

differences, although accurate to only 0.001%, are given in p. p. m. in the last column of Table II, where V represents the volume calculated from the density, and V_a the volume calculated additively. It is evident that, even at this temperature, the solutions are ideal. The average deviation from ideality is somewhat smaller than the experimental error, and the largest deviation is only twice the experimental error.

Lewis and Macdonald¹¹ have pointed out that if the molecular volumes of light and heavy water were the same, the density of deuterium oxide should be 1.1116 instead of 1.1076. Robinson and Bell¹² have shown that in dioxane solutions the partial molal volume of deuterium oxide is even smaller than that of protium oxide over a wide range of concentration, and so we might expect to find an even greater density for deuterium oxide than 1.1116. That this is not the case has been ascribed to a greater coördination of the molecules in deuterium oxide, producing a more open structure in the liquid. Cross, Burnham and Leighton¹³ have shown that the coördination

(11) G. N. Lewis and R. T. Macdonald, *THIS JOURNAL*, **55**, 3057 (1933).

(12) R. A. Robinson and R. P. Bell, *Trans. Faraday Soc.*, **33**, 650 (1937).

(13) P. C. Cross, J. Burnham and P. A. Leighton, *THIS JOURNAL*, **59**, 1134 (1937).

in liquid water can be shown to be due to bonds between neighboring oxygens through hydrogens. These bonds are much stronger in deuterium oxide than in protium oxide, and it would appear that the amount of bonding in mixtures of the two is intermediate and directly proportional to the mole fraction. That this is true, even at 5°, where the amount of four-coördination is quite large for both species, would be supported by the results of this research.

The author wishes to express his appreciation of the helpful suggestions and criticisms of Drs. C. H. Greene and L. G. Longworth, and wishes to thank Dr. R. J. Voskuyl and Mr. F. C. Novello for assistance in some preliminary work.

Summary

1. The densities of a series of mixtures of protium and deuterium oxides have been measured at 5 and 25°.

2. From the standpoint of density, these mixtures form ideal solutions at both temperatures.

3. The equation derived for ideal solutions is recommended for calculating the composition of a mixture from the density.

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[CONTRIBUTIONS FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. V. Lanthanum Chloride at 25°

BY THEODORE SHEDLOVSKY AND DUNCAN A. MACINNES

The previous papers in this series¹⁻³ described the underlying theory and the experimental procedure for obtaining activity coefficients from potential measurements on concentration cells with transference of the form



in which M represents the positive ion constituent. The results obtained for aqueous solutions of sodium chloride,¹ hydrochloric acid,² potassium chloride and calcium chloride³ were shown to be in excellent accord with the Debye-Hückel theory at low concentrations. Lanthanum chloride has been chosen for this series as an example of a tri-

valent electrolyte. Unlike other trivalent chlorides it has the advantage of being practically free from hydrolysis.

The thermodynamic equation connecting the potential E of cell (A) for this salt, the transference number t of the positive ion, the concentration C in gram moles per liter of solution and the activity coefficient f is

$$-E = \frac{4RT}{3F} \int_{C_1}^{C_2} t \, d \log (Cf) \quad (1)$$

The factor $\frac{4}{3}$ arises from the fact that four gram moles of ions—one of lanthanum and three of chloride—are transported in the passages of 3 faradays of current through a corresponding concentration cell without transference. The apparatus, experimental procedure and method of compu-

(1) Brown and MacInnes, *THIS JOURNAL*, **57**, 1356 (1935).

(2) Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936).

(3) Shedlovsky and MacInnes, *ibid.*, **59**, 503 (1937).

