[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Aqueous Solutions as a Function of the Concentration. II. Potassium Ferrocyanide

BY GRINNELL JONES AND FREDERIC C. JELEN

Introduction

The conductance of solutions is greatly influenced by the valence type of salt and therefore data on salts of a high valence type may serve as a severe and useful test of the validity and generality of the various equations which have been proposed for the conductance as a function of the concentration. For an historical review of the more important of these equations and the background of the problem the reader is referred to a recent paper by Jones and Bickford.[1] Potassium ferrocyanide seemed to be the most suitable salt of the 1–4 valence type because it is only very slightly hydrolyzed and is sufficiently soluble and stable and was therefore selected for this investigation.

Experimental

Potassium ferrocyanide was prepared for this investigation by two different methods. The best material available by purchase was twice recrystallized from conductivity water by dissolving at 60°, filtering through a sintered glass filter and cooling to 0°, followed by centrifugal drainage. Since there was a slight indication of instability of these solutions at 60°, we also prepared other samples by dissolving the salt in cold water and precipitating it by adding redistilled ethyl alcohol followed by centrifugal drainage. The entire process was then repeated. This method gave small crystals which were almost white in color. No difference in the conductivity could be detected between the salt prepared by the two methods of purification.

The salt was then placed in a platinum boat in a tube and heated at 90° in a stream of dry nitrogen for about two hours. The salt was cooled in nitrogen and the nitrogen replaced by dry air. The boat and salt was then bottled without exposure to the moist air of the laboratory in a Richards bottling apparatus. Repeated experiments demonstrated that a repetition of the heating and drying process did not change the weight by as much as 0.01%. The preparation of the solutions and the measurement of their conductivity at 25 and 0° were so similar to the procedure used by Jones and Bickford that no further description is needed. The cell constants were determined by the use of the values for the conductance of standard potassium chloride solutions determined by Jones and Bradshaw.[2] The density of each solution was determined by means of a large (65 cc.) pycnometer at both 25 and 0°. At each concentration at least two but sometimes three or four independent solutions were prepared. The actual concentrations were commonly slightly different from the round concentrations desired. Slight corrections were applied to bring the results for the conductivity to the round concentration. These corrections were rarely more than 0.01% and in only one case more than 0.05%. The detailed data on each solution and the corrections to round concentration are omitted to save space in printing.

No corrections have been applied for hydrolysis because tests made by indicators and a quinhydrone electrode on a 0.01 molar solution gave a *p*H of 7.5, from which it may be inferred that the effect of hydrolysis would be negligible. The results are shown in Tables I and II, in which c is the concentration in moles per liter and Λ is the molar conductance.

Interpretation of the Data

Figure 1 is a plot of the molar conductance against the square root of the concentration. The experimental data at 25° are represented by the centers of the circles. This gives a curve which is similar to the curves given by salts of lower valence types except that the slope and curvature in the dilute end are greater than has been found for salts of lower valence type. The curve is nearly straight at the dilute end but there is evidently some curvature even below 0.001 molar. Putting a straight line through the four lowest concentrations gives the equation $\Lambda = 741.9 - 4637\sqrt{c}$ (line K in Fig. 1). This method of extrapolation must give a value for the limiting conductance and limiting slope at infinite dilution which is too low unless there is a change in curvature at extreme dilution for which there is no experimental evidence or theoretical warrant. This equation, which has the form suggested by Kohlrausch, fails completely above 0.001 molar as is evident from the figure.

The coefficients of the Jones and Dole equation were determined by the method of least squares using all the experimental points including c = 0.5 molar or 2 N, giving the equation

$$\Lambda = 785.16 - \frac{9171.38\sqrt{c}}{1 + 17.106\sqrt{c}} - 12.84c.$$

The curve marked J in Fig. 1 is the plot of this equation and as will be seen it agrees with the experimental data so closely that the deviations are not apparent on the scale that can be printed.

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[1] Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 602 (1934).

