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Effect of High Pressure on Sound Absorption and Chemical Equilibrium*

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Interest in acquiring more definite knowledge of the mechanism of sound absorption in electrolytic solutions led to this experimental investigation of the pressure dependence of this phenomenon. A technique was evolved to measure sound absorption in liquids as a function of pressure at frequencies of 100–600 kc. The following properties of a 0.5-molar solution of $MgSO_4$ were measured up to 20 000 psi at 26°C: absorption, relaxation frequency and velocity. The absorption at 20 000 psi is less than one quarter that at atmospheric pressure and the relaxation frequency remains constant at 1.2×10^6 rad/sec over this pressure interval within the estimated experimental error of $\pm10\%$. The velocity increases linearly with pressure at the rate 0.1588 m/atmos. From these data the chemical and adiabatic compressibilities are computed.

In an effort to secure quantitative agreement with experimental results some new aspects of the dissociation theory are discussed.

INTRODUCTION

THE anomalous sound absorption exhibited by $MgSO_4$ solutions has spurred the interest of many researchers[1–6] in the general problem of sound absorption in solutions. In treating this phenomenon Liebermann[1] proposed two relaxation mechanisms to account for the observed excess absorption; (1) a partial specific heat, and (2) a partial chemical compressibility. For the particular case of a 0.02-molar solution of $MgSO_4$ in water he showed that the partial chemical compressibility could account for virtually all of the excess absorption while the partial specific heat accounted for only five percent. Presumably this chemical compressibility arises from the lack of pressure equilibrium between the molecule and its ions; neither $MgCl_2$ nor Na_2SO_4 exhibits this phenomenon which indicates both the magnesium and sulfate ions are involved in the absorption mechanism.

Sound absorption resulting from lack of equilibrium between a molecule and its ions is particularly significant in that it offers a means of exploring experimentally the kinetics of chemical equilibria in electrolytic solutions. For example, whenever pressure dependent chemical reactions are responsible for excess absorption a change in hydrostatic pressure should produce a shift in chemical equilibria and therefore a corresponding change in acoustic absorption.

Liebermann[1] showed that a liquid exhibiting a chemical compressibility will have an unusual property in that its total compressibility, β, depends on the rate of compression; that is

$$\beta=\beta_0-\beta_0'+\beta_0'/(1+i\omega/\kappa), \tag{1}$$

where β_0 is the isothermal compressibility, β_0' the chemical compressibility and κ the relaxation frequency associated with β_0'. Suppose the pressure on such a liquid is varied by a sound wave of angular frequency ω.

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[1] Liebermann, Phys. Rev. **76**, 1520 (1949).

[2] Leonard, Technical Report No. I, UCLA Physics Dept. (1950).

[3] Kurtz and Tamm, Acustica **3**, 33 (1953).

[4] Milton Manes, J. Chem. Phys. **21**, 1791 (1953).

[5] David A. Bies, J. Chem. Phys. **23**, 428 (1955).

[6] O. B. Wilson and R. W. Leonard, J. Acoust. Soc. Am. **26**, 223 (1954).

From Eq. (1) it is seen that the compressibility is greatest when $\omega=0$, the static case for which $\beta=\beta_0$. As ω increases the total compressibility decreases until $\beta=\beta_0-\beta_0'$ for $\omega=\infty$. Physically this means that the volume change due to the chemical reaction diminishes as the frequency increases because the finite rate of the chemical reaction gradually renders the reaction less sensitive to the more rapid pressure variations.

A fluid whose compressibility is of the form shown in Eq. (1) (complex compressibility) exhibits acoustic absorption which is related to chemical compressibility by the following equation[1]:

$$2\alpha=\frac{\beta_0'}{\beta_0 c}\left(\frac{\omega^2\kappa}{\omega^2+\kappa^2}\right), \tag{2}$$

where α is the acoustic absorption coefficient and c is the sound velocity. It will be shown later how β_0' is related to equilibrium properties of the chemical reaction.

