. Skrifter naturvidenskab. Math. Afdel.*, [7], XII, 241 (1914); *ibid., Math.-fys. Medd.*, III, 9 (1920), and reference 6, p. 519–521.

[10] La Mer and Mason, This Journal, **49**, 410 (1927).

[11] G. N. Lewis, *Z. physik. Chem.*, **70**, 212 (1909), points out that the classical dissociation constant of potassium ferricyanide changes about one million fold in passing from 0.0001 *M* to 1.0 *M*.

There are several factors which contribute to make this method an accurate one for determining the concentrations at equilibrium. The forward reaction is of the second and first orders, respectively, for iodide and ferricyanide. Fifteen-fold dilution alone is thus amply sufficient to check the reaction. Furthermore, this dilution displaces the equilibrium almost completely to the left and the instantaneous removal of iodine by the thiosulfate prevents the reverse reaction from proceeding. That this is really the case was proved by allowing samples at the titration end-point to stand overnight. No perceptible color change occurred.

All salts employed were of C. P. grade and the potassium ferricyanide was recrystallized twice from water. The potassium chloride used in Expts. 1 to 16 was recrystallized twice.

IV. Discussion of Results

The Tri-iodide Equilibrium

Cols. 5, 6 and 7 of Table I give the concentrations of the solutions, respectively, in terms of the sum of the KI and KCl, the total equivalent concentration or ΣK, and the ionic strength μ defined as $\mu = {}^1/_2\ \Sigma c_i z_i^2$. Since the concentrations of I_2 and I^- are influenced by the well-known equilibrium

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (6)$$

the amount of iodine titrated is recorded in Col. 9 in terms of its stoichiometric equivalent potassium ferrocyanide.

In the most recent investigations for the constant

$$L = \frac{c_{I^-} \cdot c_{I_2}}{c_{I_3^-}} \cdot \frac{f_{I^-} \cdot f_{I_2}}{f_{I_3^-}} \qquad (7)$$

is given as 0.00153 for water as solvent by Bray and MacKay,[12] whereas Brönsted and Pederson found 0.00502 at 15° and 0.00540 at 18.5°, and give an extrapolated value of 0.00611 for 25° using 1.65 M KCl + 0.1 M HCl as solvent. The latter value appears to be quite trustworthy and was used in all the further calculations.

By applying the law of mass action to Equations 1 and 6, the following expression for the concentration of the complex ion I_3^- results

$$c_{I_3^-} = \frac{b + L - x/2 - \sqrt{(b + L - x/2)^2 - 2\,x\,(b - x)}}{2} \qquad (8)$$

where b = initial concentration of KI, x = concentration of $K_4Fe(CN)_6$ formed, and $x/2$ = concentration of I_2 formed.

It is at once apparent from the I_3^- values tabulated in Col. 9 of the table that almost all of the iodine formed exists in the form of the complex ion, since the values in Col. 8 are only a little more than twice those of Col. 9. For this reason it is more convenient to compute the equilibrium constant (Col. 11)

$$K_c' = \frac{x^2 \cdot c_{I_3^-}}{(a - x)^2(b - x - c_{I_3^-})^3} \qquad (9)$$

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[12] Bray and MacKay, THIS JOURNAL, **32**, 914 (1910).

TABLE I

$K'_a = 0.199 \times 10^{-3}$

(Expts. 27–33 by Mr. W. G. Parks)