[2] Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

TABLE I

CONDUCTANCE OF POTASSIUM FERROCYANIDE SOLUTIONS AT 25°

1 c	2 Λ	3 J + D $\Delta\Lambda$	4 η	5 $\Lambda\eta$	6 J + D $\Delta\Lambda\eta$	7 Onsager Λ_0'	8 O + F $\Delta\Lambda$
0.00025	668.94	−2.08	1.00055	669.31	−2.07	724.45	+15.76
.00036	653.52	−0.26	1.00080	654.04	−0.33	719.95	−10.53
.0005	638.04	+1.22	1.00103	638.70	+1.08	716.14	+ 5.83
.00075	615.11	+1.00	1.00138	615.96	+0.81	710.40	− 1.83
.001	598.33	+1.40	1.00163	599.31	+1.15	708.21	− 6.25
.002	554.18	+1.43	1.00244	555.53	+1.11	709.70	+15.04
.005	491.29	−0.30	1.00451	493.52	−0.40	742.39	−18.10
.01	445.28	−1.40	1.00744	448.59	−1.18	817.10	−10.67
.02	403.72	−1.84	1.01255	408.79	−1.25	981	+ 2.56
.0475	360.45	−1.35	1.02525	369.55	−0.57	1507	+18.53
.05	(358.14)						
.1	332.01	+0.63	1.04839	348.08	+0.87		+12.09
.2	310.90	+2.48	1.09414	340.17	+1.41		−17.89
.5	282.63	−0.90	1.26347	357.09	−0.60		+ 2.63

Equations: Jones and Dole, column 3; $\Lambda = 785.16 - \dfrac{9171.38\sqrt{c}}{1 + 17.106\sqrt{c}} - 12.84c$

Jones and Dole, column 5; $\Lambda\eta = 783.75 - \dfrac{9000.35\sqrt{c}}{1 + 16.8424\sqrt{c}} + 133.9c$

Onsager and Fuoss, column 8; $\Lambda = 709.96 - 3954.98\sqrt{c} + 3063.41c - 5542.93c \log c$

TABLE II

CONDUCTANCE OF POTASSIUM FERROCYANIDE SOLUTIONS AT 0°

1 c	2 Λ	3 $\Delta\Lambda$ J + D	4 η	5 $\Lambda\eta$	6 $\Delta\Lambda\eta$ J + D	7 $\dfrac{\Lambda^{25}}{\Lambda^{0}}$
0.001	321.00	−0.25	1.00120	321.39	−0.19	1.8640
.002	298.01	+ .38	1.00164	298.50	+ .32	1.8596
.005	264.83	+ .10	1.00255	265.50	.00	1.8551
.01	240.34	− .17	1.00376	241.24	− .16	1.8527
.02	218.23	− .18	1.00554	219.44	− .07	1.8500
.0477	195.26	− .08	1.00981	197.17	+ .03	
.05	(194.19)					1.8443
.1	181.08	+ .33	1.01803	184.34	+ .22	1.8355
.2	171.96	− .13	1.03903	178.67	− .05	1.8080

Equations: Jones and Dole

$$\Lambda = 420.40 - \frac{4768.73\sqrt{c}}{1 + 16.4586\sqrt{c}} + 33.87c$$

Jones and Dole; column 6,

$$\Lambda\eta = 418.79 - \frac{4635.89\sqrt{c}}{1 + 16.0335\sqrt{c}} + 68.40c$$

Nevertheless, an examination of column 3 in Table I indicates that there are deviations which are probably greater than the experimental error. These deviations are substantially greater than were found for lanthanum chloride, and barium chloride and potassium bromide. This equation is clearly the best formula known to us for the more concentrated solutions of salts of all valence types but there are indications that it gives too great a curvature in the dilute end and too high a value of the limiting conductance and limiting slope.

Since the concentrated solutions of this salt are exceptionally viscous, the effect of applying a viscosity correction is of special interest. The viscosities of these solutions, η, have been determined for this and other purposes (see the preceding paper) as is shown in column 4 of Table I and the values of $\Lambda\eta$ are shown in column 5 and are plotted as the points within the triangle in Fig. 1. The Jones and Dole equation was then fitted to these values, giving

$$\Lambda\eta = 783.75 - \frac{9000.35\sqrt{c}}{1 + 16.8424\sqrt{c}} + 133.9c$$

The upper curve in Fig. 1 is the plot of this equation and, as will be seen, the deviations are so slight that they are not apparent on the scale that can be printed. Column 6 in Table I shows the computed deviations. The application of the viscosity correction substantially reduces the deviations in the more concentrated solutions but has little effect in the dilute range where the viscosity correction is small. It should be noticed that the curve depicting $\Lambda\eta$ has a flat minimum at about 0.2 molar.