EXPERIMENTAL WORK

Resonator Technique

In order to obtain the relaxation frequency of magnesium sulfate solutions as a function of pressure the absorption should be measured above and below the relaxation frequency if possible. Leonard,[2] Kurtz and Tamm,[3] and Wilson and Leonard[6] have measured the relaxation frequencies of magnesium sulfate solutions at atmospheric pressure and found them to be relatively insensitive to concentration. For solutions up to 0.1 molar concentration the relaxation frequencies lie in the 140-kc region.

The method chosen for absorption measurements in this frequency region was the resonator technique.[2] Basically this technique consists of exciting a single normal mode of the resonator, stopping the excitation and measuring the rate of decay of the sound field for this mode. The decay measured is the sum of losses due to the liquid and the resonator. Losses due to the resonator can be determined by using a liquid with negligible absorption.

Apparatus

The resonator was the most crucial piece of apparatus. It had to withstand high pressure, not corrode in water or salt solutions, and yet have thin walls to minimize absorption losses.

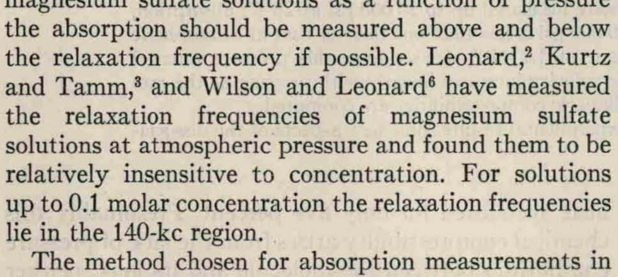

FIG. 1. Block diagram of apparatus.

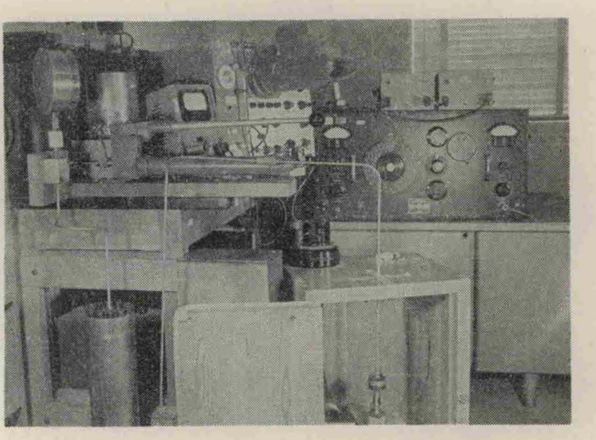

FIG. 2. High pressure absorption apparatus.

Consideration of machining problems led to the choice of a cylinder for the resonator. It was made long compared to its diameter in order to lessen end effects. The radius of the cylinder was determined by estimating the desired spacing of radial modes which should have the lowest losses. A cylinder with approximately a one inch inside radius proved to be satisfactory in the 100-kc region but exploded before satisfactory measurements could be made near 500 kc. Another cylinder, essentially a four-to-one reduction of the one which exploded, was built to make measurements in the 400–600-kc region.

Except for the resonant cylinders and the exchanger necessary for applying the hydrostatic pressure to them the apparatus consisted almost entirely of commercially available equipment. Figure 1 is a block diagram of the apparatus which is shown in Fig. 2. Filters were used in the receiver circuit.

The high pressure gauge, connectors, and one-fourth inch tubing were stock items from the American Instrument Company. The pressure calibration of the gauge was checked by measuring the velocity of sound in water as a function of pressure, correcting for expansion of the resonator walls and comparing results with known values.[7,8] As a precaution against explosions the resonators were enclosed in a box shown in Fig. 2 which also facilitated maintaining the temperature at 26±0.5°C.

Each cylinder was excited by a barium titanate transducer attached as shown in the block diagram and in Fig. 3. The response to the excitation was observed on the oscilloscope by means of a similar transducer mounted approximately opposite the other one.

High Pressure Technique

To measure absorption as a function of pressure required that a normal mode be followed as the pressure

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[7] Gerald Holton, J. Appl. Phys. **22**, 1407 (1951).

