terms of the other by a trial and error process. None of the observed vapor pressures differ from those calculated from equation 6 by more than 0.5 mm. The probable error of the determinations is considered to be somewhat less than 0.5 mm.

The excess partial molal free energy of the hydrocarbons at infinite dilution was calculated from equations 4 and 6. Vapor pressures of propane and *n*-butane required in this calculation were obtained from the equations published by Thodos[25] and that of isobutane was interpolated from the measurements of Aston[26] and Beattie.[15] The partial molal heats of mixing and excess entropies at infinite dilution were obtained from the free energies by standard thermodynamic formulas. The values are listed in Table IV. The excess entropy is seen to be negative, as it is for higher hydrocarbons in ethanol.[7,9,23] The excess partial molal free energy, which is a measure of the deviation from ideal behavior, increases on going from propane to the butanes, and for isoöctane in ethanol it amounts to 1470 cal./mole at 50°.[7]

TABLE IV

EXCESS PARTIAL MOLAL THERMODYNAMIC FUNCTIONS OF HYDROCARBONS AT INFINITE DILUTION, CAL./MOLE

Temp., °C.	$\overline{F}_2^E$	$\overline{H}_2^M$	$-T\overline{S}_2^E$
	Propane		
0	1020	147	873
25	1096	244	851
50	1164	315	848
	n-Butane		
25	1187	395	792
35	1213	439	774
50	1249	511	738
	Isobutane		
10	1158	227	931
25	1205	362	843
35	1231	456	775
50	1266	573	693

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[25] G. Thodos, *Ind. Eng. Chem.*, **42**, 1514 (1950).

[26] J. G. Aston, R. M. Kennedy and S. C. Schumann, THIS JOURNAL, **62**, 2059 (1940).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Zinc Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

The diffusion coefficient of zinc sulfate from 0.001 to 0.005 molar concentration has been determined by the conductometric method. The experimental results are considerably higher than those computed by the Onsager and Fuoss theory unless the influence of ion-pair formation is taken into consideration. A correction factor has been introduced for ion-pair formation which leads to a reasonable interpretation of the results.

Diffusion coefficients of lithium, sodium[1] and potassium chlorides[2] and potassium nitrate[3] in dilute aqueous solutions determined by the conductance method agree within very narrow limits with the theory of Onsager and Fuoss.[4] Conformity with theory is also found for lithium sulfate while the diffusion of sodium sulfate[5] appears to be somewhat higher than the theoretical value and the diffusion coefficient of calcium chloride[6] is considerably below the theoretical prediction.

To illustrate the behavior of another type of electrolyte, we have measured the diffusion coefficient of zinc sulfate from 0.001 to 0.005 molar. The behavior of this substance in relation to the theory should be interesting since its conductance indicates considerable ion-pair formation and recent work[7,8] has indicated dissociation constants of the order of 0.005 for 2–2 valence type electrolytes. The activity coefficient of zinc sulfate has been determined in dilute solutions from the electromotive forces of cells without liquid junctions by Cowperthwaite and LaMer[9] who found that the extended theory[10] was required to interpret the results. These activity coefficients prove useful in evaluating the thermodynamic factor required by the theory of diffusion.

Experimental Results

The apparatus and technique used in these conductometric measurements is the same as that previously employed in this Laboratory and described in detail.[2] As in the earlier investigations, it is assumed that the difference in conductance at the bottom and top electrodes in the cell is proportional to the difference in salt concentrations at these two positions. That no appreciable error is caused by this approximation is apparent from the data in Table I in which the specific conductances L_1 and L_2, at round concentrations, c_1 and c_2, taken from the measurements of Owen and Gurry are recorded. The last column contains the coefficient $(L_1 - L_2)/(c_1 - c_2)$ when $c_1 + c_2 = 0.011$. This quantity is fairly constant throughout the range considered.

TABLE I

SPECIFIC CONDUCTANCES OF ZINC SULFATE AT 25°

c_1	$L_1 \times 10^3$	c_2	$L_2 \times 10^3$	$[(L_1 - L_2)/(b_1 - c_2)]_{c_1+c_2-0.01}$
0.009	0.77822	0.002	0.21622	0.08029
.008	.70623	.003	.30841	.07956
.007	.63316	.004	.39452	.07955
.006	.55744	.005	.47746	.07998

Highest grade analytical zinc sulfate was purified by twice dissolving in conductivity water and pre-

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

[2] Harned and Nuttall, *ibid.*, **69**, 737 (1947); **71**, 1460 (1949); Harned and Blake, *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 Blake, THIS JOURNAL, **73**, 2448 (1951).