It is next of interest to apply the Onsager–Shedlovsky method of extrapolation to the data. If the Onsager equation is transformed by using molar concentrations (gram molecules per liter) and molar conductances, and by introducing the appropriate numerical values for water at 25°, namely, $\eta = 0.008949$ and $D = 78.57$ and $T = 298.1$, the Onsager equation becomes

$$\Lambda = \Lambda_0 - [0.27446 w \Lambda_0 + 21.138 z_1 z_2 (z_1 + z_2)] \sqrt{z_1 z_2 (z_1 + z_2) c}$$

where $w = 2qz_1z_2/(1 + \sqrt{q})$

and $q = \dfrac{z_1 z_2 \Lambda_0}{(z_1 + z_2)\ \{\Lambda_0 + (z_2^2 - z_2)\Lambda_1^0 + (z_1^2 - z_1)\Lambda_2^0\}}$

for potassium ferrocyanide we substitute $z_1 = 1$ and $z_2 = 4$ giving $\Lambda = \Lambda_0 - (1.22742\ w\ \Lambda_0 + 1890.64)\sqrt{c}$

$$w = \frac{8q}{1 + \sqrt{q}}$$

$$q = \frac{4\Lambda_0}{5(\Lambda_0 + 12\Lambda_K^0)}$$

It is evident that the limiting slope cannot be computed from these equations without first assuming that the values of the limiting conductances of the two ions are known because the value of w depends on Λ_0 and Λ_K^0 in the complicated manner indicated by the equations. However, the value of w is rather insensitive to the value of Λ_0 so that we may proceed by a method of successive approximations and obtain a result if the equations are really valid.

If we take as a first approximation the value of $\Lambda_0 = 741.9$ obtained by putting a straight line through the four lowest points and assume that the limiting conductance of the potassium ion is 73.5 then $q = 0.36549$ and $w = 1.82226$ and the Onsager equation becomes $\Lambda = \Lambda_0 - (2.23668\ \Lambda_0 + 1890.64)\sqrt{c}$ or $\Lambda_0 = (\Lambda + 1890.64\sqrt{c})/(1 - 2.23668\sqrt{c})$.

If the Onsager equation were valid over any range accessible to experimentation, the values of Λ_0 computed from this equation should be a constant over the range of validity of the equation. The values of Λ_0 computed by this equation are given in column 7 of Table I. As will be evident from the table, the values of Λ_0 are far from being constant. Attempts were made to obtain constancy by varying the value of Λ_0 assumed in the computation of w but no appreciable improvement could be obtained in this manner. This proves that Onsager's equation is not valid for potassium ferrocyanide even up to 0.001 molar.

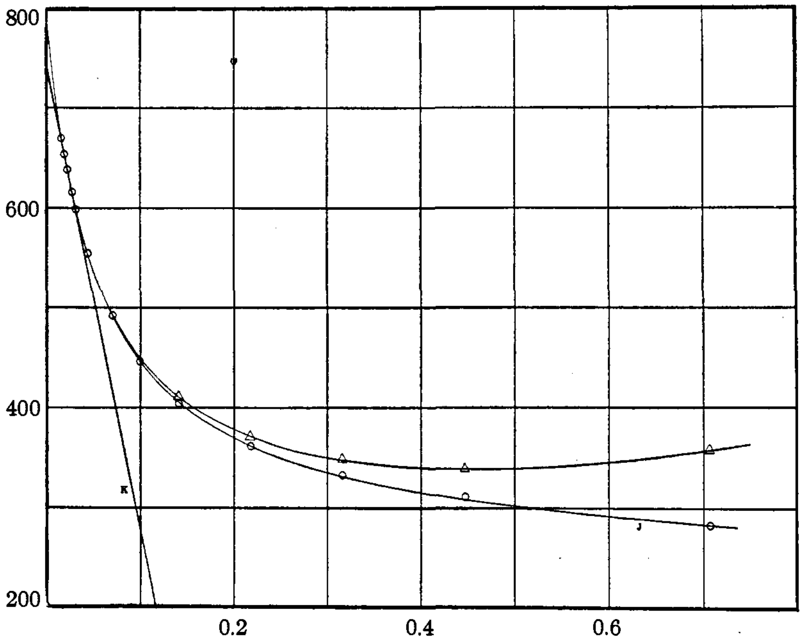

Fig. 1.

It has been demonstrated previously that the values of Λ_0 computed by this method are not constant for salts of any valence type. Shedlovsky[3] found for many uni-univalent salts that if the values of Λ_0 computed by the Onsager formula were plotted against c a straight line was obtained up to about 0.1 molar and he proposed to use this method to obtain Λ_0 by extrapolation and also suggested a modified Onsager equation $\Lambda_0 = \dfrac{\Lambda + \beta\sqrt{c}}{1 - \alpha c} + Bc$ which fitted the data up to about 0.1 *N*. In this Shedlovsky equation definite numerical values can be assigned to α and β from the Onsager theory and only Λ_0 and B are arbitrary parameters selected to fit the data for each salt. Some uni-univalent salts did not obey this equation. Shedlovsky suggests that this exceptional behavior is due to association.