Expt.	$C_{K_3Fe(CN)_6}$	C_{KI}	C_{KCl}	$C_{KI} + C_{KCl}$	Equiv. concn., ΣK	μ	$C_{K_4Fe(CN)_6} \times 10^3$ formed	$C_{I_3^-} \times 10^3$	% conv. of ferricyanide	$K'_c \times 10^3$	K'_f
1	0.10	0.25	...	0.25	0.55	0.85	5.486	2.674	5.49	0.637	0.312
2	.10	.20	...	.20	.50	.80	4.104	1.989	4.10	.500	.398
3	.075	.20	...	.20	.425	.65	3.240	1.570	4.32	.430	.463
4	.075	.15	...	.15	.375	.60	2.236	1.071	2.98	.320	.622
5	.075	.20	1.00	1.20	1.425	1.65	6.685	3.240	8.91	4.52	.0440
6	.075	.20	1.00	1.20	1.425	1.65	6.664	3.230	8.89	4.47	.0445
7	.075	.20	1.00	1.20	1.425	1.65	6.674	3.232	8.90	4.49	.0443[a]
8	.075	.175	1.025	1.20	1.425	1.65	5.864	2.829	7.82	4.43	.0449
9	.075	.15	1.05	1.20	1.425	1.65	5.087	2.433	6.78	4.45	.0447
10	.10	.25	0.80	1.05	1.35	1.65	9.763	4.754	9.76	4.26	.0467
11	.10	.25	.875	1.125	1.425	1.675	10.120	4.930	10.12	4.82	.0413
12	.10	.25	.825	1.075	1.375	1.625	9.882	4.815	9.88	4.44	.0448
13	.10	.20	.875	1.075	1.375	1.625	8.014	3.877	8.01	4.42	.0450
14	.10	.15	.925	1.075	1.375	1.625	6.113	2.927	6.11	4.43	.0449
15	.05	.20	1.125	1.325	1.475	1.625	5.230	2.533	10.46	4.86	.0409
16	.05	.20	1.075	1.275	1.425	1.575	5.103	2.474	10.20	4.48	.0444
17	.05	.15	1.125	1.275	1.425	1.575	3.915	1.876	7.83	4.51	.0441
18	.05	.15	0.50	0.65	0.80	0.95	2.711	1.302	5.42	1.38	.144
19	.05	.20	.45	.65	.80	.95	3.650	1.768	7.30	1.49	.134
20	.05	.10	.55	.65	.80	.95	1.793	0.842	3.58	1.25	.159
21	.10	.15	.925	1.075	1.387	1.705	4.402	2.110	4.40	4.29	.0464[b]
22	.05	.20	1.075	1.275	1.437	1.605	3.512	1.702	7.02	4.52	.0440[b]
23	.075	.20	2.00	2.20	2.425	2.65	9.963	4.824	13.28	17.8	.0112
24	.075	.10	1.90	2.00	2.225	2.45	4.775	2.240	6.37	12.9	.0154
25	.075	.15	1.95	2.10	2.325	2.55	7.448	3.568	9.93	16.2	.0123
26	.075	.20	1.00	1.20	1.425	1.65	7.214	3.497	9.60	5.84	.034[c]
27	.075	.20	2.00	2.20	2.425	2.65	9.85	4.77	13.13	17.11	.0116[d]
28	.075	.10	2.10	2.20	2.425	2.65	5.09	2.388	6.79	16.0	.0125[d]
29	.10	.20	1.925	2.125	2.425	2.725	12.00	5.808	12.00	17.8	.0112[d]
30	.10	.20	1.85	2.05	2.35	2.65	11.73	5.68	11.73	16.5	.0121[d]
31	.075	.20	1.00	1.20	1.425	1.65	6.63	3.21	8.84	4.39	.0453
32	.075	.20	1.00	1.20	1.425	1.65	7.26	3.52	9.68	5.97	.0333[e]
33	.075	.20	1.00	1.20	1.435	1.66	10.20	4.93	13.60	19.33	.0103[f]

[a] 2×10^{-4} *M* HCl. [b] 0.003 *M* $K_4Fe(CN)_6$. [c] 1.73×10^{-3} *M* HCl.

[d] Average of two experiments.

[e] 0.001 *M* HCl.

[f] 0.01 *M* HCl.

corresponding to the reaction

$$2Fe(CN)_6^{---} + 3I^- \rightleftharpoons 2Fe(CN)_6^{----} + I_3^- \qquad (10)$$

where a = initial concentration of ferricyanide. The mass action function for (10) will be designated by primes to distinguish it from (3); namely,

$$K'_c \cdot K'_f = K'_a \text{ where } K'_f = \frac{f^2_{IV}}{f^2_{III}} \cdot \frac{f_{I_3^-}}{f^3_{I^-}} \qquad (11)$$

The equilibrium constants for the original Equation 1 can be obtained when desired by multiplying the figures in Col. 11 with the appropriate value of L for the solvent employed. We have not done this because systematic studies on the variation of L for potassium chloride additions have not been made. That L changes markedly when chlorides are added is evident from the values given by Bray and MacKay and by Brönsted and Pedersen. For an accurate calculation the L value used in (8) should of course correspond with the measured value for the particular solvent employed. However, we have proved to our satisfaction that the $c_{I_3^-}$, as computed from (8), is not appreciably affected by using either the Bray or the Brönsted value. For example, $10^3K'_c$ in Expts. 1 and 23 is changed from 0.637, and 17.8 to 0.649, and 18.3 when L is assigned the values 0.00611 and 0.00143, respectively. Since the μ value of 1.65 lies intermediate in our range of salt concentrations, the value $L = 0.00611$ is more appropriate for the calculations in Tables I and II.

