measure of the relative flow rates of the ion-pair and the electrolyte. This may be expressed by the equivalent conductances by multiplying both numerator and denominator of this fraction by the faraday. Thus

$$\mathfrak{D}_{\text{obsd}}/\mathfrak{D}_{\text{calcd}} = 1 + (1 - \alpha)\left[\lambda^0_{\text{m}}\Big/\frac{\lambda^0_1\lambda^0_2}{\lambda^0_1 + \lambda^0_2} - 1\right] \quad (6)$$

where λ^0_{m} is 96,500 ω_{m}. This equation yields

$$\mathfrak{D}_{\text{obsd}}/\mathfrak{D}_{\text{calcd}} = 1 + (1 - \alpha)[0.0314\ \lambda_{\text{m}} - 1] \quad (7)$$

upon substituting the numerical values of λ^0_1 and λ^0_2 for the equivalent conductances of the magnesium and sulfate ions.

By utilizing the values of α for zinc sulfate given in the fourth column of Table I, the values of λ^0_{m} recorded in the last column are obtained. It is to be observed that these results do not vary greatly with concentration. The mean value of 46 is slightly greater than that of 44 obtained for λ^0_{m} of zinc sulfate. Both of these results are greater than $\lambda^0_1\lambda^0_2/(\lambda^0_1 + \lambda^0_2)$ which computation shows to 31.9. The higher flow rate for the ion-pairs may be explained by the loss of water of hydration as a result of their formation.

DEPT. OF CHEMISTRY
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The Diffusion Coefficient of Cesium Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND CHARLES A. BLAKE, JR.

The present series of results supplements our earlier determinations of the diffusion coefficients of lithium and sodium sulfates.[1] When these measurements were made the limiting equivalent conductance of the cesium ion was not known with sufficient accuracy to permit a precise application of theory. This discrepancy in our knowledge has been remedied by recent accurate measurements of the conductance of cesium chloride in water.[2]

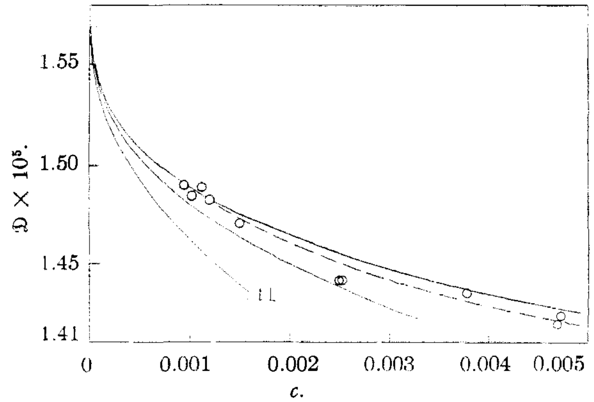

Fig. 1.—The diffusion coefficient of cesium sulfate as function of concentration in dilute aqueous solution: top curve, complete theory; circles, experimental results; dashed curve represents mean of experimental results; center solid curve, equation (6); lower curve, limiting law.

Experimental Results and Theoretical Calculations

The apparatus and technique were the same as those described in detail by Harned and Nuttall[3] and require no amplification. Cesium sulfate was prepared from a carefully purified sample of cesium chloride. The chloride was converted to sulfate by addition of the required amount of sulfuric acid and by surface evaporation. The dried salt was dissolved in water and precipitated with a large volume of ethyl alcohol. Further purification was obtained by recrystallization from water. Spectrographic analysis of this material showed no potassium, less than 0.001% of sodium or lithium, and less than 0.01% of rubidium. The *p*H of a 0.01 solution was found to be 6.