Jones and Bickford applied Shedlovsky's method to lanthanum chloride, obtaining a curve which was approximately straight between 0.0025 and 0.01 molar but had a definite positive curvature in the more dilute range and a negative curvature between 0.01 and 0.1 molar. At the dilute end the plot appeared to be curving so as to enter the axis horizontally, which is the behavior to be expected if Onsager's law is valid as a limiting law. However, Shedlovsky's method

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[3] T. Shedlovsky, THIS JOURNAL, 54, 1405, 1411 (1932).

of straight line extrapolation could not be applied to this tri-univalent salt.

Shortly afterward Shedlovsky and Brown[4] reported measurements on the chlorides of four divalent metals which when plotted gave a similar curvature at the dilute end. They, therefore, abandoned extrapolation along a straight line and recommended extrapolation along a curve and thus in effect for divalent salts abandoned the Shedlovsky equation, although they are not clear as to whether or not this curve is assumed to enter the axis horizontally. They propose a modification of the original Shedlovsky equation by the addition of two more terms each containing an arbitrary parameter giving the equation

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} + Bc + Dc \log c - Ec^2$$

This equation, of course, can be made to fit the data better than the original Shedlovsky equation because it contains two more parameters selected to fit the data for their four divalent salts. But they do not give a detailed comparison of the data for the four divalent salts with the results computed by their equation.

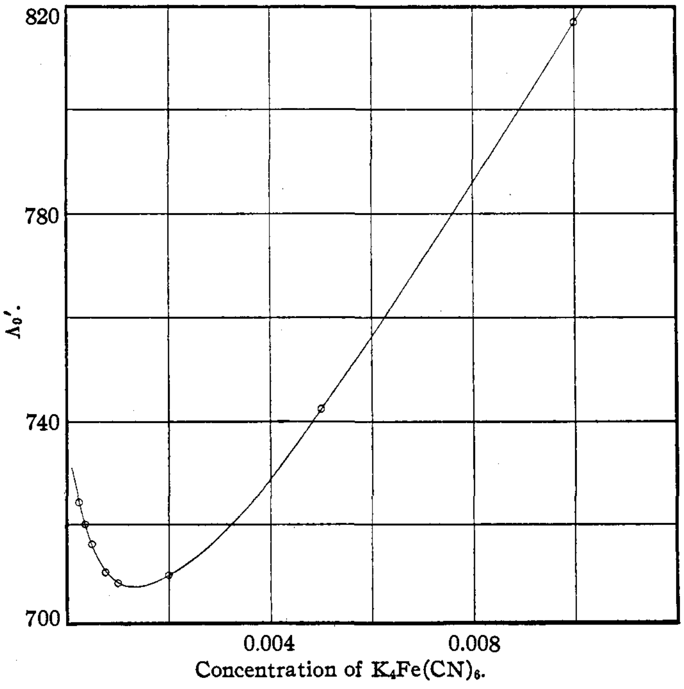

Fig. 2.

Shedlovsky, Brown and MacInnes[5] have shown that this equation may be applied successfully to potassium chloride up to 0.12 N.

The results of an attempt to apply the Shedlovsky method of extrapolation to obtain Λ_0 by plotting $\Lambda_0' = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}}$ against c with our data on potassium ferrocyanide are shown in Fig. 2. In this case the plot has a very definite minimum and the portion of the curve which must be extended for extrapolation has a pronounced curvature. Any attempt to extrapolate such a curve depends too much on a guess as to the curvature to have much value. The influence of making other assumptions as to the value of Λ_0 in the computation of w and hence of Λ_0' was tried but there was no change in the character of the curves. These curves are so close together that only one can be shown without confusion on the scale which can be printed and, therefore, only one curve is shown in Fig. 2.

Onsager and Fuoss[6] have suggested a generalized equation for the properties of solutions of the form $F(c) = F(o) - A\sqrt{c} + Bc - Dc \log c + \ldots$ It seemed worthwhile, therefore, to attempt to apply this generalized equation to conductance in the form $\Lambda = \Lambda_0 - A\sqrt{c} + Bc - Dc \log c$. Although in principle the value of A might be computed theoretically if the value of Λ_0 were known, yet since Λ_0 is not known and the results depend so greatly on the value of A, it seemed best to treat A as a parameter and evaluate it from the data by the method of least squares. The result is $\Lambda = 709.96 - 3954.98\sqrt{c} + 3063.41\,c - 5542.92\,c \log c$. The values computed by this equation and the deviations between the experimental and computed results are shown in column 8 of Table I. As will be seen, the results are disappointing. The average deviation is more than eight times as great as for the Jones and Dole equation, although both are four parameter equations. The value of Λ_0 is substantially below that given by Kohlrausch's method of extrapolation (741.9), although there is strong reason for believing that the Kohlrausch method gives too low a result. Moreover, the equation gives a curve having a minimum at about 0.1 molar and a maximum at about 0.25 molar whereas

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(4) T. Shedlovsky and A. S. Brown, THIS JOURNAL, **56**, 1066 (1934).