[8] T. A. Litovitz and E. H. Carnevale, J. Appl. Phys. **26**, 816 (1955).

increased; that is, the oscillator frequency had to be increased as the resonant frequency of the mode varied according to the change in sound velocity of the solution and the expansion of the resonator walls (see Fig. 4). Positive identification of liquid modes was assured by the sound velocity *vs* pressure data for water[7,8] and sound velocity *vs* concentration data at atmospheric pressure for aqueous solutions.[9–11]

Because the wall losses of the cylinders were large, it was necessary to use high concentrations of $MgSO_4$ in order to observe the effect of pressure on absorption. The concentration had to be great enough so that the absorption could still be measured at high pressures where it was less than one-third the value measured at atmospheric pressure. For this reason a concentration of 0.5 molarity was selected.

Ideally resonator loss data for a given mode should be obtained at the identical frequency using the nonabsorbing liquid. In previous work at lower concentrations water has been used to obtain correction data because the resonant frequencies in water and the solution of interest were practically identical. In this experiment the difference between the resonant frequencies in water and in 0.5 molar $MgSO_4$ is approximately four percent, too great to obtain valid correction data (see Fig. 4). Aqueous solutions of sodium chloride show negligible absorption; hence, the velocity of such solutions can be adjusted independently of absorption by varying concentration. By selecting the proper concentration the resonant frequencies in NaCl could be matched with those in $MgSO_4$ and correction data could be obtained satisfactorily. The match was not perfect over the entire pressure range (Fig. 4) but the difference was very small, less than 1.7 kc at 20 000 psi for the high frequency mode.

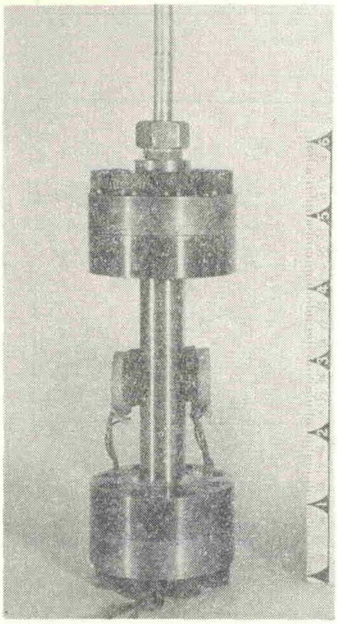

FIG. 3. Small stainless steel resonant cylinder.

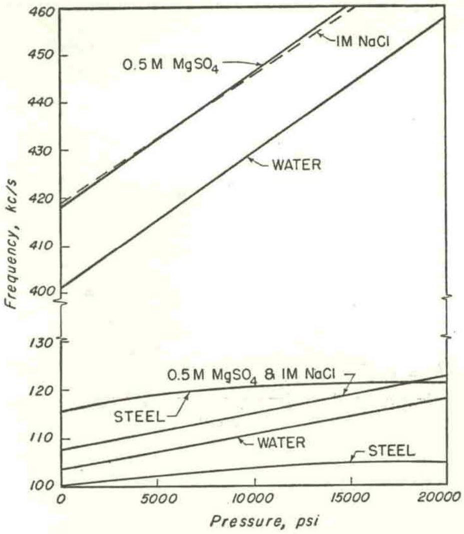

FIG. 4. Typical graph of shift of resonant frequency *vs* pressure for various solutions.

A major difficulty in measuring absorption as a function of pressure arises from the existence of resonant steel modes (modes in the walls of the cylinder) which at various pressures were observed to cross the liquid modes and make impossible the identification of liquid modes. Figure 4, which shows some typical steel and liquid modes as a function of pressure, illustrates this interfering behavior. Fortunately, it was found that the Q of the steel modes was lowered greatly by touching the cylinder at various places while the Q of the liquid modes was lowered only slightly. In order to exploit this damping the cylinder was wrapped with a layer of masking tape, a device which proved to be successful in permitting modes to be followed up to 20 000 psi. This procedure was resorted to only for the large cylinder. The effect of mode crossing for the large cylinder was still apparent [notice the large hump in Fig. 5(a) for both $MgSO_4$ and NaCl data] but the mode could be followed.

