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THE EFFECT OF PRESSURE ON THE EQUILIBRIUM OF MAGNESIUM SULFATE1

DEC 27 1965

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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 Conductivity at 25° of aqueous solutions of MgSQ, 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 equa-tion used by Davies, Otter, and Prue. The difference of partial molal volumes between products and reactants, $\Delta \vec{V}^{\circ}$, was found to be -7.3 ± 0.4 cc./mole. The relation of this work to results of sound absorption measurements in MgSQ, solutions is pointed out. Measurements of the effect of pressure on conductivity also were made for the following aqueous solutions: KCl, K₂SQ, MgCl₃, and NaCl at 25° over the same concentration range. Values of equivalent conductivity at infinite dilution, Λ_p° , were determined as a function of pressure for MgSO, KCl, K₂SO₄, and MgCl₂. Values of Λ_p/Λ_1 are given for MgSO₄, KCl, K₂SO₄, and MgCl₂ at each concentration. Since $V_2^{\circ} = -6.4$ 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 water and dioxane-water solvents. 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.

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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 $\Delta \overline{V}^0$ which appears in eq. 1.8 It should, in principle, be possible to use the same $(\Delta \vec{V}^0)$ and degree

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

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).

Contributions from the Scripps Institution of Oceanography, New Series, 1424

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 ΔV determined by Bies.¹¹ The molal dissociation constant $K_{\rm m}$ was calculated from equation 2, in which it is as-

$$K_{\rm m} = \frac{m\alpha^2 f_{\pm}^2}{1-\alpha} \tag{2}$$

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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

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

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

$$-\log f_{\pm} = \frac{A \left| z_1 z_2 \right| \sqrt{I}}{1 + B \delta \sqrt{I}} \tag{4}$$

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

$$\epsilon_{\rm p} = \epsilon_1 / \left[1 - 0.4060 \log \left(1 - \frac{p+1}{B+1} \right) \right] \quad (5)$$

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 $(\Delta V)^2$ reported by Bies was a factor of 10⁸ low. The corrected value is $(\Delta V)^2 = 10$ (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).

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data were interpolated graphically from the measurements of Bridgman¹⁵ and the ratio of densities $\rho_{\rm r}$ 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.		еT	(eT)1/2	$(eT)^{3/2} \times 10^{-6}$	η (poise)	Pr	
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 CON-STANTS AS A FUNCTION OF PRESSURE FOR AQUEOUS SOLU-TIONS AT 25° IN THE EQUATIONS

$$\Lambda_{p} = \Lambda_{p}^{0} - \left[\frac{R\Lambda_{p}^{0}}{1 + B\delta\sqrt{I/2}} + E\right]\frac{\sqrt{I}}{1 + B\delta\sqrt{I}}$$
$$-\log f = \frac{A|z_{1}z_{2}|\sqrt{I}}{1 + B\delta\sqrt{I}}$$

P.			+		å
atm.	R	E	В	A	MgSO
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

the solubility of the glass were made assuming the rate of solution or the change in conductivity $\Delta_{\mathbf{x}}$ proportional to pressure and time, $\Delta_{\mathbf{x}} = \Sigma \alpha P t$, 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 $25 \pm 0.05^{\circ}$.

(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 (1959).

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Materials and Method.-Aqueous solutions of potassium chloride, potassium sulfate, magnesium chloride, and mag-nesium sulfate were prepared from analytical grade reagents. Conductivities of these salts were measured at three con-centrations 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. 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.

