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DEC 27 1965

FISH FH62 0118

[Reprinted from the Journal of Physical Chemistry, 66, 1607 (1962).]
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THE EFFECT OF PRESSURE ON THE EQUILIBRIUM OF MAGNESIUM SULFATE¹

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Received February 16, 1962

Conductivity at 25° of aqueous solutions of MgSO₄ has been measured as a function of pressure up to 2000 atm. for five concentrations from 0.0005 to 0.02 *M*. The effect of pressure on the dissociation constant was calculated with the equation used by Davies, Otter, and Prue. The difference of partial molal volumes between products and reactants, $\Delta \bar{V}^0$, was found to be -7.3 ± 0.4 cc./mole. The relation of this work to results of sound absorption measurements in MgSO₄ solutions is pointed out. Measurements of the effect of pressure on conductivity also were made for the following aqueous solutions: KCl, K₂SO₄, MgCl₂, and NaCl at 25° over the same concentration range. Values of equivalent conductivity at infinite dilution, Λ_p^0 , were determined as a function of pressure for MgSO₄, KCl, K₂SO₄, and MgCl₂. Values of Λ_p/Λ_1 are given for MgSO₄, KCl, K₂SO₄, and MgCl₂ at each concentration. Since $\bar{V}_2^0 = -6.4$ cc./mole for MgSO₄, the partial molal volume of the state which dissociates into ions is $\sim +1$ cc./mole.

The unusually high sound absorption of sea water, about 30 times greater than that of fresh water, is due to a small concentration of magnesium sulfate, approximately 0.02 *M*.² Tamm and Kurtze³ found that other 2-2 sulfates exhibit similar high absorption and Eigen⁴ has discussed their significance. Liebermann⁵ showed how a pressure dependent chemical reaction could produce this sound absorption and Bies,⁶ on the basis of pressure dependent dissociation, derived a theory by which he determined equilibrium constants of magnesium sulfate from sound absorption measurements at atmospheric pressure in water and dioxane-water solvents. Verma⁷ has made a recent summary of sound absorption in electrolytes which includes measurements as a function of concentration, temperature, dielectric constant, pressure, and the effect of heavy water as solvent.

For any quantitative check of the theory of sound absorption based on pressure dependent dissociation reactions, it is vital to know the volume change upon dissociation into ions, that is $\Delta \bar{V}^0$ which appears in eq. 1.⁸ It should, in principle, be possible to use the same ($\Delta \bar{V}^0$) and degree

$$\left(\frac{\partial \ln K_m}{\partial p} \right)_{T,m} = - \frac{\Delta \bar{V}^0}{RT} \quad (1)$$

of dissociation (α) to describe results of density and conductivity measurements; if sound absorption is due to dissociation into ions, it should be possible, using the same ($\Delta \bar{V}^0$) and α , to account for it also. This has been done for a weak electrolyte in the case of ammonium hydroxide in work reported by Hamann and Strauss⁹ and by Carnevale and Litovitz.¹⁰

(1) This work represents results of research under joint sponsorship of the Office of Naval Research, Contract Nonr 2216 (05) and the Division of Physical Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia. Contribution from Scripps Institution of Oceanography, New Series.

(2) R. W. Leonard, *J. Acoust. Soc. Am.*, **20**, 254 (1948).

(3) K. Tamm and G. Kurtze, *Acustica*, **3**, 33 (1953).

(4) M. Eigen, *Discussions Faraday Soc.*, **24**, 25 (1957).

(5) L. N. Liebermann, *Phys. Rev.*, **76**, 1520 (1949).

(6) D. A. Bies, *J. Chem. Phys.*, **23**, 428 (1955).

(7) G. S. Verma, *Rev. Mod. Phys.*, **31**, 1052 (1959).

(8) B. B. Owen and S. R. Brinkley, *Chem. Rev.*, **29**, 461 (1941).

(9) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955).

Since $\Delta \bar{V}^0$ has not been determined experimentally for any of the 2-2 sulfates from conductivity measurements as a function of pressure, the object of this work is to do so at 25° to facilitate comparison with values of $\Delta \bar{V}$ determined by Bies.¹¹ The molal dissociation constant K_m was calculated from equation 2, in which it is as-

$$K_m = \frac{m\alpha^2 f_{\pm}^2}{1 - \alpha} \quad (2)$$

sumed that the activity coefficient of the associated salt is unity at all pressures and concentrations. The degree of dissociation was determined at 25° for magnesium sulfate by dividing the measured equivalent conductivity by the theoretical value determined from the equation