EXPERIMENTAL RESULTS

Absorption measurements were made in two frequency regions: in the 100-kc region with the large cylinder and in the 500-kc region with the small one. The resonant frequencies at atmospheric pressure, f_0, were 107.7 kc and 495.8 kc. All measurements were made at 26°C. The absorption measurements were made at 1000 psi intervals for both the 0.5-molar solution of $MgSO_4$ and the 1.0175-molar‡ NaCl solution. These absorption measurements are shown in Fig. 5.

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[9] Romard Barthel, J. Acoust. Soc. Am. **26**, 227 (1954).

[10] Schaafs, Z. Physik **105**, 658–75 (1937).

[11] A. Weissler and V. A. Del Grosso, J. Acoust. Soc. Am. **23**, 222 (1951).

‡ Velocity *vs* concentration data at various temperatures for $MgSO_4$[10,11] and NaCl[9,11] were used to compute concentration of NaCl solution which would have same velocity as 0.5 molar $MgSO_4$ solution.

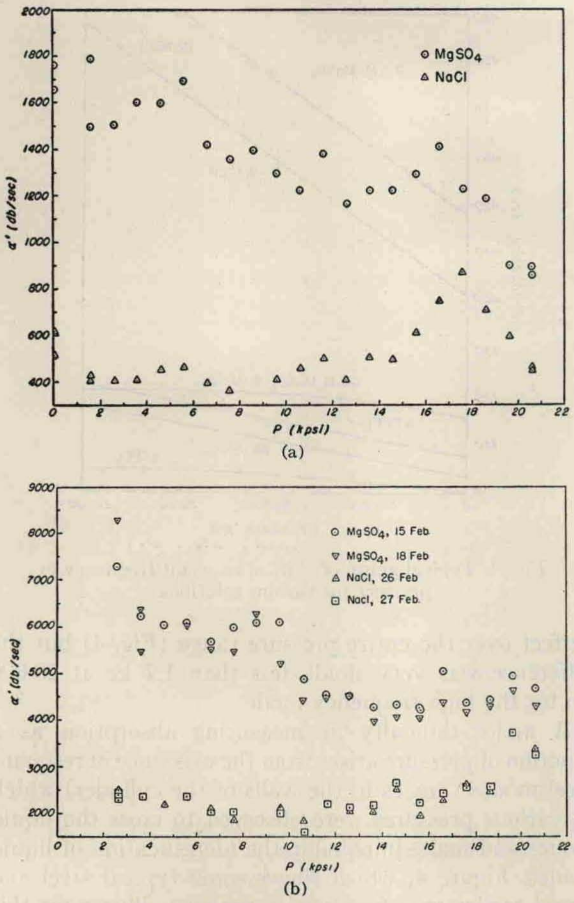

FIG. 5. Raw absorption data, 26°C. (a) Low frequency: Note the absorption peak at 18 000 psi for both solutions where a steel mode crosses the liquid mode. (b) High frequency: The mode for both solutions could not be followed down to atmospheric pressure.

The absorption of the magnesium sulfate was found by subtraction of the NaCl data point-by-point from the $MgSO_4$ data; where more than one absorption measurement was made the average was used in computation. The large cylinder exploded before more data could be taken in the low-frequency region.

The observations of the absorption of $MgSO_4$ are shown in Fig. 6 for both the low and high frequencies. The line in each figure, drawn by eye, is somewhat arbitrary because equal weight was not given to all points, especially in regions where steel modes cross the liquid ones; whenever data showed relatively slow variations with pressure these points were given more weight. Absorption is not observed for a fixed frequency because, as mentioned earlier, the frequency must be increased as the pressure is elevated in order to observe the same mode.

The relaxation frequency was calculated from the above data and Eq. (2). It was found that within the estimated accuracy of the absorption measurements, ±10%, there was no change in κ, as the pressure increased; its value was found to be 1.2×10^6 rad/sec. In Fig. 7 this result is compared with those of Wilson and Leonard[6] as a function of the square root of concentration.

Once the relaxation time was known, the absorption measurements could be reduced to absorption as a function of pressure at a fixed frequency. The absorption results at fixed frequencies, Fig. 8, show that the absorption decreases approximately by a factor of four for a change of 20 000 psi.