(5) T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Am. Electrochem. Soc.*, **165** (1934).

(6) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

the experimental data show no such minimum and maximum in this or other cases.

The data for 0° are given in Table II. These data cover a smaller range of concentration than for 25°, and therefore give a less severe test of the equations. The solubility is not great enough at 0° to make it possible to work with 0.5 molar solutions and the data below 0.001 molar were not obtained. These data are probably not quite so reliable as the data at 25°, because it is harder to control the temperature inside an oil bath at 0 than at 25°. The Kohlrausch method of extrapolating to infinite dilution using the data from 0.001 to 0.01 molar gives $\Lambda_0 = 353$ but this figure is undoubtedly much too low. The Jones and Dole equation for this case is $\Lambda = 420.40 - 4768.7 \sqrt{c}/(1 + 16.459 \sqrt{c}) + 33.87c$. The differences between the observed results and the results computed by this equation are given in column 3 of Table II. The deviations are much less than were found at 25°, but this is probably due to the fact that the data cover a smaller range of concentration and are therefore easier to fit to an equation. The deviations are probably somewhat greater than the experimental error.

By the use of the values of the relative viscosity given in the preceding paper we have computed the values of $\Lambda\eta$ given in column 5 of Table II. With the viscosity correction applied the Jones and Dole equation becomes $\Lambda\eta = 418.79 - 4635.89 \sqrt{c}/(1 + 16.0335 \sqrt{c}) + 68.40c$. As will be seen by a comparison of columns 3 and 6 the deviations are substantially reduced by the application of the viscosity correction especially in the more concentrated solutions.

The last column in Table II gives the ratio between the conductance at 25 and at 0°. As will be seen the temperature coefficient of the conductance decreases with increasing concentration.

Summary

1. The conductance of potassium ferrocyanide solutions has been determined at 25 and at 0° from great dilution up to nearly saturation.

2. The data have been used to test various equations which have been proposed to express the conductance as a function of the concentration.

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The Palladium-Hydrogen Equilibrium and New Palladium Hydrides[1]

BY LOUIS J. GILLESPIE AND LIONEL S. GALSTAUN

The early work of Troost and Hautefeuille, Hoitsema, Sieverts, Lambert and Gates and others was reviewed in the paper of Gillespie and Hall. It may be remembered that Troost and Hautefeuille[2] claimed the existence of Pd_2H on the basis of evidence just short of that demanded by the phase rule, which was about to be announced by Gibbs, and that this claim was usually disallowed after the paper of Hoitsema,[3] although Lambert and Gates[4] pointed out that their descending isotherms show "breaks" at approximately the same composition (about $Pd_{1.9}H$) at 75, 103 and 120°. Gillespie and Hall[5] worked with finely-divided palladium, allowed much time—often one to three days or longer—to elapse before recording pressures, and obtained for the first time a phase diagram for the system in obvious conformity with the phase rule. This diagram indicates the existence of Pd_2H capable of formation in definite proportions from about 80 to 180° or higher; at lower temperatures the phase contains a progressively greater excess of hydrogen.

In their first work at 0° they established the first break between the first rising isotherm and the relatively horizontal one as a sharp angle, which could be demonstrated reversibly at constant temperature. Large additions of hydrogen produced hysteresis effects. They discovered that if some hydrogen were withdrawn and the

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(1) Part of this article is taken from the thesis presented by L. S. Galstaun in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology. The work at 270, 280 and 285°, upon which the finding of new hydrides mainly rests, was done since presentation of the thesis.

(2) Troost and Hautefeuille, *Compt. rend.*, **78**, 686 (1874); *Ann. chim. phys.*, [5] **2**, 273 (1874).

(3) Hoitsema, *Z. physik. Chem.*, **17**, 25 (1895).

(4) Lambert and Gates, *Proc. Roy. Soc.* (London), **108A**, 456 (1925).

(5) Gillespie and Hall, THIS JOURNAL, **48**, 1207 (1926).