

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

Note the change in the concentration dependence of K_m as the pressure increases; the variations in K_m decrease as pressure increases and K_m shows a slight dip at the two highest pressures.

TABLE IV

 Δ_p FOR AQUEOUS $MgSO_4$ SOLUTIONS AT 25° C is atmospheric pressure concentration in moles/l.

| $C \times 10^4$ | P , atm. | | | | |
|-----------------|--------------------|-------|-------|-------|-------|
| | 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 | 101.3 ^b | 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 Taken from Dunsmore and James. ^b Av. between extrapolated value from Dunsmore and James and this work.

TABLE V

 Δ_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 |
| $MgSO_4$ | (133.07) | 135.1 | 135.5 | 133.4 | 131.2 |

TABLE VI

MOLAL DISSOCIATION CONSTANT, K_m , AND $\Delta \bar{V}^0$ FOR AQUEOUS $MgSO_4$ AT 25° C is atmospheric pressure concentration in moles/l.

| $\Delta \bar{V}^0$, cc./mole | C $\times 10^4$ | P , atm. | | | | |
|----------------------------------|----------------------|------------|--------|--------|--------|--------|
| | | 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 $MgSO_4$ AT 25° C is atmospheric pressure concentration in moles/l.

| $C \times 10^4$ | P , atm. | | | | |
|-----------------|------------|-------|-------|-------|-------|
| | 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 d 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 K_2SO_4 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 Δ 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 Δ_p/Δ_1 .

For the 0.0005 M solution at 2000 atm., the effect of an error of $\pm 0.4\%$ in the conductivity will cause $\Delta \bar{V}^0$ 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 $\Delta \bar{V}^0$. 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

 $\Delta_p p_r/\Delta_1$ FOR 0.009999 M KCl, 25°

| P , atm. | Ellis | Fisher |
|------------|-------|--------|
| 500 | 1.031 | 1.038 |
| 1000 | 1.052 | 1.060 |
| 2000 | 1.068 | 1.072 |

TABLE IX

 $\Delta_p p_r/\Delta_1$ FOR 0.01 M K_2SO_4 , 25°

| P , atm. | Adams and Hall | Fisher |
|------------|----------------|--------|
| 500 | 1.0381 | 1.041 |
| 1000 | 1.0644 | 1.065 |
| 2000 | 1.0894 | 1.084 |

TABLE X

 $\Delta_p p_r/\Delta_1$ 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 $MgSO_4$,¹⁴ the partial molal volume of the state which dissociates into ions is $+0.9 \pm 0.4$ cc./mole.

Conclusions

The value $\Delta \bar{V}^0 = -7.3$ 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).

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 MgSO_4 , as Owen and Gurry²³ did for ZnSO_4 and CuSO_4 , 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 $\Delta\bar{V}^0$ 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 Bies⁹ 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 $\Delta\bar{V}^0$ 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 $\Delta\bar{V}^0$. If the simpler Onsager-Debye-Hückel equation is used, the values of $\Delta\bar{V}^0$ 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 \bar{d} 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 cooperation 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 \bar{d} -parameter by a factor of three resulted in a decrease of $\Delta\bar{V}$ from -6.9 to -9.4 cc./mole.

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 atmospheric pressure value L_1 by L_p^*

| P , atm. | L_p^* |
|------------|---------|
| 500 | 0.995 |
| 1000 | .990 |
| 1500 | .985 |
| 2000 | .980 |

| Salt | Concn., moles/l. | L_1 |
|-------------------------|------------------|-------|
| 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 , atm. | | | | | |
|---|------------|-------|--------|-------|-------|----------------|
| | 1 | 478 | 985 | 1495 | 2001 | 1 ^a |
| 0.02 M KCl, mmho | 3.774 | 3.932 | 4.040 | 4.102 | 4.132 | 3.770 |
| 0.02 M MgSO_4 , mmho | 3.766 | 4.082 | 4.330 | 4.517 | 4.656 | 3.763 |
| 0.02207 M K_2SO_4 , mmho | 7.163 | 7.501 | 7.746 | 7.909 | 8.006 | 7.137 |
| 0.02007 M MgCl_2 , mmho | 5.699 | 5.981 | 6.6167 | 6.286 | 6.347 | 5.699 |
| 0.002 M | | | | | | |
| KCl, μmho | 404.6 | 421.5 | 433.0 | 439.9 | 443.1 | 404.0 |
| MgSO_4 | 566.8 | 600.8 | 626.2 | 643.3 | 654.7 | 565.1 |
| K_2SO_4 | 805.8 | 839.4 | 862.2 | 876.7 | 884.6 | 807.2 |
| MgCl_2 | 684.5 | 716.2 | 738.2 | 751.0 | 757.3 | 682.7 |
| 0.0005 M | | | | | | |
| KCl, mmho | 108.8 | 113.6 | 117.2 | 119.5 | 120.8 | 108.9 |
| MgSO_4 | 168.0 | 176.9 | 183.2 | 187.4 | 190.1 | 167.8 |
| K_2SO_4 | 205.0 | 213.6 | 219.7 | 223.1 | 225.7 | 205.4 |
| MgCl_2 | 174.4 | 182.5 | 188.3 | 191.6 | 193.3 | 174.5 |
| 0.01001 M MgSO_4 , mmho | 2.188 | 2.358 | 2.490 | 2.584 | 2.653 | 2.186 |
| 0.00100 M MgSO_4 , μmho | 308.2 | 325.4 | 337.7 | 346.0 | 351.1 | 3.082 |
| Water, μmho | 1.1 | 1.5 | 1.9 | 2.5 | 3.1 | |
| Series lead resistance, ohm | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | |

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

Appendix C

Notation

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}}$$

$$B = \frac{5.209 \times 10^9}{(\epsilon T)^{1/2}}$$

$$E = \frac{41.25(|z_1| + |z_2|)}{\eta(\epsilon T)^{1/2}}$$