[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Differential Diffusion Coefficient of Potassium Ferrocyanide in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

The diffusion coefficient of potassium ferrocyanide in water at 25° has been determined through a concentration range from 0.0025 to 0.006 molar. The experimental results are compared with values derived from the theory of Onsager and Fuoss.

The diffusion coefficient of potassium ferrocyanide in dilute solution has been determined in order to supplement the results so far obtained in this Laboratory[1] with 1-1,[1] 1-2,[2] 2-1,[3] 2-2[4] and 1-3[5] types of electrolytes.

Experimental Results and Theoretical Calculations

The measured diffusion coefficients at the molar concentrations designated in the first column are given in the second column of Table I. The theoretical values in the third column of the table were computed by the equations resulting from the theory of Onsager and Fuoss.[6,7,8] Upon introduction of the values of 73.52[9] and 111[10] for the equivalent conductances of the potassium and ferrocyanide ions, λ_1^0 and λ_2^0, respectively, 8.949×10^{-3} [11] for η_0, the viscosity of water, 78.54[12] for the dielectric constant of water and 278.16 for the absolute temperature, the numerical equations for the diffusion coefficient of potassium ferrocyanide reduce to

TABLE I

OBSERVED AND THEORETICALLY COMPUTED VALUES OF THE DIFFUSION COEFFICIENTS OF POTASSIUM FERROCYANIDE AT 25°

c (moles/liter)	$\mathfrak{D} \times 10^5$ (obs.)	$\mathfrak{D} \times 10^5$ (calcd.)
0.00000	...	(1.473)
.00269	1.218	1.221
.00384	1.197	1.200
.00396	1.198	1.199
.00474	1.183	1.189
.00556	1.178	1.179

$$\mathfrak{D} = 1.2395 \times 10^{14} \left(\frac{\mathfrak{M}}{c}\right)\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (1)$$

$$\left(\frac{\mathfrak{M}}{c}\right) \times 10^{20} = 11.885 - 5.0362 \frac{\sqrt{c}}{(1 + A'\sqrt{c})} + 923.02c\, \phi\, (A'\sqrt{c}) \quad (2)$$

$$\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{7.4147\sqrt{c}}{(1 + 4.59\sqrt{c})^2} - 0.5988c \quad (3)$$

Unfortunately, no accurate data on the activity coefficient of potassium ferrocyanide in dilute solution at 25° are available. Therefore, the tentative expedient of extrapolating the values of the activity coefficient determined from isopiestic vapor pressure measurements by Robinson and Stokes[13] by means of the equation

$$\log y_{\pm} = -\frac{\mathcal{S}_{(f)}\sqrt{c}}{1 + A'\sqrt{c}} + 2BC - \log\left(1 + \frac{\nu m M}{1000}\right) \quad (4)$$

This equation was applied to their data over a concentration range of 0.1 to 0.5 molal upon introducing 6.4397[14] for $\mathcal{S}_{(f)}$, the Debye and Hückel function. This procedure led to the values of 4.59 for A' and -0.260 for B. The density term, $c\psi(d)$, which appears in these calculations and which contributes only to the third decimal place of the diffusion coefficient in solutions as dilute as those under consideration, has been omitted due to lack of

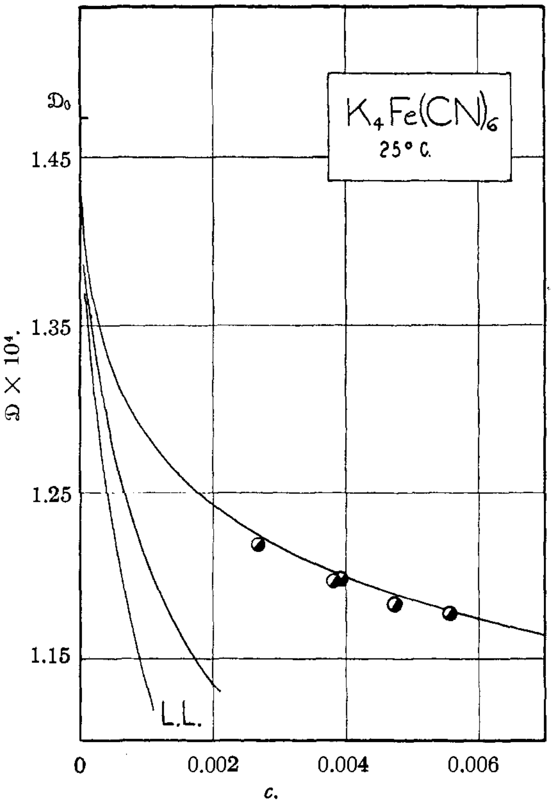

Fig. 1.—The diffusion coefficient of potassium ferrocyanide in water at 25°: upper curve, complete theory; middle curve, mobility term constant; lowest curve, limiting law.

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(9) Ref. 8, p. 172.

(10) G. Jones and F. C. Jelen, THIS JOURNAL, **58**, 2561 (1936).