TABLE I

THE POTENTIALS OF THE CONCENTRATION CELL: Ag; AgCl, LaCl₃ (0.033333): LaCl₃ (C₂), AgCl; Ag at 25°, AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF LANTHANUM CHLORIDE IN AQUEOUS SOLUTION

1	2	3	4	5	6	7
Concn. in moles per liter at 25°, C ₂	E. m. f., mv., E	Trans. no., t	Log activity coeff. ratio - Δ log f	Activity coefficients f exptl.	f ₁ computed equation (5)	δ (mv.)
0.0006070	52.694	0.4701	0.2551	0.8817	0.8825	0.014
.0016628	38.140	.4663	.2215	.8160	.8169	.017
.0032179	29.052	.4627	.1910	.7607	.7600	-.014
.004885	23.500	.4600	.1664	.7188	.7180	-.017
.010936	13.242	.4530	.1059	.6253	.6256	-.007
.017188	7.746	.4478	.0657	.5700	.5699	-.003
.025257	3.209	.4423	.0280	.5226	.5225	-.003
.033333	0.000	.4375	.0000	.4900	.4899	-.003

tation of the results have been described in previous papers.²⁻⁴

Lanthanum chloride of a high grade of purity was recrystallized, and the salt was shown to be pure by photospectroscopic analysis except for a possible trace of cerium. Stock solutions were prepared with conductivity water at a concentration of $1/30$ mole per liter (*i. e.*, 0.1 normal), the reference solution C₁ used in all the determinations. An accurate check on the concentration of these stock solutions was made by conductivity measurements, using our own results on the conductance of the salt solutions, which were found to be in good agreement with those reported by Jones and Bickford.⁵ The dilute solutions, C₂, were prepared by weight dilution of the solutions C₁, using the density data of Jones and Bickford⁵ in computing their concentrations. Measurements of pH on the solutions showed them to be neutral.

Results and Discussion

The results of the measurements on the potentials of lanthanum chloride concentration cells at 25° are given in Table I. The first column of the table contains the concentration C₂ in moles per liter. The second column contains the potentials, E, in millivolts of a concentration cell (A), C₁ being 0.033333 mole (0.1 N) in every case.

(4) A simple alternative method for computing values of Δ log f from the measurements is the following

$$dE = -\frac{\nu RT}{F} t d(\log Cf)$$

in which ν is the number of gram moles of ions transported per faraday in a concentration cell without transference. Let $\delta = \frac{1}{t} - \frac{1}{t_1}$

Substituting $\delta + \frac{1}{t_1}$ for $\frac{1}{t}$ and integrating, there results

$$-\Delta \log f = -\frac{FE}{\nu RT t_1} - \log \frac{C_2}{C_1} - \frac{F}{\nu RT} \int_0^E \delta dE$$

The integral in the last term is evaluated graphically from a plot of δ vs. E.

(5) Jones and Bickford, THIS JOURNAL, 56, 606 (1934).

The transference numbers for the lanthanum ion at the concentrations C₂ have been computed from the measurements of Dr. L. G. Longworth⁶ of this Laboratory and are given in column 3. Column 4 lists values of the logarithms of the activity coefficient ratios $-\Delta \log f \equiv \log f/f_1$ computed from these data by the methods already described.^{1,3,4} In order to obtain the activity coefficients, f , from $-\Delta \log f$, it is necessary to evaluate the activity coefficient, f_1 , of the reference solution. For the uni-univalent electrolytes, sodium chloride, potassium chloride, hydrochloric acid and the bi-univalent calcium chloride, discussed in the former papers of this series,¹⁻³ it was possible to do so by extrapolating with the aid of the Debye-Hückel equation

$$-\log f = \Delta \log f - A = \alpha \sqrt{C}/(1 + \beta \sqrt{C}) \quad (2)$$

in which $A = \log f_1$, α is a theoretical constant depending on the valence type of the electrolyte, the solvent and the temperature, and β is an empirical constant related to the size of the ions. For a tri-univalent electrolyte, the value of α in water at 25° is 3.715. With this value it was found impossible to make a satisfactory extrapolation for obtaining A from the data on lanthanum chloride, using equation (2). Consequently, an attempt was made to interpret the results with the aid of the "extended theory" for the activity coefficients of unsymmetrical electrolytes of La Mer, Gronwall and Greiff.⁷ This met with no greater success. Kirkwood⁸ recently has derived an equation for activity coefficients, which takes into account close range ion interactions which become relatively more important with higher valence electrolytes. His equation reduces to the Debye-Hückel formulation for low concentrations and avoids the convergence difficulties of La Mer,

(6) Longworth, *ibid.*, 60, 3070 (1938).

(7) La Mer, Gronwall and Greiff, *J. Phys. Chem.*, 35, 2245 (1931).

(8) Private communication from Dr. J. G. Kirkwood (1937).