To calculate the chemical compressibility using Eq. (2) the isothermal compressibility and sound velocity must be known in addition to the absorption and relaxation frequency which were measured. Using instead the adiabatic compressibility[12] $(\rho c^2)^{-1}$ for β_0 in Eq. (2), one obtains

$$\beta_0'=\frac{2\alpha}{\rho c}\left(\frac{\omega^2+\kappa^2}{\omega^2\kappa}\right). \tag{2a}$$

The experiment itself yields sound velocity *vs* pressure; density *vs* pressure at 25°C can be calculated.[13] The

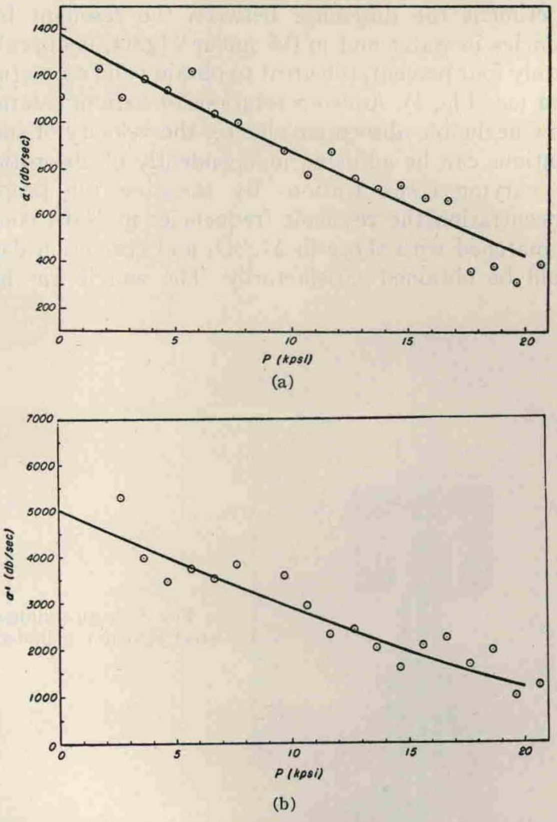

FIG. 6. Absorption of 0.5 molar $MgSO_4$ solution, 26°C. Note that as the pressure increases the frequency of the resonant mode increases from the atmospheric pressure frequency, f_0. (a) $f_0=107.7$ kc. (b) $f_0=495.8$ kc.

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[12] Harned and Owen, *Physical Chemistry of Electrolyte Solutions* (Reinhold Publishing Corporation, New York, 1950). For aqueous solutions at 25°C the adiabatic and isothermal compressibilities differ by only about one percent.

[13] Gibson, J. Am. Chem. Soc. **56** : 1, 4 (1934).

chemical compressibility was computed from the fixed frequency absorption results at both the high and low frequencies. The discrepancy between values shown in Fig. 9 at 26°C is an indication of the accuracy of the experiment. No attempt was made to reconcile the differences. Note that at atmospheric pressure the chemical compressibility is approximately a factor of 1000 smaller than the isothermal compressibility.

It has been mentioned earlier that it was necessary to increase the frequency in order to follow a given mode as the pressure was increased. By calculating the change in the dimensions of the cylinder as a function of pressure it was possible to obtain relative velocity measurements accurate to one part in a thousand. Although the experiment was done at 26°C the velocity is presented in Table I as a function of pressure at 25°C since chemical and physical data are usually determined at this temperature. The velocity of sound at 25°C for $MgSO_4$ was found by interpolation from the data of Schaafs[10] and Weissler and Del Grosso.[11] In doing so it has been assumed that variation of velocity with pressure is the same at the two temperatures.

Since the velocity and density are known as a function of pressure the adiabatic compressibility can be computed; the results at 25°C are presented in Fig. 10.