[6] Harned and Levy, *ibid.*, **71**, 2781 (1949).

[7] Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

[8] Owen and Gurry, THIS JOURNAL, **60**, 3078 (1938).

[9] Cowperthwaite and LaMer, *ibid.*, **53**, 4333 (1931).

[10] Gronwall, LaMer and Sandved, *Physik Z.*, **29**, 358 (1928).

cipitating with methanol. A final crystallization was made from conductivity water. The *p*H of all solutions was greater than 6.

The calculation of the diffusion coefficient was effected by the same procedure as described in our earlier communications.[2] No unusual behaviors were noticed which might disturb the consistency of the experiments. The final values obtained for the diffusion coefficient are recorded in the second column of Table II.

TABLE II

OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF ZINC SULFATE AT 25°

c	$\mathfrak{D} \times 10^5$ (obsd.)	$\mathfrak{D} \times 10^5$ (calcd.)	α	λ_m
0.00000	...	0.8486	1.00	..
.00108	0.747	.721	0.885	42
.00139	.739	.708	.86	42
.00192	.733	.690	.84	44
.00256	.728	.673	.81	45
.00260	.731	.672	.81	46
.00263	.732	.671	.81	47
.00308	.721	.664	.79	45
.00439	.714	.647	.76	46
.00471	.707	.644	.75	44
			Mean	44

Theoretical Calculations

For an electrolyte dissociating into two ions, the theoretical equations for the diffusion coefficient,[11] $\mathfrak{D}$, are

$$\mathfrak{D} = 16.629 \times 10^{10}\, T \left(\frac{\bar{M}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (1)$$

where

$$\left(\frac{\bar{M}}{c}\right) \times 10^{20} = \frac{1.0748}{z}\left(\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) - \frac{0.4404}{\mathring{a}\eta_0}\left(\frac{\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \frac{\kappa a}{1 + \kappa a} + \left(\frac{z}{\mathring{a}}\right)^2 \frac{36790}{\eta_0(DT)}(\kappa a)^2\phi(\kappa a) \quad (2)$$

T is the absolute temperature, $y_{\pm}$ the mean activity coefficient on the molar scale, c the concentration in moles per liter, z the valence of the cation or anion, λ_1^0 and λ_2^0, the limiting ionic conductances, η_0 the viscosity of water, D its dielectric constant, κ the Debye and Hückel reciprocal radius, a the mean distance of approach of the ions in cm., $\mathring{a}$ the same in ångstrom units, and $\phi(\kappa a)$ the exponential integral function of the theory. Upon substituting the values $\lambda_1^0 = 53$[8]; $\lambda_2^0 = 79.8$[12]; $\mathring{a} = 3.64$[9]; D[13] $= 78.54$; $\eta_0 = 8.949 \times 10^{-3}$ [13]; $z = 2$; and $T = 298.16$ in equation (2), we obtain

$$\left(\frac{\bar{M}}{c}\right) \times 10^{20} = 17.115 - \frac{1.3173\sqrt{c}}{1 + 2.3922\sqrt{c}} + 303.35\, c\phi(2.3922\sqrt{c}) \quad (3)$$

The thermodynamic term in equation (1) was estimated from the activity coefficients obtained by Cowperthwaite and LaMer[9] from cells without liquid junctions. By applying the method of least squares to their data for the concentration range 0.000498 to 0.0099 mole per liter, we find that

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 + 28.48c - 6.187c^{1/2} \quad (4)$$

The theoretical values in the third column in Table II were computed by equations (1), (3) and (4).

It is apparent from the second and third columns of Table II that the observed results are considerably higher than those calculated on the basis of the theory without further modification. The obvious explanation of this difference lies in the fact that 2–2 electrolytes exhibit considerable ion-pair formation. From conductance measurements of copper and zinc sulfate solutions, Owen and Gurry[8] obtained 0.0049 and 0.0043 for their dissociation constants at 25° while Davies[7] obtained 0.0045 at 18° for both of these salts.