$$(\pi'_{\rm salt} - H_{\rm 2O})L_{\rm p} = \pi_{\rm p}$$

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_0/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, a	tm	
	$C \times 10^4$	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
	200.0	1.058	1.094	1.116	1.126
K ₂ SO ₄	5.000	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 $(x_p/x_1) = (\Lambda_{ppr}/\lambda_1)$ by p_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 $(\Lambda_p^o/\Lambda_1^o)$, and multiply by respective conductivities at infinite dilution. For MgSO₄, calculate Λ_p^o/Λ_1^o according to the equation

$$[\Lambda_{\mathbf{p}}^{0}] Mg SO_{4} = [\Lambda_{\mathbf{p}}^{0}] K_{2} SO_{4} + [\Lambda_{\mathbf{p}}^{0}] Mg Cl_{2} - [\Lambda_{\mathbf{p}}^{0}] KCl$$

where

$$\Lambda_{\rm p}^{0} = \Lambda_{\rm 1}^{0} (\Lambda_{\rm p}^{0} / \Lambda_{\rm 1}^{0})$$

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.

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

values were obtained graphically from the slope of log $K_{\rm m}$ plotted against pressure and are listed in Table VI. Although the 0.0005 molar value of $\Delta \tilde{V}^0$ is much less than the other values, it is included in the average $\Delta \tilde{V}^0 = -7.3$ cc./mole.

Note the change in the concentration dependence of $K_{\rm m}$ as the pressure increases; the variations in $K_{\rm m}$ decrease as pressure increases and $K_{\rm m}$ shows a slight dip at the two highest pressures.

TABLE IV

Λ_p FOR AQUEOUS MgSO₄ SOLUTIONS AT 25° C is atmospheric pressure concentration in moles/l.

			-P. atm		
$C \times 10^4$	1	500	1000	1500	2000
5.000	116.6^{a}	119.5	120.4	120.1	119.0
10.01	109.6^{a}	112.7	114.1	114.0	113.2
20.00	101.30	104.6	106.4	106.9	106.4
100.1	78.6	82.6	85.1	86.3	86.8
200.0	69.0	73.0	75.5	77.0	77.7
a m.1	Duran	and Tem	b Arr	hotmoon out	

^a Taken from Dunsmore and James. ^b Av. between extrapolated value from Dunsmore and James and this work.

TABLE V

Λ_p^0 for Aqueous Solutions at 25°

	P. atm.						
	1	500	1000	1500	2000		
K_2SO_4	(153.52)	155.7	155.8	154.0	152.1		
$MgCl_2$	(129.40)	131.6	132.2	130.7	128.4		
KCl	(149.85)	152.2	152.5	151.3	149.3		
MgSO4	(133.07)	135.1	135.5	133.4	131.2		

TABLE VI

Molal Dissociation Constant, $K_{\rm m}$, and $\Delta\,\overline{V}{}^{\rm 0}$ for Aqueous MgSO4 at $25\,^{\rm o}$

C is atmospheric pressure concentration in moles/l.

ΔV^{0} .	C			-P, atm.		
cc./mole	$\times 10^{4}$	1	500	1000	1500	2000
-8.5	5.000	0.0047	0.0054	0.0058	0.0078	0.0091
-7.0	10.01	.0048	.0055	.0062	.0075	.0086
-7.0	20.00	.0052	.0059	.0066	.0080	.0090
-7.3	100.1	.0063	.0073	.0083	.0097	.0111
-6.9	200.0	.0071	.0079	.0094	.0109	.0123
-7.3 Av						

TABLE VII

Degree of Association (1 - $\alpha)$ for Aqueous MgSO4 at 25°

C is atmospheric pressure concentration in moles/l.

			-P. atm		
$C \times 10^4$	1	500	1000	1500	2000
5.000	0.067	0.059	0.056	0.043	0.037
10.01	.107	.096	.089	.075	.068
20.00	.158	.144	.133	.115	.105
100.1	.314	.290	.271	.248	.230
200.0	.386	.360	.340	.315	.297

At the lowest concentration and the highest pressure, the value of $\Delta \bar{V}^0$ is very sensitive to the change in a as a function of pressure because $(1 - \alpha)$ is very small, as shown in Table VII. Errors in the conductivity measurement, of course, have a large effect of the value of $(1 - \alpha)$, especially at the lowest concentration.