A comprehensive study of the behavior of L in salt solutions, particularly the halides, by the method given by Brönsted and Pedersen, is needed since this constant enters into the interpretation of all kinetic and equilibrium studies involving iodine.

V. Determination of K_a and K'_a from e.m.f. Data

Although we cannot measure K'_c at sufficient dilution to extrapolate safely to infinite dilution to determine K'_a, we can by a combination of existing free energy data arrive at what should be very trustworthy values for K'_a and K_a.

Linhart's[13] careful measurements on the cell

$$\text{Hg, Hg Cl (S)} + \text{KCl (M)}, \left(\begin{matrix}\text{K}_3\text{Fe(CN)}_6(\text{c}_1)\\ \text{K}_4\text{Fe(CN)}_6(\text{c}_2)\end{matrix} + \text{KCl (M)}\right)\text{Au} \qquad (12)$$

give, when corrected for the activity of potassium chloride as Linhart has done using the measurements of Harned, the free energy of the reaction

$$\text{Hg (S)} + \text{Fe (CN)}_6^{---} + \text{Cl}^- = \text{Fe(CN)}_6^{--} + \text{HgCl (S)} \qquad (13)$$

$$\mathbf{E}_0 = 0.2188 \pm 0.0002;\ \Delta F^\circ_{298.1} = -5049 \pm 5$$

In these experiments no liquid junction potential exists since the potassium chloride was in great excess and of the same concentration in both half-cells. Eight molalities of potassium chloride were used, ranging between 0.05 M and 4.284 M. The concentration ratio c_1/c_2 was varied between 2 to $^1/_2$ and $(c_1 + c_2)$ between 0.0005 to 0.02 M at the highest concentrations of potassium chloride.

When the concentration of potassium chloride was greater than 0.1 M, Linhart found that the activities of potassium ferrocyanide and potassium ferricyanide were proportional to their concentrations, a result which Brönsted's principle demands. The greatest variation which $\mathbf{E}_0$ exhibited is only 0.4 mv. in changing from $c_1/c_2 = 2$ to $^1/_2$, which corresponds to a change of 2.5% in K'_c. Linhart speaks of this result as in accord with the view that potassium ferrocyanide and potassium ferricyanide are

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[13] Linhart, This Journal, 39, 615 (1917).

undissociated or at least that the ionization of intermediate ions is completely repressed. This is not necessarily true. Linhart's results only prove that both salts are dissociated to the same extent in potassium chloride solutions. The data may be taken equally well as proof for the hypothesis of complete dissociation as for any definite degree of incomplete dissociation.

Linhart also shows that Lewis and Sargent's[14] data yield the same average value for $\mathbf{E}_0$ when the differences in potassium chloride concentration in the oxidation cell and normal calomel cell are taken into account. Lewis and Sargent's measurements consequently serve as a good check upon his results.

On the other hand, the measurements of Schoch and Felsing[15] involve concentrations of ferro- and ferricyanide relative to potassium chloride which are too large to determine $\mathbf{E}_0$ accurately. Nevertheless, the trend of their values is also consistent with a value $\mathbf{E}_0 = 0.2188$.

The other data needed for the calculation are taken from Lewis and Randall's "Thermodynamics" with the exception of cell (14). For 25°

$$\mathrm{Hg\,Cl\,(S)} + \mathrm{E}^- = \mathrm{Hg} + \mathrm{Cl}^-;\ \mathbf{E}_0 = 0.2676;\text{[16]}\ \Delta F^\circ = -6175 \qquad (14)$$

$$\mathrm{I}^- = \mathrm{E}^- + \frac{1}{2}\,\mathrm{I}_2\,(\mathrm{S});\ \mathbf{E}_0 = -0.5357 \pm 0.0004;\ \Delta F^\circ = 12{,}361 \pm 10 \qquad (15)$$

$$\frac{1}{2}\,\mathrm{I}_2\,(\mathrm{S}) = \frac{1}{2}\,\mathrm{I}_2\,(\mathrm{aq.});\ \mathbf{E}_0 = -0.0851;\ \Delta F^\circ = 1963 \qquad (16)$$

$$\frac{1}{2}\,\mathrm{I}_3^- = \frac{1}{2}\,\mathrm{I}^- + \frac{1}{2}\,\mathrm{I}_2(\mathrm{S});\ \mathbf{E}_0 = +0.0010;\ \Delta F^\circ = -23 \qquad (17)$$

By combining (13) and (14), we get (18)

$$\mathrm{Fe(CN)}_6^{---} + \mathrm{E}^- = \mathrm{Fe(CN)}_6^{--},\ \mathbf{E}_0 = +0.4864;\ \Delta F^\circ = -11{,}224 \qquad (18)$$

with an uncertainty which should be less than 1 mv.