The influence of ion-pair formation on the diffusion coefficient may be computed in the following manner for an electrolyte dissociating into two kinds of ions. If n_1, n_2 and n_m are the concentrations, ω_1, ω_2 and ω_m, the mobilities of the cation, anion and ion-pair, respectively, then the total flow J is expressed by

$$J = -(n_1\omega_1\nabla\bar{\mu}_1 + n_2\omega_2\nabla\bar{\mu}_2) - n_m\omega_m\nabla\mu \quad (5)$$

where $\bar{\mu}_1$ and $\bar{\mu}_2$ are the electrochemical potentials of the ions, and μ, the chemical potential of the undissociated ion pairs. Since in diffusion, the ions migrate with the same velocity, $\omega_1\nabla\bar{\mu}_1 = \omega_2 \cdot \nabla\bar{\mu}_2$. Utilizing this equality, the mass action law, $\mu = \mu_1 + \mu_2$, and recalling[11] that $\mu = \bar{\mu}_1 + \bar{\mu}_2$, we find that

$$J = -\left[n_1\left(\frac{\omega_1\omega_2}{\omega_1 + \omega_2}\right) + n_m\omega_m\right]\nabla\mu \quad (6)$$

for zinc sulfate since n_1 equals n_2. Since the salt concentration n equals $n_1 + n_m$, this equation may be rearranged to give

$$J = -n\left(\frac{\omega_1\omega_2}{\omega_1 + \omega_2}\right)\left[1 + \frac{n_m}{n}\left(\frac{\omega_m}{\omega_1} + \frac{\omega_m}{\omega_2} - 1\right)\right] \quad (7)$$

The term in brackets is the correction factor to be applied to the values of the diffusion coefficient, $\mathfrak{D}_{\text{calcd.}}$, as calculated by equations (1) to (4). Thus, since $n_m/n = 1 - \alpha$, where α is the degree of dissociation, and since the mobilities are proportional to the conductances, the correction factor for ion-pair formation becomes

$$1 + (1 - \alpha)\left[\lambda_m^0\left(\frac{1}{\lambda_1^0} + \frac{1}{\lambda_2^0}\right) - 1\right] = \mathfrak{D}_{\text{obsd.}}/\mathfrak{D}_{\text{calcd.}} \quad (8)$$

Upon substitution of the values of λ_1^0 and λ_2^0 for the zinc and sulfate ions, we obtain

$$1 + (1 - \alpha)[0.0314\lambda_m^0 - 1] = \mathfrak{D}_{\text{obsd.}}/\mathfrak{D}_{\text{calcd.}} \quad (9)$$

which permits the evaluation of the mobility of the ion pair if the degree of dissociation is known.

These values of λ_m, given in the last column of Table II are approximately constant throughout the measured range of concentration. The mean value of 44 may be compared to 31.9 obtained for the ion mobility term $\lambda_1^0\lambda_2^0/(\lambda_1^0 + \lambda_2^0)$ which is not an unreasonable result. This higher value may be explained by the loss of water of hydration of the zinc ion in forming the ion-pair.

Although this first estimation of the mobility of

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(11) Harned, *Chem. Revs.*, **40**, 461 (1947), Eq. (178).

(12) MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1938, p. 342.

(13) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, pp. 118, 128.

an ion-pair is very interesting, the approximate nature of the calculations involved should not be overlooked. The estimation of the thermodynamic term in equation (1) directly from experimental data should be fairly reliable. On the other hand, the two terms in equation (2) which represent the effect of electrophoresis depends on the value of 3.64 Å. assigned to the mean distance of approach a and of course this may be in error. However, this uncertainty does not invalidate the qualitative nature of the estimate of λ^0_m for if we assumed an extreme value of a of 10.8 Å., we find that λ^0_m is about 50. A further uncertainty resides in the values of α derived from conductance data.

Although these calculations are approximate, the theory of ion-pair formation in the case of zinc sulfate is consistent with our data in diffusion, the theory of electrophoresis of Onsager and Fuoss, the determination of the degree of dissociation by the conductance method and known behavior of the activity coefficient.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Conductances of Potassium Iodide, Silver Nitrate and Some Alkaline Earth Halides in Methanol at 20° and 0°[1,1a]

BY LYLE R. DAWSON AND WILLIAM M. KEELY[2]

Conductance studies have shown that for solutions of potassium iodide and silver nitrate in methanol the equivalent conductance is a linear function of the square root of the concentration over the range 1.6×10^{-5} to 2.0×10^{-2} N at 0 and 20°. Linearity was observed also at concentrations below 0.001 N for magnesium, strontium and barium chlorides and strontium bromide and iodide. The experimental slope is less than the theoretical for potassium iodide, but greater for all others with the deviation becoming less with increasing atomic weight of the bivalent cation. Considering the dielectric constant to be the principal variable, the effective dielectric constants have been calculated. The data give evidence that the principal temperature effect is its influence on the viscosity. Indications that solvation and acid–base effects are complicating factors appear also.

