[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficients of Lithium and Sodium Sulfates in Dilute Aqueous Solution at 25°

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The diffusion coefficients of lithium and sodium sulfates from 0.001 to 0.005 molar at 25° have been determined by the conductometric method with an accuracy of the order of 0.1 to 0.2%. The results for lithium sulfate agree with values calculated by the theory of Onsager and Fuoss while those for sodium sulfate are somewhat higher than the theoretically estimated ones.

Diffusion coefficients of the uni-univalent electrolytes, lithium, sodium[1] and potassium chlorides[2] and potassium nitrate[3] at high dilutions in water, determined by the conductance method, have been found to conform accurately with the theory of Onsager and Fuoss.[4] On the other hand, the diffusion coefficient of calcium chloride[5] at concentrations from 0.001 to 0.005 M differs considerably from the theoretical prediction. One possible cause of this discrepancy may be that the theory is unable to account for the behaviors of unsymmetrical polyvalent electrolytes. To test this possibility, the diffusion coefficients of lithium and sodium sulfates have been determined in dilute solutions.

Experimental Results and Theoretical Calculations

The equations derived from the theory and required in the subsequent calculations are[6,7]

$$\mathfrak{D} = 1000RT\,(\nu_1 + \nu_2)(\bar{M}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \qquad (1)$$

where

$$(\bar{M}/c) = \frac{1.0748 \times 10^{-20}}{\nu_1|z_1|}\left(\frac{\lambda_1^0\lambda_2^0}{(\lambda_1^0 + \lambda_2^0)}\right) - \frac{3.1322 \times 10^{-19}}{(\nu_1 z_1^2 + \nu_2 z_2^2)^{1/2}\eta_0(DT)^{1/2}}\left(\frac{|z_2|\lambda_1^0 - |z_1|\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \left(\frac{z_2^2\lambda_1^0 + z_1^2\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \frac{9.304 \times 10^{-13}}{\eta_0(DT)^2}\,c\phi(A'\sqrt{c}) \qquad (2)$$

In these equations, $\mathfrak{D}$ is the differential diffusion coefficient, R the gas constant in ergs, T the absolute temperature, c the concentration in moles per liter, $(\bar{M}/c)$ is denoted the mobility term and $\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right)$ the thermodynamic term. In the equation which expresses the mobility term, z_1, z_2 are the valences of the ions of the electrolyte, $|z_1|$, $|z_2|$ their magnitudes, ν_1, ν_2 the number of kinds of ions obtained by the dissociation of the electrolyte and λ_1^0, and λ_2^0 are the equivalent conductances of the ions at infinite dilution. D is the dielectric constant of the solvent and η_0 is its viscosity. $A'\sqrt{c} = \kappa a$, where κ is the reciprocal radius of the Debye and Hückel theory and a the mean distances of approach of the ions. The exponential integral term of the theory, $\phi(A'\sqrt{c})$, for various values of $A'\sqrt{c}$ may be obtained from the table compiled by Harned and Owen.[6]

From these equations one may derive the limiting law

$$\mathfrak{D} = \mathfrak{D}_0 - \mathcal{S}_{(\mathfrak{D})}\sqrt{c} \qquad (3)$$

where the limiting value of the diffusion coefficient, $\mathfrak{D}_0$, is given by the Nernst equation

$$\mathfrak{D}_0 = \frac{(\nu_1 + \nu_2)RT\,1.0748 \times 10^{-17}}{\nu_1|z_1|}\left(\frac{\lambda_1^0\lambda_2^0}{(\lambda_1^0 + \lambda_2^0)}\right) \qquad (4)$$

and where

$$\mathcal{S}_{(\mathfrak{D})} = \frac{1.3273 \times 10^{-3}\,(\Sigma\nu_i z_i^2)^{3/2}}{\nu_1|z_1|D^{3/2}T^{1/2}}\,\frac{\lambda_1^0\lambda_2^0}{(\lambda_1^0 + \lambda_2^0)} + \frac{2.6042 \times 10^{-8}(\Sigma\nu_i z_i^2)^{1/2}}{\eta_0 D^{1/2}T^{-1/2}|z_1 z_2|}\left(\frac{|z_2|\lambda_1^0 - |z_1|\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \qquad (5)$$

The thermodynamic term in equation (1) may be evaluated by the equation

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514\,\mathcal{S}_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 2.303\,BC - c\psi(d) \qquad (6)$$

where

$$\psi(d) = \frac{\partial d/\partial c + 0.001\,(\nu M_1 - M_2)}{d + 0.001c(\nu M_1 - M_2)} \qquad (7)$$

In these expressions, $y_\pm$ is the activity coefficient in moles per liter, $\mathcal{S}_{(f)}$, the Debye and Hückel factor, B, an empirical constant, d, the density of the solution, $\nu = \nu_1 + \nu_2$, and M_1 and M_2, the molecular weights of the solvent and solute, respectively.