Original data and cell constants are listed in the Appendix. Results obtained in this work for $0.009999 \ M \ KCl$ are compared with those obtained by Ellis¹⁸ in Table VIII. Results interpolated for

0.01 M K₂SO₄ from this work are compared with those obtained by Adams and Hall²⁰ in Table IX. Results obtained in this work for 0.01 KCl also are compared with values reported by Adams and Hall²⁰ in Table X. This work shows smaller differences with the results of Adams and Hall than with those of Ellis. The average deviation of these results from those of Adams and Hall is under 0.4% and with those of Ellis over 0.6%. The error in A shows up in the equilibrium constant almost completely in the $(1 - \alpha)$ term. For this type of experiment, Hamann estimated that accuracy was about $\pm 0.3\%$ in Λ_p/Λ_1 . For the 0.0005 M solution at 2000 atm., the effect

For the 0.0005 M solution at 2000 atm., the effect of an error of $\pm 0.4\%$ in the conductivity will cause $\Delta \overline{V^0}$ to vary by approximately 1 cc./mole. The data at low concentration are not accurate enough to enable us to say anything about a possible concentration dependence of $\Delta \overline{V^0}$. The average of all five concentrations and the average deviation are

$\Delta \bar{V}^0 = -7.3 \pm 0.4 \text{ cc./mole}$

TABLE VIII

Appr/A1 FOR 0.009999 M KCl. 25°

	1226 3 2 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	/
P, atm.	Ellis	Fisher
500	1.031	1.038
1000	1.052	1.060
2000	1.068	1.072
	TABLE IX	
$\Lambda_{\rm p}\rho$	$_r/\Lambda_1$ for 0.01 M K ₂ SO ₄ ,	25°
P, atm.	Adams and Hall	Fisher
500	1.0381	1.041

500	1.0381	1.041
1000	1.0644	1.065
2000	1.0894	1.084

TABLE X

$\Lambda_{p,\rho_{\rm f}}/\Lambda_1$ FOR 0.02 M NaCl, 25°

P, atm.	Adams and Hall	Fisher
500	1.0343	1.039
1000	1.0566	1.060
2000	1.0727	1.070

Using the value $\bar{V}_2^0 = -6.4$ cc./mole for Mg-SO₄,¹⁴ the partial molal volume of the state which dissociates into ions is $+0.9 \pm 0.4$ cc./mole.

Conclusions

The value $\Delta \tilde{V}^0 = -7.3$ cc./mole does not agree by a factor of two with that deduced by Bies⁶ on the assumption that a pressure dependent dissociation reaction is responsible for sound absorption.

It also disagrees with the values of $\Delta \bar{V}^0$ of -15 to -20 cc./mole quoted by Eigen, Kurtze, and Tamm.²¹

The authors indicate that $\Delta \bar{V}^0$ which appears in eq. 1 is not the same one which appears in the sound absorption equation. However, they say that for concentrations below 0.02 M, the difference between the two is less than 0.7 cc./mole. These authors explicitly showed the relationship

(20) L. H. Adams and R. E. Hall, J. Phys. Chem., 35, 2145 (1931).
 (21) M. Eigen, G. Kurtze, and K. Tamm, Z. Elektrochem., 57, 114, 118 (1953).

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between density and sound absorption data in terms of α and $\Delta \bar{V}^0$, but did not have conductivity data available to provide an independent measurement of $\Delta \bar{V}^{0,22}$

The reasons for the discrepancies are not clear at this time. Although hydrolysis corrections were not applied in determining equivalent conductivity for MgSO₄ as Owen and Gurry²³ did for ZnSO₄ and CuSO₄, the maximum values of their corrections are small at atmospheric pressure (0.2 and 0.8 conductance unit, respectively) and if relatively pressure independent, these corrections would not affect the $\Delta \hat{V}^0$ values significantly.