Conductance studies of solutions of silver nitrate and the halides of some of the alkali and alkaline earth metals were made for the purpose of testing the applicability of the Onsager equation[3] to solutions of these salts in a non-aqueous medium. Previous studies[4] have shown fair agreement between the observed values of the slopes of plots of equivalent conductance *versus* the square root of the concentration and the values predicted by the Onsager equation for uni-univalent electrolytes in methanol. However, this agreement does not extend to the results for bi-univalent salts, indicating that there is considerable tendency for association of ions which results in values for the equivalent conductance being less than that predicted by theory. It has been reported[5] that the thiocyanates of barium, strontium, calcium and magnesium behave like nearly completely dissociated bi-univalent electrolytes at low concentrations in methanol, but the thiocyanates of zinc and cadmium appear to be weak electrolytes. Data reported by Kanning and coworkers[6] suggest that sulfuric acid is an incompletely dissociate uni-univalent electrolyte in methanol.

Experimental

Apparatus.—The bridge assembly was essentially the same as that described by Shedlovsky.[7]

Four Washburn-type cells, having constants ranging from 0.07292 to 2.166, were used. The cell constants were determined by the method of Jones and Bradshaw.[8] The electrodes were coated lightly with platinum black and errors which might result from adsorption were minimized by agitating the solution in the cell. The cells were held in a thermostated bath which maintained a constant temperature to within ±0.01°.

Salts.—C.P. potassium iodide was recrystallized twice from conductivity water. C.P. silver nitrate was dissolved in hot conductivity water and recrystallized by slowly adding freshly distilled ethanol. Both of these salts used in this research were better than 99.9% pure.

Anhydrous magnesium chloride was prepared by the method described by Davidson[9] in which a pyridine–magnesium chloride complex was formed. The complex was decomposed under vacuum into anhydrous magnesium chloride and pyridine which volatilized. Analyses showed purities greater than 99% for all samples used. Anhydrous barium chloride and anhydrous halides of strontium were obtained from W. D. Mackay Co. In every case, analysis showed the purity to be greater than 99.9%.

Solvent.—Commercial reagent grade methanol was purified by the method described by Kanning, Bobalek and Byrne.[6] Specific conductances of the samples used ranged from 1.5×10^{-7} to 3.0×10^{-7} ohm^{-1} cm.$^{-1}$ at 20°. The Karl Fischer reagent gave no evidence of water in either the solvent or the solutions used in this research.

Solutions.—Solutions were prepared on a weight basis and molarities calculated, assuming the density of the solution to be the same as that of the pure solvent. All transfers were made in a dry atmosphere.

Results

Experimental conductivities were corrected for the conductivity of the solvent, and averages of two

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(1) This work was supported in part by a research contract with the U. S. Army Signal Corps.

(1a) For detailed tables order Document 3239 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) Abstracted from a Ph.D. dissertation submitted by William M. Keely.

(3) L. Onsager, *Physik Z.*, **27**, 388 (1926); **28**, 277 (1927).

(4) (a) A. Unmack, E. Bullock, D. A. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (*London*), **A132**, 427 (1931); (b) J. E. Frazer and H. Hartley, *ibid.*, **A109**, 351 (1925); (c) T. H. Mead, O. L. Hughes and H. Hartley, *J. Chem. Soc.*, 1207 (1933); (d) L. Thomas and E. Marum, *Z. physik. Chem.*, *Abt A*, **143**, 191 (1929).

(5) A. Unmack, D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (*London*), **A127**, 228 (1928).

(6) E. W. Kanning, E. G. Bobalek and J. B. Byrne, THIS JOURNAL, **65**, 1111 (1943).

(7) T. Shedlovsky, *ibid.*, **52**, 1793 (1930).

(8) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

(9) H. L. Davidson, M.S. Thesis, University of Kentucky, 1948.