Table I contains the quantities which are necessary for the theoretical computations and their sources. The densities required by equation[7]

TABLE I

CONSTANTS AND PARAMETERS EMPLOYED IN THEORETICAL COMPUTATIONS

	Li_2SO_4	Na_2SO_4
λ_1^0	38.69[6]	50.11[6]
λ_2^0	79.8[7]	79.8[7]
A'	2.220[6]	1.982[9]
a(Å.)	3.9[6]	3.48[6]
$\mathcal{S}_{(f)}$	1.7636[6]	1.7636[6]
B	0.0[8]	−0.058[8,9]
d_0	0.997	0.997
M_2	109.94	142.05
ϕ_v^0	12.7[6]	11.47[6]
S_v	10.8[6]	12.16[6]
$\mathcal{S}(\mathfrak{D})$	2.1146	2.5154

$\eta_0 = 8.949 \times 10^{-3}$; $D = 78.54$; $R = 8.31436 \times 10^7$; $T = 298.16$.

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[1] Harned and Hildreth, THIS JOURNAL, **73**, 650 (1951).

[2] Harned and Nuttall, *ibid.*, **69**, 736 (1947); **71**, 1460 (1949); Harned and Blake, Jr., *ibid.*, **72**, 2265 (1950).

[3] Harned and Hudson, *ibid.*, **73**, 652 (1951).

[4] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[5] Harned and Levy, THIS JOURNAL, **71**, 2781 (1949).

[6] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950; Harned. *Chem. Revs.*, **40**, 461 (1947).

[7] MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 342.

[8] Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

[9] Harned and Hecker, THIS JOURNAL, **56**, 650 (1934).

may be obtained from the equation

$$d = d_0 + \frac{(M_2 - d_0\phi_v{}^0)c}{1000} - \frac{(S_v d_0)c^{3/2}}{1000} \qquad (8)$$

and the table of parameters given by Harned and Owen.[10] The final equations for the densities obtained in this manner are

$$d_{25} = 0.997 + 0.09731c - 0.0108c^{3/2} \qquad (9)$$

for the lithium sulfate solutions, and

$$d_{25} = 0.997 + 0.13061c - 0.01212c^{3/2} \qquad (10)$$

for the sodium sulfate solutions.

Table II contains the experimental results and the values obtained by the theory. It is apparent that the agreement of the theoretical values with the observed ones is very close for the lithium sulfate solutions. On the other hand, the observed results for sodium sulfate are somewhat higher than the calculated ones. For this latter case, the maximum deviation is 1% at 0.00147 *M* which is considerably larger than the estimated experimental error.

TABLE II

OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF LITHIUM AND SODIUM SULFATES AT 25°

c	Li_2SO_4 $\mathfrak{D} \times 10^5$ (obsd.)	$\mathfrak{D} \times 10^5$ (calcd.)	*c*	Na_2SO_4 $\mathfrak{D} \times 10^5$ (obsd.)	$\mathfrak{D} \times 10^5$ (calcd.)
0.00000	...	(1.0413)	0.00000	...	(1.2302)
.00064	1.000	.999	.00081	1.178	1.173
.00071	0.997	.998	.00081	1.177	1.173
.00071	.998	.998	.00147	1.170	1.158
.00085	.993	.994	.00199	1.160	1.150
.00210	.973	.975	.00268	1.151	1.142
.00267	.968	.968	.00356	1.137	1.132
.00348	.961	.961	.00448	1.129	1.124
.00440	.954	.955	.00449	1.132	1.124
.00573	.946	.948	.00479	1.124	1.122

Detailed Considerations

Some valuable conclusions may be derived from the results by a critical examination of the theoretical computations. Figures 1 and 2 show graphs which illustrate the details of the calculations for the lithium and sodium sulfate solutions, respectively. The diffusion coefficients have been plotted against *c* rather than $c^{1/2}$ for the purpose of spreading the results. The curve A represents the complete theoretical computation. If the mobility term, $\overline{M}/c$, remained constant (not a function of *c*) and equal to its value at infinite dilution, curve B is obtained. The limiting law given by equation (3) is represented by the bottom curves in the figures. $\mathfrak{D}_0$ and $\mathcal{S}(\mathfrak{D})$ given in Tables I and II were computed by equations (4) and (5), respectively.