Similarly, by combining (18) and (15)

$$\mathrm{Fe(CN)}_6^{---} + \mathrm{I}^- = \frac{1}{2}\,\mathrm{I}_2(\mathrm{S}) + \mathrm{Fe(CN)}_6^{--};\ \mathbf{E}_0 = -0.0493;\ \Delta F^\circ = 1137 \qquad (19)$$

or by combining (18), (15) and (16), we obtain

$$\mathrm{Fe(CN)}_6^{---} + \mathrm{I}^- = \frac{1}{2}\,\mathrm{I}_2\,(\mathrm{aq.}) + \mathrm{Fe(CN)}_6^{--};\ \mathbf{E}_0 = -0.1344;\ \Delta F^\circ = 3100 \qquad (20)$$

To take into account tri-iodide formation, we have on combining (19) and (17)

$$\mathrm{Fe(CN)}_6^{---} + {}^3/_2\,\mathrm{I}^- = \frac{1}{2}\,\mathrm{I}_3^- + \mathrm{Fe(CN)}_6^{--};\ \mathbf{E}_0 = -0.0503;\ \Delta F^\circ = 1160 \qquad (21)$$

By introducing the well-known formula

$$-\Delta F^\circ = \mathbf{N\,F\,E}_0 = RT \ln K$$

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[14] Lewis and Sargent, THIS JOURNAL, **31**, 355 (1909).

[15] Schoch and Felsing, *ibid.*, **38**, 1928 (1916).

[16] Revised value, Randall and Young, *ibid.*, **50**, 989 (1928). The older value given by Lewis and Randall was $\mathbf{E}_0 = 0.2700$.

we obtain the following values for the equilibrium constants K_a and K'_a, corresponding to Equations 1 and 10 for **N** = 2 when the activities of all components are one (hypothetical) molal; namely,

$$K_a = 2.89 \times 10^{-5} \qquad (22)$$

$$K'_a = 0.199 \times 10^{-3} \qquad (23)$$

which corresponds to

$$L_a = \frac{a_{I_2} \cdot a_{I^-}}{a_{I_3^-}} = \frac{K_a}{K'_a} = 0.00143 \qquad (24)$$

in substantial agreement with Bray and MacKay's value.[17]

VI. The Influence of Environment

In Col. (12), K'_f is computed by dividing K'_a by the stoichiometric quantity, K'_c, and in accordance with expectation K'_f decreases markedly with increasing salt concentration. The most striking result of the investigation is the marked dependence of K'_c, in the absence of foreign neutral salts, arising from comparatively small variations in the initial ferricyanide and iodide concentrations, and the almost complete obliteration of this dependence in the presence of excess potassium chloride. Thus Expts. 1–4 show a change in K'_c or K'_f of 35% when potassium iodide is varied from 0.15 to 0.20 *M* in the absence of potassium chloride and the concentration of potassium ferricyanide is held constant at 0.075 *M*.

In the next group of experiments (5–9), potassium chloride is added to maintain the sum of potassium chloride and potassium iodide constant at 1.20 *M*. K'_c now shows a variation of less than 2% which is within the experimental error. Expts. 5–9, 12–14 and 16–17 may therefore be taken as an excellent confirmation of Brönsted's principle. Expts. 18–20 indicate that 0.50 *M* potassium chloride is hardly sufficient to maintain a constant environment, a change in potassium iodide from 0.10 to 0.20 causing K'_c to increase by about 20%.

In Expts. 27 and 28, the same change in potassium iodide produces a 6% change in K'_c in the presence of 2.00 *M* potassium chloride. This variation is about three times as great as the probable error in K'_c and is most likely to be ascribed to the fact that the value of *L* employed does not correspond to this salt concentration and therefore does not yield exactly comparable results for $c_{I_3^-}$ when potassium iodide is varied as is the case for the experiments where μ = 1.65 for which environment *L* has been determined.