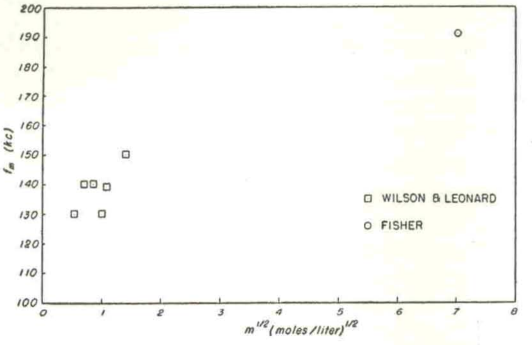

FIG. 7. Relaxation frequency *vs* (concentration)$^{\frac{1}{2}}$, 23–26°C.

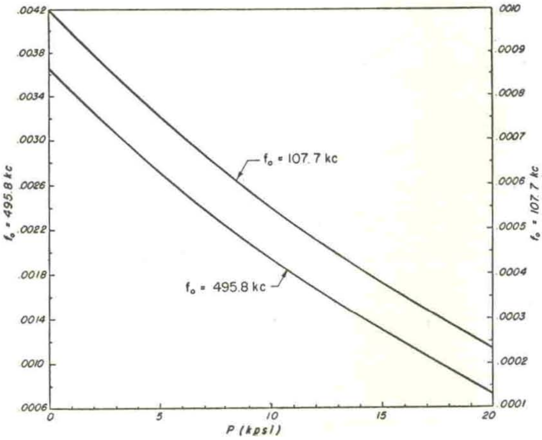

FIG. 8. Absorption of 0.5 molar $MgSO_4$ solution at 26°C.

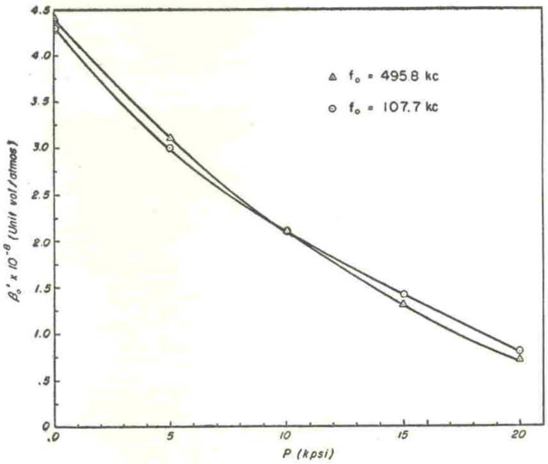

FIG. 9. Chemical compressibility *vs* pressure, 26°C.

COMPARISON OF THEORY AND EXPERIMENT

The chemical compressibility, β_0', can be related to chemical thermodynamic properties as was pointed out by Liebermann.[1] For example,

$$\beta_0' = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial \ln K}\right)_{T,p}\left(\frac{\partial \ln K}{\partial p}\right)_T, \quad (3)$$

which relates the volume, V, of the solution and the equilibrium constant K to chemical compressibility. The pressure dependence of K is expressed by the standard thermodynamic equation[14]

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^0}{RT}, \quad (4)$$

where ΔV^0 is the algebraic difference between the partial molal volumes of the products and reactants in their standard states. A more specific expression for β_0' for the case of a salt dissociating into two ions has been given by Bies.[5] However, his expression for β_0' includes the explicit ratio of two kinetic quantities, reaction rate and relaxation frequency, in spite of the fact that β_0' is an equilibrium property; he subsequently shows an equilibrium relation between these two quantities. A more direct relation can be derived from the Manes[4] expression for relaxation frequency and for this case it can be shown that the ratio of the specific reaction rate for dissociation, k_1, to relaxation

TABLE I. Velocity *vs* pressure, 25°C 0.5 molar $MgSO_4$.

P (psi)	c(m/sec)
15	1558
5 000	1612
10 000	1666
15 000	1720
20 000	1774

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[14] Owen and Brinkley, Chem. Revs. **29**, 461 (1941). A detailed discussion is given of Eq. (4).