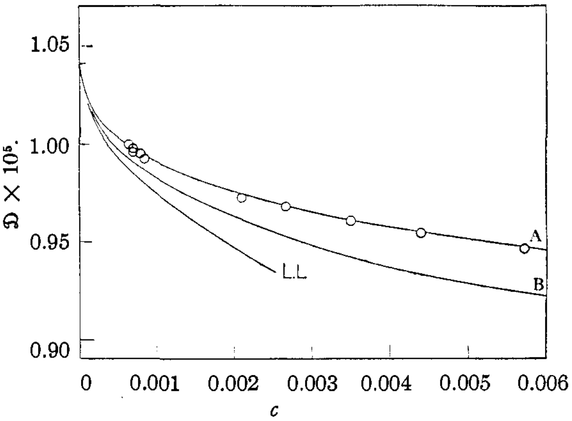

Fig. 1.—The diffusion coefficient of lithium sulfate as a function of its concentration: A, complete theory; B, mobility term constant; L.L., limiting law; circles represent observed results.

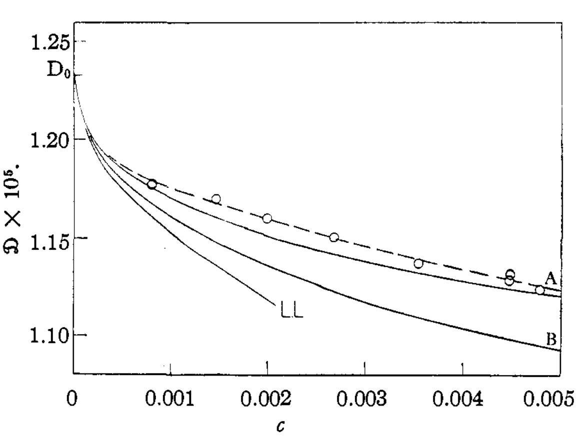

Fig. 2.—The diffusion coefficient of sodium sulfate in dilute solutions: A, complete theory; B, mobility term constant; L.L., limiting law; circles represent experimental results.

Although the lithium sulfate results indicate complete agreement with theory at these low salt concentrations, care must be exercised in this case because of some uncertainties inherent in the quantities used in this complicated calculation. In particular, the thermodynamic term was obtained from activity coefficients computed by equation (6) from electromotive force and isopiestic vapor pressure measurements of concentrations from 0.05 to 0.5 *M*. Unfortunately, there are few accurate activity coefficient measurements (of high accuracy) of electrolytes at 25° and at low concentrations, and one must relay on lengthy extrapolations. On the other hand, the variation of the quantity, $\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right)$ with concentration is about one-half of that of $y_\pm$, a fact which is of advantage in reducing the error in the calculation of the thermodynamic term. The sodium sulfate results illustrated in Fig. 2 indicate a departure from theory of the order of 0.5%. This discrepancy may be real but more must be known concerning the activity coefficients at these low concentrations before we can be certain.

In both cases the estimation of the mobility terms, based as they are upon accurate conductance measurements should be reliable. Figures 1 and 2 show definitely that the complete theoretical calculation is more valid than that which neglects the variation of the mobility term with the concentration.

Both series of results approach the values predicted by the limiting law as the concentrations approach zero. Further, since these are absolute computations of the diffusion coefficients, the re-

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(10) Ref. (6), p. 233.

sults yield further confirmation of the validity of the Nernst limiting equation.

The diffusion coefficients of the three unsymmetrical type electrolytes, lithium sulfate, sodium sulfate and calcium chloride at concentrations below 0.005 *M* exhibit considerable individualistic behaviors. Assuming for the time being that the theoretical computations are correct, we find that lithium sulfate conforms with theory. On the other hand, the observed values of sodium sulfate are somewhat higher than those calculated while those for calcium chloride lie considerably below the theoretical values. These observations prove that the explanation of the deviations does not reside in the unsymmetrical nature of these salts but in specific interactions between the ions themselves or between the ions and the solvent molecules.