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(12) Ref. 8, p. 128.

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(14) Ref. 8, p. 587.

density data in dilute potassium ferrocyanide solutions.

For a 1–4 electrolyte, the limiting law of the theory for the diffusion coefficient is

$$\mathfrak{D} = \mathfrak{D}_0 - \mathcal{S}_{(\mathfrak{D})}\sqrt{c} \qquad (5)$$

where

$$\mathfrak{D}_0 = 11.1705 \times 10^{10}\, T\left(\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) \qquad (6)$$

and

$$\mathcal{S}_{(\mathfrak{D})} = \frac{29.679 \times 10^{-3}}{D^{3/2}T^{1/2}}\left(\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) + \frac{2.9117 \times 10^{-8}}{\eta_0 D^{1/2}T^{1/2}}\left(\frac{4\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \qquad (7)$$

For potassium ferrocyanide at 25°, these equations yield

$$\mathfrak{D} \times 10^5 = 1.4731\text{–}10.925\sqrt{c} \qquad (8)$$

The values of the diffusion coefficient computed by equations (1) to (3) and given in the third column of Table I agree surprisingly well with the observed results. In Fig. 1, the diffusion coefficient is plotted against the molar concentration. The upper curve represents the values obtained from the complete theory. The middle graph is obtained when the mobility term, $(\mathfrak{M}/c)$, is constant and equal to its value when c equals zero. The difference between the upper and middle curves represent the contribution of electrophoresis. The lowest curve represents the limiting law.

It would be presumptuous to take too seriously the agreement between theory and experiment for an electrolyte as complicated as potassium ferrocyanide since the calculated values are derived by a theory which assumes complete dissociation. Such a calculation involves only the mean mobilities of the ions, K^+ and $Fe(CN)_6^{----}$. A completely detailed computation would require a knowledge of the degrees of dissociation and mobilities of other ions such as $KFe(CN)_6^{---}$, $K_2Fe(CN)_6^{--}$ etc. which are probably present and this information is not available. A second difficulty resides in the long extrapolation required to evaluate the thermodynamic term due to lack of information regarding the activity coefficient of potassium ferrocyanide in dilute solution. However, it may be stated that there is evidence that the experimental observations approach the expected theoretical values as the concentration approaches zero.

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Barium Cobalt Oxide of the Perowskite Type[1,2]

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The system barium–cobalt–oxygen was studied over the temperature range 500 to 1300°. Three distinct new phases were found by means of X-ray and chemical analysis. The formulas assigned to these phases are $BaCoO_{2.72}$, $BaCoO_{2.31}$ and $BaCoO_{2.23}$. The latter has the perowskite structure.

The reaction of cobalt oxides with barium peroxide was studied by Hedvall and von Zweiberg[5] by means of heating curves from which they concluded that a reaction occurred and suggested that a cobaltite was formed. The composition of the product was not determined. Some previous investigations[6–9] in this Laboratory established that ternary compounds in this system were formed in which the average valence of the cobalt in the reaction products was greater than 3. X-Ray analysis showed that more than one new phase was formed. The expected perowskite type structure was not obtained in these investigations although this is readily obtained when lanthanum is substituted for barium.[10] The results reported here offer an explanation of the barium–cobalt–oxygen system within a limited composition range.

Experimental

The materials used were Baker analyzed C.P. chemicals. Intimate mixtures of barium nitrate and cobaltous nitrate were heated in platinum boats in an atmosphere of oxygen at constant temperatures over a temperature range of 500 to 1300°. The products were examined with X-rays and the average valence of the cobalt was estimated by determining the amount of chlorine liberated on dissolving a sample in dilute hydrochloric acid.

It was found that mixtures, in which the barium to cobalt atomic ratios were greater than one, gave products the diffraction pattern of which contained the lines of barium oxide. The barium oxide could be extracted with water leaving a residue in which Ba/Co = 1. When the barium to cobalt atomic ratio in the starting mixture was less than one, the product gave the lines of Co_3O_4 in the diffraction pattern. With equimolar mixtures the diffraction patterns of the products obtained by prolonged heating above 650° corresponded to new phases. Attempts to prepare a cobalt compound analogous to $BaO \cdot 6Fe_2O_3$[11] were not successful.

The product obtained by heating the equimolar mixture of barium nitrate and cobaltous nitrate at 650°, an opaque material with a metallic luster, gave an average oxidation number for cobalt of 3.44. The spacings from the diffraction pattern correspond to a cubic structure with a primitive cell a = 4.82 Å. and are listed in Table I. The measured density of the product was 3.72 g./cc. which is about 5.4% higher than the calculated density based on the formula $BaCoO_{2.72}$. Virtually no change occurred upon

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[1] Abstracted in part from a dissertation presented by Simon W. Strauss to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1950.

[2] Part of the work described in this paper was performed under contract W36-039 Sc 33719 with the U. S. Army Signal Corps Engineering Laboratories, Belmar, N. J.

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[4] University of Connecticut, Storrs, Connecticut.

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