Considering now those experiments in which ferricyanide is varied, it is evident that the ionic strength does not function as an entirely satis-

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[17] The minor difference between Lewis and Randall's value for L_a and Bray and MacKay's value is due to a slightly different assumption in regard to the behavior of the activity coefficients of I^- and I_3^- ions. See Lewis and Randall, "Thermodynamics," p. 527.

factory measure of the electric environment, although it is perhaps the best of all proposed measures. Comparing Expt. 10 with Expts. 5–9, and Expt. 15 with Expts. 12–14, it is seen that for constant ionic strength produced by interchanging potassium chloride for potassium ferricyanide K'_c becomes smaller as potassium ferricyanide is increased.

The principle of ionic strength assumes that the square of the valence is the appropriate function to take into account changes in the concentration of ions of different valences. The Debye-Hückel theory yields this theorem as a limiting law for extreme dilution, but it is certainly not universally true when any appreciable concentrations of *high valence* ions are present.[18] This inadequacy of the principle of ionic strength has already been demonstrated for other systems of high valence ions and for far more dilute solutions than those now under consideration, namely, as low as 0.0005 μ.[19]

If we compute the appropriate valence exponent in order to maintain constant values of K'_c by changing the c_{KCl} when the ferricyanide concentration changes from 0.075 M to 0.10 M, we find that an exponent of 1.75 is satisfactory for Expts. 5–9 and 12–14, but groups 12–14 and 16–17 require an exponent of 1.1 for a corresponding change in ferricyanide concentration from 0.10 to 0.05 M. It will be of interest to carry out experiments with the ferricyanide concentration at still lower values to see if in the limit the equilibrium constant is determined by the equivalent concentration which demands a valence exponent of unity.

The addition of 0.003 M potassium ferrocyanide, although of considerable influence upon the percentage conversion and the observed rate of reaction, is without influence upon K'_c, as is to be expected (Expts. 16 and 22). A qualitative experiment using 0.5 M HCl + 1.00 M KCl showed a percentage conversion about 5 times that found in the absence of hydrochloric acid, and a few experiments were accordingly undertaken to determine the influence of P_{H}. Expts. 7, 26, 32 and 33 show that although acidity has no effect up to a P_{H} of about 3.7, a very noticeable increase in the oxidizing action of ferricyanide is apparent as the hydrochloric acid is increased above 0.001 M. Kolthoff[20] states that hydroferrocyanic acid is a weak acid with a dissociation constant of about 5.10^{-4} and the oxidation potential of the ferro–ferricyanide system is increased

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[18] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[19] La Mer and Mason, *ibid.*, **49**, 410 (1927); Graham Cook, *Dissertation*, Columbia University, **1928**. Further experimental work on this problem by F. H. Goldman and one of us shows that quite similar results are also obtained for the solubility of $La(IO_3)_3$ in sulfate solvents, and that the anomalous results obtained by La Mer and Mason in highly dilute solutions are not restricted to salts of the cobaltammine family. A theoretical explanation for these results on the basis of the Debye theory is given by Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[20] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **110**, 143 (1920).

owing to removal of ferrocyanide ion in acid solution. Our experiments are consistent with this prediction but hardly support Kolthoff's statement that ferrocyanide will *quantitatively* reduce iodine in neutral solution, except, of course, the presence of excess ferrocyanide. The validity of his empirical expression for the influence of hydrochloric acid, upon which this statement seems to be based is restricted to the concentration range studied, namely, 0.0125 *N* to 1.00 *N* HCl, and should be modified to take in the influence of the dissociation constant.[20]

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Summary

The equilibrium state for the reaction

$$2\text{Fe(CN)}_6^{---} + 3\text{I}^- \rightleftharpoons 2\text{Fe(CN)}_6^{----} + \text{I}_3^-$$

has been studied analytically for the potassium salts in pure water as well as in aqueous potassium chloride solutions as solvents.

Using water as solvent the value of $K_{\text{eq.}}$ changes 35% when the concentration of potassium iodide is increased from 0.15 *M* to 0.20 *M*, but the corresponding change is less than 2% in the presence of 1.0 *M* KCl. The data confirm the principle that the law of mass action holds for ionic systems when a sufficient excess of neutral salts is present to maintain a constant electrical environment, although this law fails completely in the absence of excess of neutral salts.

The inadequacy of the principle of ionic strength for high valence ions is also evident in this system.

The equilibrium constant in the absence of salt effects has been computed from e.m.f. data and found to be $0.199 \cdot 10^{-3}$.

Addition of hydrochloric acid up to a *P*H value of about 3.5 is without influence upon $K_{\text{eq.}}$ but is of marked influence in more acid ranges.

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