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The Phase System BaO–NiO

BY J. J. LANDER

The phase system BaO–NiO has been studied largely by means of X-ray diffraction. The two compounds NiO·BaO and NiO·3BaO occur in the system. Their preparation and properties are described. NiO·BaO is black, stable in air, orthorhombic, and melts at 1240°. NiO·3BaO is gray-green, unstable in air, hexagonal, and melts at 1160°. A eutectic melting at 1080° is observed between these compounds, but none between NiO·3BaO and BaO. Intersolubility of all solid phases in the system is small, even at high temperatures, but quantitative data have not been obtained.

1. **Introduction.**—The purpose of this paper is to give an account of the preparation and properties of phases in the system bivalent nickel ion, oxygen ion and barium ion. The following paper describes the synthesis and properties of compounds containing oxygen ion, barium ion and nickel in higher states of oxidation.

2. **Chemical Background.**—BaO may be obtained by decomposition of $BaCO_3$, BaO_2, $Ba(OH)_2$, etc. It may then be mixed with NiO and heated until reaction takes place. But one would like to mix BaO and NiO in a predetermined ratio. Since BaO rapidly absorbs moisture, techniques for doing this are generally not convenient. $BaCO_3$ is, from this point of view, a more convenient starting material, and moreover it can be obtained very pure. It has been found that decomposition of the carbonate and reaction with NiO proceed rapidly if the mixture is maintained in vacuum (1 mm. or less) at 900° or higher. Reaction between several grams of material in a small volume is then complete in a few hours.

The atmosphere in which reaction takes place is critical. The products react with oxygen at temperatures above 450°. In one atmosphere of oxygen and below 730° divalent nickel compounded with oxygen and barium is oxidized to the tetravalent state. Between 730° and about 1200° it is also oxidized. But at high temperatures and in the absence of oxidizing agents divalent nickel compounded with oxygen and barium is reduced to metallic nickel. Exact conditions for the stability of divalent nickel products containing barium and oxygen have not been determined.

Reactions carried out in vacuum at a high temperature may easily result in reduction of the nickel. The residual atmosphere in a vacuum system tends to be reducing and when $BaCO_3$ is a starting material, once decomposition of the carbonate is complete, reduction of nickel may take place. Above 900° this danger becomes increasingly acute. Reactions carried out in nitrogen present much the same problem.

The danger of oxidation or reduction is largely avoided by starting with large amounts of anhydrous BaO and NiO and either fusing rapidly, or reacting below the fusion temperature in a small closed system. However, it may also be avoided, if $BaCO_3$ is used, by exercising simple precautions. Use of a vacuum system eliminates the danger of oxidation. Reduction of nickel or incomplete decomposition of the carbonate may be avoided by monitoring the decomposition (measuring the pressure of released CO_2). In a well-mixed sample reaction with NiO and decomposition of the carbonate are completed simultaneously. If the reaction mixture is loosely packed the pressure drop is fairly sharp. If the products are immediately cooled carbon dioxide and/or nickel are normally found in no more than trace amount.

3. **Materials and Apparatus.**—All chemicals used were highly pure except BaO_2. The grade of BaO_2 available and used in a few experiments contained 89% peroxide and about 1% silica.

Two types of furnaces were used. Heats made at atmospheric pressure were run either in a 1.25″ i.d. long alundum tube the center portion of which was surrounded by a nichrome heater, or in a 0.5″ i.d. alundum tube wound with Pt–Rh heater wire and inserted in the larger alundum tube. Vacuum heats were made in a Pt–Rh wound vacuum furnace of conventional design.

Both platinum and nickel crucibles were used. In general platinum crucibles were used for vacuum heats and nickel crucibles for heats carried out at atmospheric pressure. These latter heats generally had for purpose the fusion of products in a flux in order to obtain single crystals and comparatively large amounts of material were used.

4. **Technique.**—In the initial and largest phase of the work weighed amounts of $BaCO_3$ and NiO were mixed in acetone in a ball mill. A platinum crucible was filled loosely with several grams of the dried material and slowly heated in the vacuum furnace. After several hours heating at 900 to 950° the pressure normally dropped in a few minutes from about 1 mm. to about 0.1 mm. The furnace was then turned off.

When cool the furnace was opened and the reaction products transferred rapidly to a small vial. A fraction of a gram was placed under a few drops of dried pump oil in an agate mortar and ground. This material was drawn into a thin walled 15 mil glass capillary and an X-ray powder pattern obtained from it. CuKα radiation was used. It was found that this capillary-immersion in oil technique