$$\Lambda = \Lambda^0 - \left[\frac{R\Lambda^0}{1 + B\bar{a}\sqrt{I}/2} + E \right] \frac{\sqrt{I}}{1 + B\bar{a}\sqrt{I}} \quad (3)$$

used by Davies, Otter, and Prue.¹² The activity coefficients were calculated from the Debye-Hückel equation

$$- \log f_{\pm} = \frac{A |z_1 z_2| \sqrt{I}}{1 + B\bar{a}\sqrt{I}} \quad (4)$$

In both eq. 3 and 4 molar concentrations varying with pressure were used. In eq. 2 the rational activity coefficient is used for the molal activity coefficient. Tables I and II list constants for aqueous solutions useful in evaluating eq. 3 and 4.

The dielectric constant ϵ was calculated using the Owen and Brinkley¹³ equation

$$\epsilon_p = \epsilon_1 \sqrt[3]{1 - 0.4060 \log \left(1 - \frac{p+1}{B+1} \right)} \quad (5)$$

where p is in atmospheres and the 25° value $B = 2885$ atm. from Gibson¹⁴ is used. The viscosity

(10) (a) M. Eigen, *Z. Physik. Chem. (Frankfurt)*, **1**, 176 (1954); (b) E. H. Carnevale and T. A. Litovitz, *J. Acoust. Soc. Am.*, **30**, 610 (1958).

(11) Because of an error in concentration (ΔV)² reported by Bies was a factor of 10³ low. The corrected value is (ΔV)² = 10 (cc./mole)².

(12) W. G. Davies, R. J. Otter, and J. E. Prue, *Discussions Faraday Soc.*, **24**, 103 (1957).

(13) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, **64**, 32 (1943).

(14) R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4 (1934).

data were interpolated graphically from the measurements of Bridgman¹⁵ and the ratio of densities ρ_r was calculated from Dorsey.¹⁶ The value $\alpha = 14.28$ at atmospheric pressure is that used by Robinson and Stokes¹⁷; it decreases as a function of pressure, varying inversely as the dielectric constant.

TABLE I

CONSTANTS FOR WATER AS A FUNCTION OF PRESSURE AT 25°

P, atm.	ϵ	ϵT	$(\epsilon T)^{1/2}$	$(\epsilon T)^{3/2} \times 10^{-3}$	η (poise)	ρ_r
1	78.54	23,417	153.0	3.583	0.008937	1.0000
500	80.81	24,094	155.2	3.739	.009014	1.0220
1000	82.88	24,712	157.2	3.885	.009132	1.0416
1500	84.80	25,284	159.0	4.020	.009314	1.0595
2000	86.57	25,812	160.7	4.148	.009604	1.0758

TABLE II

CONDUCTIVITY AND ACTIVITY COEFFICIENT EQUATION CONSTANTS AS A FUNCTION OF PRESSURE FOR AQUEOUS SOLUTIONS AT 25° IN THE EQUATIONS

$$\Lambda_p = \Lambda_p^0 - \left[\frac{R\Lambda_p^0}{1 + B\alpha\sqrt{I}/2} + E \right] \frac{\sqrt{I}}{1 + B\alpha\sqrt{I}}$$

$$-\log f = \frac{A|z_1z_2|\sqrt{I}}{1 + B\alpha\sqrt{I}}$$

P, atm.	R	E	B	A	$\frac{d}{MgSO_4}$
1	0.9157	120.64	0.3286	0.5092	14.28
500	.8775	117.9	.3239	.4880	13.88
1000	.8445	114.8	.3198	.4696	13.53
1500	.8161	111.4	.3162	.4538	13.23
2000	.7910	106.9	.3129	.4398	12.95

Experimental

Apparatus.—The apparatus was essentially that described by Ellis.¹⁸ The conductivity cell consisted of a cylindrical Teflon tube closed at one end; a sliding Teflon plug inserted at the other end of the cell supported the electrodes, transmitted the pressure, and isolated the conductivity cell from white paraffin oil used in the pressure vessel. Heavy platinum wire pins were mounted parallel to the axis of the cylindrical plug and went all the way through it to provide electrical contact with the electrodes. Corrections to the cell constant as a function of pressure due to compression of the Teflon were obtained by comparing potassium chloride conductivity results. These were obtained with a sliding plug in which one electrode was supported by heavy platinum wire as above; the other electrode was supported by a glass rod located at the edge of both electrodes and whose axis was perpendicular to the plane of both electrodes and perpendicular to the axis of the cylindrical plug. A fine platinum wire provided electrical contact between the glass supported electrode and a shorter heavy platinum wire mounted in the sliding plug. Corrections for the solubility of the glass were made assuming the rate of solution or the change in conductivity $\Delta\kappa$ proportional to pressure and time, $\Delta\kappa = \Sigma\alpha Pt$, where α is assumed to be independent of pressure. A Wayne-Kerr universal bridge B221 was used for measuring conductance. The effects of series lead resistance and shunt resistance of the hydraulic oil as a function of pressure were measured; corrections for the 0.2 ohm series lead resistance were made where necessary. The temperature was $25 \pm 0.05^\circ$.