The second column of Table I contains the observed diffusion coefficients at the concentrations designated in the first column. The theoretical equations[4] are written in full in our earlier communication[1] and only the final numerical equations derived from the quantities recorded at the bottom of the table will be given. Thus

$$\mathfrak{D} = 7.437 \times 10^{13}(\overline{\mathfrak{M}}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 21.097 - \frac{2.114\sqrt{c}}{1 + 2.135\sqrt{c}} + 116.21c\,\phi\,(2.135\sqrt{c}) \quad (2)$$

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{2.0306\sqrt{c}}{(1 + 2.135\sqrt{c})^2} - 0.157c - c\,\psi\,(d) \quad (3)$$

$$c\,\psi\,(d) = \frac{-0.0026c - 0.1824c^{3/2}}{0.9970 - 0.0026c - 0.01216c^{3/2}} \quad (4)$$

The theoretical limiting equation is

$$\mathfrak{D} \times 10^5 = 1.569 - 3.343\sqrt{c} \quad (5)$$

TABLE I

OBSERVED AND CALCULATED DIFFUSION COEFFICIENT OF CESIUM SULFATE

c	$\mathfrak{D} \times 10^5$ Obsd.	Calcd.
0.00000	...	1.569
.00096	1.490	1.490
.00102	1.484	1.488
.00112	1.489	1.485
.00120	1.482	1.482
.00150	1.470	1.475
.00248	1.442	1.455
.00251	1.441	1.454
.00378	1.435	1.436
.00468	1.419	1.426
.00472	1.424	1.426

$\lambda^0_1 = 77.27^2$; $\lambda^0_2 = 79.8^5$; $A'^{(6)} = 2.135$; a (Å.) $= 3.75$; $\mathcal{S}_{(f)} = 1.7636^7$; $B = -0.068^6$; $d_0 = 0.9970$; $M_2 = 361.88$; $\phi^0_{\text{v}} = 56.9^7$; $S_{\text{v}} = 12.2^7$ $\mathcal{S}_{(\mathfrak{D})} = 3.343 \times 10^{-5}$; $D = 78.54$; $\eta_0 = 8.949 \times 10^{-3}$.

It is apparent from comparison of the values in columns two and three of Table I that the agree-

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(1) H. S. Harned and C. A. Blake, THIS JOURNAL, **73**, 2448 (1951).

(2) W. E. Voisinet, Jr., Dissertation, Yale University, June, 1951.

(3) H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 737 (1947).

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

(5) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 342.

(6) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1943, p. 233 or 587.

ment of the observed with the results computed by equations (1) to (4) is good. A more detailed illustration of the calculation is shown in Fig. 1 in which the diffusion coefficient is plotted against the concentration in moles per liter. The curve at the top represents the complete calculation according to equations (1) to (4) while the bottom curve is the graph of equation (5). The solid graph in the center is the plot of equation (1) when $(\mathfrak{M}/c)$ is constant and equal to its value when c equals zero. Under this condition equation (1) becomes

$$\mathfrak{D} = 7.437 \times 21.097 \times 10^{-7}\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (6)$$

The difference between the graph of this equation and the top curve in Fig. 1 represents the calculated effect of electrophoresis.

The dashed graph, drawn through the experimental results, exhibits a maximum deviation from theory of 0.4%. It appears that the two results at 0.0025 molar concentration are low. In any case, when the complicated nature of the calculation is considered, good concordance with the theory is obtained. Further, the results confirm the essential correctness of the electrophoretic terms.

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The Solubility of Aromatic Hydrocarbons in Water

BY E. F. G. HERINGTON

In a recent paper under the above title Bohon and Claussen[1] have described the determination of the solubility of various aromatic hydrocarbons including benzene, toluene, ethylbenzene, *m*- and *p*-xylene in water for the temperature range 0–40°. The partial molar heats of solution ($\Delta\bar{H}_{sol}$) were calculated by the aid of equation 1 where m is the molar solubility and R and T have their usual significance.

$$\Delta\bar{H}_{sol} = RT^2[d(\ln m)/dT] \quad (1)$$

The authors state that, "Since the process of solution of the hydrocarbon into water can be considered an isothermal equilibrium reaction, the free energy change is zero and the entropy of solution, $\Delta\bar{S}_{sol}$, is given by $\Delta\bar{S}_{sol} = \Delta\bar{H}_{sol}/T$." The large variation of the quantity $\Delta\bar{H}_{sol}$ with temperature and the values of $\Delta\bar{S}_{sol}$ found in this manner were examined in terms of the possible nature of the aqueous solutions.