It may be, as Eigen⁴ suggests, that observed sound absorption relaxation effects are due to intermediate reactions preceding dissociation into ions and that the lower relaxation frequency $f \sim 10^5$ c.p.s. which Bies⁶ observed is associated with an intermediate chemical reaction. On the basis of another model, Fisher²⁴ calculated from density and sound absorption data values of degree of dissociation which agreed with conductivity data within 5%; one assumption was that the partial molal volume of the intermediate state preceding dissociation was zero, an assumption to which this work gives support.

Whatever the final interpretation of the mechanism of sound absorption, it is necessary to have quantitative values of partial molal volumes in order to check the theory.

The calculations of $\Delta \tilde{V}^0$ made herein are based on a particular equation from electrolyte theory, the selection of the closest distance of approach of ions, and the assumption that it varies inversely with the dielectric constant as pressure increases. Changes in the theory will undoubtedly affect the value of $\Delta \tilde{V}^0$. If the simpler Onsager-Debye-Hückel equation is used, the values of $\Delta \tilde{V}^0$ are about -10 cc./mole and show no concentration dependence. However, new values can be calculated from the data presented here. Changes in α due to changes in closest distance of approach were shown by Davies, Otter, and Prue¹³ to be very small, 0.4% at 0.0004 mole/l. as $\hat{\alpha}$ varied from 10 to 14 Å.²⁵

The type of work reported here also will be of use in evaluating the theoretical equations giving the pressure dependence of activity coefficients.

Acknowledgment.—The author wishes to thank Dr. S. D. Hamman, Chief of the Division of Physical Chemistry of C.S.I.R.O., Fisherman's Bend, Melbourne, Australia, for his stimulating help and keen interest in this work and for his most generous coöperation in making his high pressure equipment available and ready for these measurements. Without his help it would not have been

(22) M. Eigen and K. Tamm, J. Phys. Chem., 66, 93 (1962), propose a multistate dissociation model in which volume changes obtained acoustically and by conductivity methods are related but are not numerically the same.

(23) B. B. Owen and R. W. Gurry, J. Am. Chem. Soc., 60, 3074 (1938).

(24) F. H. Fisher, Marine Physical Laboratory Technical Memorandum 113, University of California, Marine Physical Laboratory of the Scripps Institution of Oceanography, 1960.

(25) At the highest concentration, m = 0.02, the effect of reducing the 4-parameter by a factor of three resulted in a decrease of $\Delta \overline{V}$ from -6.9 to -9.4 cc./mole.

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possible to do this work in the short time allotted. The author also wishes to thank the Office of Naval Research and the Director of the Marine Physical Laboratory, Dr. F. N. Spiess, for making it possible to do this work.

Appendix A

Cell Constants To find cell constant, L_{p} , at pressure P multiply atmos-

pheric	pressure value L_1 b	y Lp*
P, atm.		L_{p}^{*}
500		0.995
1000		.990
1500		.985
2000		.980
Salt	Concn., moles/l.	L
MgSO ₄	0.0005000	0.686
	.001001	.719
	.002000	.723
	.01001	.719
	.02000	.732
K_2SO_4	.0005000	.696
	.002000	. 699
	.02207	.732
MgCl ₂	.0005000	.696
	.002000	. 699
	.02007	.732

Appendix B

Copy of original conductivity data measured for electrolytes at 25° in aqueous solutions; Teflon cell without glass bar