Gronwall and Greiff's equations. For a tri-univalent salt his equation is

$$\Delta \log f - A \equiv -\log f = 3.715\sqrt{C} + 32.7C \log C + BC \quad (3)$$

in which B is a constant depending on the ion radii. Within the region of validity of this equation, a plot of $(\Delta \log f - 3.715\sqrt{C} - 32.7C \log C)$ vs. C should be linear with a slope of B , cutting the ordinate axis at a value equal to A . Such a plot showed curvature which, however, decreased at the lower concentrations. Although no linear extrapolation was possible through the experimental points, the curve was carried to the axis with a limiting tangent which corresponds to a "distance of closest approach" for the ions of about 23 Å., a rather improbable value.

A simple plot of $-\Delta \log f$ vs. \sqrt{C} shows comparatively little curvature. It was therefore decided to try an equation of the form

$$\Delta \log f - A \equiv -\log f = a\sqrt{C} - bC \quad (4)$$

with both a and b empirical constants. Such an equation proved to be in excellent accord with the entire set of measurements well within the limit of experimental error. The values for the constants are $A = -0.3098$, $a = 2.282$ and $b = 3.20$; *i. e.*

$$-\log f = 2.282\sqrt{C} - 3.20C \quad (5)$$

The fifth column of Table I gives the activity coefficients on the basis of $A = -0.3098$. The corresponding values computed from equation (5) are listed in column 6. The last column in the table gives the difference in potential, δ , in millivolts between the measured values of E and those that would be required to be in complete accord with equation (5). In no case is the discrepancy as great as 0.02 millivolt. A plot of the results is shown in Fig. 1. Here values of $-\log f$ are

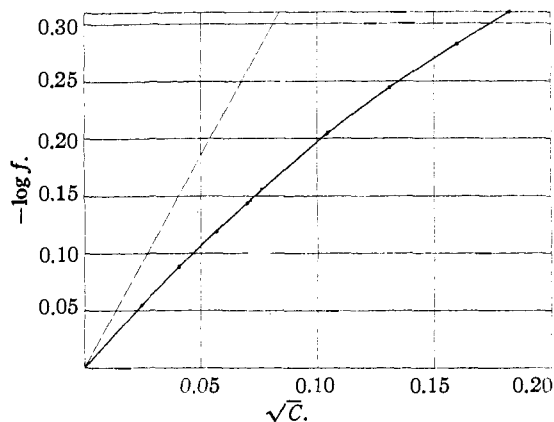


Fig. 1.

plotted against the square root of the concentration. The curve through the experimental results is a plot of equation (5). The broken line is the Debye-Hückel limiting slope for a tri-univalent salt. It is quite apparent that in the concentration range measured, the curve through even the most dilute points does not merge with the line representing the theoretical limiting slope. It will be observed that the coefficient of the square root term is considerably smaller than is required by the Debye-Hückel theory, namely, 3.715. That is, the activity coefficients for lanthanum chloride decrease less rapidly with concentration than we should expect from the interionic attraction theory. This is surprising since the deviations are opposite in direction to those which would result from ion pair formation. That is to say, the salt appears to be a "stronger" electrolyte than one would expect on the basis of present theory. On the other hand, there is the interesting fact that our conductivity measurements and those of Jones and Bickford⁵ on dilute lanthanum chloride solutions are in good accord with the interionic attraction theory for conductance. It is difficult to reconcile normal conductance behavior with the quite abnormal activity coefficients.

The values for f presented in this paper are, it must be emphasized, only relative, depending on the value $f = 0.4900$ at $C = 0.033333$ mole per liter. However, equation (5) accurately represents such activity coefficients for the concentration range $C = 0.0006$ to $C = 0.033$. The corresponding equation on a molality basis is

$$-\log \gamma = 2.279 \sqrt{m} - 3.19 m \quad (6)$$

in which m is in moles per 1000 g. of water, and γ is the corresponding activity coefficient.