(15) P. W. Bridgman, "Physics of High Pressure," Bell and Sons, 1949.

(16) E. N. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publ. Co., New York, N. Y., 1940.

(17) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, p. 401.

(18) A. J. Ellis, *J. Chem. Soc.*, 3689 (1950).

(1130)

Materials and Method.—Aqueous solutions of potassium chloride, potassium sulfate, magnesium chloride, and magnesium sulfate were prepared from analytical grade reagents. Conductivities of these salts were measured at three concentrations and for magnesium sulfate, for two additional concentrations. Solvent conductivity corrections were made using experimentally measured values. Measured equivalent conductivities and calculated values at infinite dilution as a function of pressure were obtained as follows.

1. **Water Conductivity Correction.**—Subtract water conductance measured in same cell at same pressure.

$$\kappa'_{\text{salt}} - \kappa'_{\text{H}_2\text{O}} = \kappa'_{\text{salt}} - \text{H}_2\text{O}$$

2. **Specific Conductivity.**—Multiply water corrected conductance by pressure dependent cell constant to get specific conductivity as a function of pressure; cell constant was measured for each concentration.

$$(\kappa'_{\text{salt}} - \text{H}_2\text{O})L_p = \kappa_p$$

Pressure dependence of cell constant for the Teflon cell was determined by comparing 0.02 M KCl data in the Teflon cell with 0.01 M KCl data for the cell with a glass bar. It is assumed that Λ_p/Λ_1 for KCl is independent of concentration.¹⁹

TABLE III

 Λ_p/Λ_1 FOR AQUEOUS SOLUTIONS AT 25°
C is atmospheric pressure concentration in moles/l.

	P, atm.				
	$C \times 10^4$	500	1000	1500	2000
MgSO ₄	5.000	1.025	1.033	1.030	1.021
	10.01	1.028	1.041	1.040	1.033
	20.00	1.033	1.050	1.055	1.050
	100.1	1.051	1.083	1.098	1.104
K ₂ SO ₄	5.000	1.058	1.094	1.116	1.126
	20.00	1.015	1.016	1.007	0.995
	20.00	1.016	1.017	1.011	0.998
	220.6	1.021	1.029	1.026	1.018
MgCl ₂	5.000	1.019	1.023	1.015	0.999
	20.000	1.021	1.024	1.019	1.005
	200.7	1.023	1.029	1.025	1.014
KCl	5.000	1.015	1.018	1.010	0.996
	20.00	1.015	1.016	1.008	.994
	99.99	1.016	1.018	1.010	.996
200.0	1.016	1.018	1.012	.998	

3. **Ratio of Equivalent Conductivities.**—Divide $(\kappa_p/\kappa_1) = (\Lambda_p\rho_r/\Lambda_1)$ by ρ_r to get (Λ_p/Λ_1) for each pressure at each concentration. Plot (Λ_p/Λ_1) for each pressure vs. the square root of the molality, extrapolate to find $(\Lambda_p^0/\Lambda_1^0)$, and multiply by respective conductivities at infinite dilution. For MgSO₄, calculate Λ_p^0/Λ_1^0 according to the equation

$$[\Lambda_p^0]\text{MgSO}_4 = [\Lambda_p^0]\text{K}_2\text{SO}_4 + [\Lambda_p^0]\text{MgCl}_2 - [\Lambda_p^0]\text{KCl}$$

where

$$\Lambda_p^0 = \Lambda_1^0(\Lambda_p^0/\Lambda_1^0)$$

Results

The values of Λ_p/Λ_1 for all the salts used are listed in Table III. Equivalent conductance for MgSO₄ is listed in Table IV and equivalent conductances at infinite dilution are presented in Table V. The dissociation constants, K_m , and degree of association $(1 - \alpha)$ calculated using eq. 2, 3, and 4 are shown in Tables VI and VII for each concentration as a function of pressure; the $\Delta\bar{V}^0$

(19) The deviations of Λ_p/Λ_1 in Table III are within the limits of experimental error.