		P	etm —		
1	478	985	1495	2001	1ª
3.774	3.932	4.040	4.102	4.132	3.770
3.766	4.082	4.330	4.517	4.656	3.763
7.163	7.501	7.746	7.909	8.006	7.137
5.699	5.981	6.6167	6.286	6.347	5.699
404.6	421.5	433.0	439.9	443.1	404.0
566.6	600.8	626.2	643.3	654.7	565.1
805.8	839.4	862.2	876.7	884.6	807.2
684.5	716.2	738.2	751.0	757.3	682.7
108.8	113.6	117.2	119.5	120.8	108.9
168.0	176.9	183.2	187.4	190.1	167.8
205.0	213.6	219.7	223.1	225.7	205.4
174.4	182.5	188.3	191.6	193.3	174.5
2.188	2.358	2.490	2.584	2.653	2.186
308.2	325.4	337.7	346.0	351.1	3.082
1.1	1.5	1.9	2.5	3.1	
0.2	0.2	0.2	0.2	0.2	
	1 3.774 3.766 7.163 5.699 404.6 566.6 805.8 680.5 8 684.5 108.8 168.0 205.0 174.4 2.188 308.2 1.1 0.2	1 478 3.774 3.932 3.766 4.082 7.163 7.501 5.609 5.981 404.6 421.5 566.6 600.8 805.8 839.4 684.5 716.2 108.8 131.6 174.4 182.5 2.188 2.358 308.2 325.4 1.1 1.5 0.2 0.2	1 478 985 3.774 3.932 4.040 3.766 4.082 4.330 7.163 7.501 7.746 5.699 5.981 6.6167 404.6 421.5 433.0 566.6 600.8 626.2 805.8 839.4 862.2 684.5 716.2 738.2 108.8 113.6 117.2 168.0 176.9 183.2 205.0 213.6 219.7 174.4 182.5 188.3 2.188 2.358 2.490 308.2 325.4 337.7 1.1 1.5 1.9 0.2 0.2 0.2 0.2	1 478 985 1495 1 478 985 1495 3.774 3.932 4.040 4.102 3.766 4.082 4.330 4.517 7.163 7.501 7.746 7.909 5.699 5.981 6.6167 6.286 404.6 421.5 433.0 439.9 566.6 600.8 620.2 643.3 805.8 839.4 862.2 876.7 684.5 716.2 738.2 751.0 108.8 113.6 117.2 119.5 168.0 176.9 183.2 187.4 205.0 213.6 219.7 223.1 174.4 182.5 188.3 191.6 2.188 2.358 2.490 2.584 308.2 325.4 337.7 346.0 1.1 1.5 1.9 2.5 0.2 0.2 0.2 0.2	1 478 985 1495 2001 3.774 3.932 4.040 4.102 4.132 3.766 4.082 4.330 4.617 4.656 7.163 7.501 7.746 7.909 8.006 5.699 5.981 6.6167 6.286 6.347 404.6 421.5 433.0 439.9 443.1 566.6 600.8 626.2 643.3 654.7 805.8 839.4 862.2 876.7 884.6 684.5 716.2 738.2 751.0 757.3 108.8 113.6 117.2 119.5 120.8 168.0 176.9 183.2 187.4 190.1 205.0 213.6 219.7 223.1 225.7 174.4 182.5 188.3 191.6 193.3 2.188 2.358 2.490 2.584 2.653 308.2 325.4 337.7 346.0 351.1 1.1 1

^a The readings in this column were obtained the day after the pressure run was made.

Appendix C

Notation

$$A = \frac{1.8246 \times 10^{6}}{(\epsilon T)^{1/4}}$$

$$B = \frac{5.209 \times 10^{9}}{(\epsilon T)^{1/4}}$$

$$E = \frac{41.25(|z_{1}| + |z_{2}|)}{\eta(\epsilon T)^{1/4}}$$

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- $R = \frac{2.801 \times 10^{6} |z_{1}z_{2}| q}{(\epsilon T)^{3/2} (1 + \sqrt{q})}$
- a = 14.28, Bjerrum critical distance in Ångstroms for a 2:2 electrolyte in water at 25°. This varies as a function of pressure
- c = concentration in moles/l.
- m = concentration in moles of solute/kg. of solvent $\rho_r = \text{relative density of water}$
- $q = \frac{1}{2}$ for symmetrical electrolytes, $z_1 = z_2$; $z_1 =$ $z_2 = 2$ for MgSO₄
- $I = 4c\alpha$, ionic strength of 2-2 salt
- T = absolute temperature
- $\alpha = \text{degree of dissociation}$
- ϵ = dielectric constant
- $\eta = \text{viscosity}$