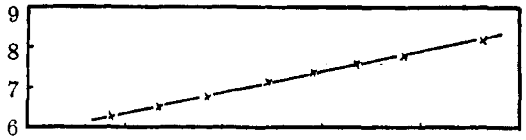
Since the solution of a hydrocarbon in water is in fact accompanied by a free energy change and since Bohon and Claussen's choice of the liquid hydrocarbon as a standard state is not a very convenient one for the discussion of the nature of the aqueous solutions because the liquid hydrocarbons themselves exhibit some structure,[2] the experimental data have been examined on a different basis. The treatment adopted follows that developed by Butler[3] and the thermodynamic quantities ΔF, ΔS and ΔH have been calculated from the experimental results by means of equations 2, 3 and 4 where p is the vapor pressure of the hydrocarbon in mm., and N is the mole fraction of the hydrocarbon in solution.

$$\Delta F = RT \ln (p/N) \quad (2)$$

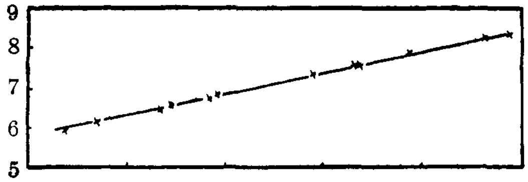
$$\Delta S = -[d\Delta F/dT] \quad (3)$$

$$\Delta H = \Delta F - T[d\Delta F/dT] \quad (4)$$

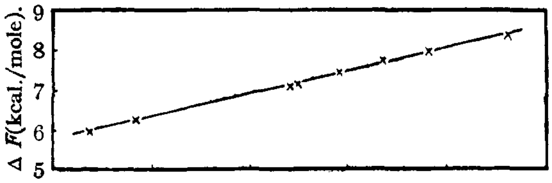
The quantity ΔF is the free energy of hydration[4] and is equal to the difference between the molar free energy of the hydrocarbon in the standard state referred to the infinitely dilute aqueous solution and at 1 mm. pressure in the vapor while ΔS and ΔH are the corresponding entropy and heat terms. Hildebrand[5] has recently re-emphasized the importance of adopting a constant pressure of the vapor as the standard state of the solute for the discussion of the structure of solutions. The vapor pressures of liquid benzene, toluene, ethylbenzene, *m*- and *p*-xylene were calculated from the Antoine equation using the accurate data for these compounds presented by the A.P.I.



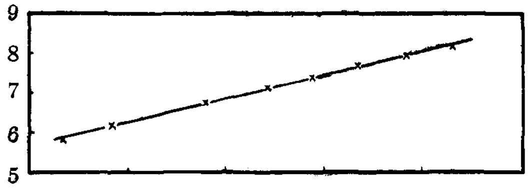
Benzene.



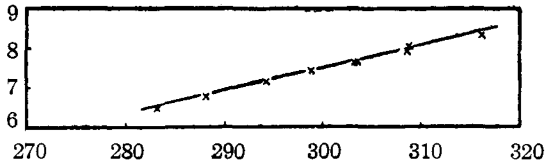
Toluene.



Ethylbenzene.



m-Xylene.



p-Xylene.

Fig. 1.—Free energy of hydration, ΔF, plotted against the temperature, T, in degrees absolute.

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(1) Bohon and Claussen, THIS JOURNAL, **73**, 1571 (1951).

(2) Herington, *Trans. Faraday Soc.*, **40**, 481 (1944).

(3) Butler, "Chemical Thermodynamics," 4th ed. (1 Vol.), The Macmillan Co., London, 1946, p. 389.

(4) ΔF is the Gibbs free energy change and is represented in Britain by the symbol ΔG.

(5) Hildebrand, *J. Phys. Colloid Chem.*, **53**, 973 (1949).