The osmotic coefficients of trivalent metal chloride solutions have been measured recently by Mason⁹ at 25° with the isopiestic vapor pressure method. From his data for lanthanum chloride, covering a concentration range between 0.06 and 2 molal, he has computed activity coefficients, γ , which are much lower than our values. In fixing his scale for activity coefficients, Mason assumed the equation of Hückel¹⁰ (*i. e.*, equation (2) with the addition of a linear term in concentration) to be valid from $m = 0$ to 1.5. The necessary constants were determined from data for concentrated solutions at $m = 0.5$, 1.0 and 1.5.

(9) Mason, *THIS JOURNAL*, **60**, 1638 (1938).

(10) Hückel, *Physik. Z.*, **26**, 93 (1925).

On the basis of work published from this Laboratory on the activity coefficients of dilute univalent chlorides,¹⁻³ we are convinced that such a procedure results in equations which fail to hold for low concentrations. The inadequacy of various extensions of the Debye-Hückel equation for dilute lanthanum chloride solutions has, in addition, been discussed in this paper. However, the serious discrepancy between Mason's and our activity coefficient scales is due to his method of computation and not to inconsistency in the experimental work. The osmotic coefficient, ϕ , is related to the activity coefficient, γ , by the equation

$$\phi = 1 + \frac{1}{m} \int_0^m m \, d \log_e \gamma \quad (7)$$

To compare our activity coefficient values with Mason's measurements we have evaluated the integral in equation (7) analytically, using equation (6). The resulting equation is

$$\phi = 1 - 1.749\sqrt{m} + 3.673m \quad (8)$$

from which we can compute values of osmotic coefficients corresponding to our measurements on the basis of the activity coefficient scale implied in equations (4), (5) or (6).

Figure 2 shows a graph of osmotic coefficient values, ϕ , plotted against the square root of the molal concentration, \sqrt{m} . Mason's measurements appear as the black circles in this figure, whereas the open circles correspond to our values. It is evident that a smooth curve could readily be drawn through both sets of points. The solid and dotted curves in the figure correspond to Mason's smoothed values and our equation (8),

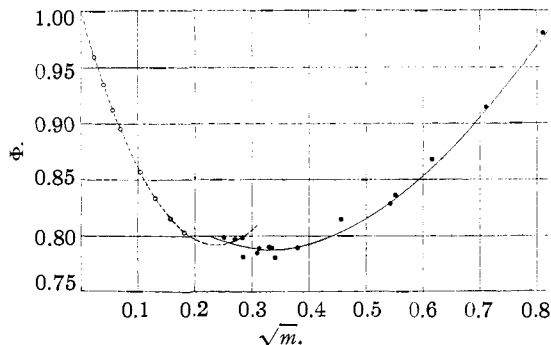


Fig. 2.

respectively. It is clear that equation (8) should not be used beyond a concentration of about 0.05 molal. The two sets of data, based on very different experimental methods, appear, however, to be quite consistent.

Summary

Measurements have been made on the potentials of lanthanum chloride concentration cells with transference from $C = 0.0006$ to 0.0333 mole per liter at 25° . From these data and accurate transference numbers, activity coefficients have been computed. The results do not appear to be in harmony with the available equations based on the interionic attraction theory since the values decrease less rapidly with increasing concentration than the theory predicts. Osmotic coefficients obtained from our results have been shown to be consistent with recent isopiestic measurements.

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The Specific Heats at Low Temperatures of Manganese, Manganous Selenide, and Manganous Telluride¹

By K. K. KELLEY²

In two earlier papers^{3,4} from the Metallurgical Fundamentals Section, Metallurgical Division, Bureau of Mines, data were reported for the specific heats at low temperatures of manganous oxide and manganous sulfide. Both of these sub-

(1) Published by permission of the Director, Bureau of Mines, United States Department of the Interior. (Not subject to copyright.)

(2) Chemist, Metallurgical Fundamentals Section, Metallurgical Division, Bureau of Mines.

(3) Millar, *THIS JOURNAL*, **50**, 1875 (1928).

(4) Anderson, *ibid.*, **53**, 476 (1931).

stances behave anomalously, the manganous oxide having a high "hump" in its specific heat curve around 116°K . and the manganous sulfide having a two-cusped "hump" in the region around 140°K . It was thought worth while to extend these measurements to the selenide and telluride, as by analogy these substances might be expected to show anomalous behavior and thus data would exist for a series of four similar but irregularly behaving compounds.