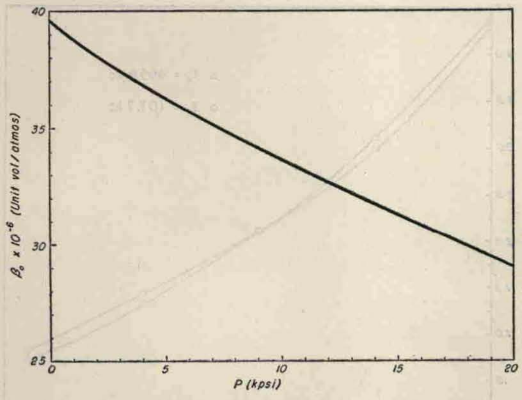

FIG. 10. Adiabatic compressibility *vs* pressure, 25°C.

frequency, κ, is

$$\frac{k_1}{\kappa}=1+\frac{\bar{V}_2-\bar{V}_2^0}{\Delta V^0}, \tag{5}$$

where $\bar{V}_2$ is the partial molal volume of the solute at the concentration to which κ refers and $\bar{V}_2^0$ is the partial molal volume of the solute at infinite dilution.

By evaluating the Manes[4] expression for β_0' the chemical compressibility is expressed as

$$\beta_0'=\frac{\Delta V'\Delta V^0 c_s(1-\theta)}{RT}\left[1+\frac{\bar{V}_2-\bar{V}_2^0}{\Delta V^0}\right], \tag{6}$$

in which unit volume has been assumed, c_s is the concentration in moles/cc,§ and θ is the degree of dissociation. The quantity $\Delta V'$ is closely related to ΔV^0.‖ Liebermann, Bies, and Manes set $\Delta V'=\Delta V^0$ in their work although Bies,[15] as well as Manes, suggested that this may not be true. In the absence of any data by which $\partial\bar{V}_1/\partial\xi$ can be accurately evaluated in the expression for $\Delta V'$ given in the footnote below, it will be assumed that $\Delta V'$ is independent of pressure.

Whenever the dissociation reaction is responsible for sound absorption its pressure dependence can be calculated by combining Eqs. (2) and (6); the result is

$$2\alpha=\frac{\Delta V'\Delta V^0 c_s(1-\theta)}{c\beta_0 RT}\left[1+\frac{\bar{V}_2-\bar{V}_2^0}{\Delta V^0}\right]\left[\frac{\omega^2\kappa}{\omega^2+\kappa^2}\right]. \tag{7}$$

Equation (7) may be rearranged by lumping terms independent of pressure ($\Delta V'$, ω and κ) into a constant; hence

$$\alpha=\text{constant}\times|\Delta V^0|\rho c c_s(1-\theta)\left[1+\frac{\bar{V}_2-\bar{V}_2^0}{\Delta V^0}\right], \tag{8}$$

in which β_0 is expressed as $(\rho c^2)^{-1}$. A numerical evaluation of the effect of pressure on sound absorption using Eq. (8) can be made provided data on the pressure dependent variables are known.

Some of the pressure dependent variables are readily calculated, namely, ρ, c_s, and c. The pressure dependence of ΔV^0 and of the dissociation constant, K, is obtained by the method of Owen and Brinkley[14] up to 15 000 psi.

In order to calculate the degree of dissociation, θ, it is necessary to use the equation for thermodynamic equilibrium

$$K=c_s'\gamma_\pm^2/(1-\theta), \tag{9}$$

in which c_s' is in units of moles/liter and $\gamma_\pm$ is the stoichiometric activity coefficient.[16]

The pressure dependence of $\gamma_\pm$ may be calculated[17] by making use of the equation

$$\partial \ln\gamma_\pm/\partial p=(\bar{V}_2-\bar{V}_2^0)/2RT, \tag{10}$$

in which account is taken of the pressure dependence of $(\bar{V}_2-\bar{V}_2^0)$. Once K, $\gamma_\pm$ and c_s' are known as functions of pressure, the degree of dissociation can be calculated. All calculations have been made on the assumption that the activity coefficient of the undissociated solute is unity.

The effect of pressure on some of these quantities is by no means negligible. For example, in a 0.5-molar $MgSO_4$ solution the following changes are found for a pressure increase from atmospheric pressure to 15 000 psi: K increases by a factor of approximately 6.6; ΔV^0 increases from -51.7 cc/mole to -39.9 cc/mole; if one uses the atmospheric pressure values of 0.0882 for $\gamma_\pm$ [18] and 0.00616 for K,[19] the degree of dissociation

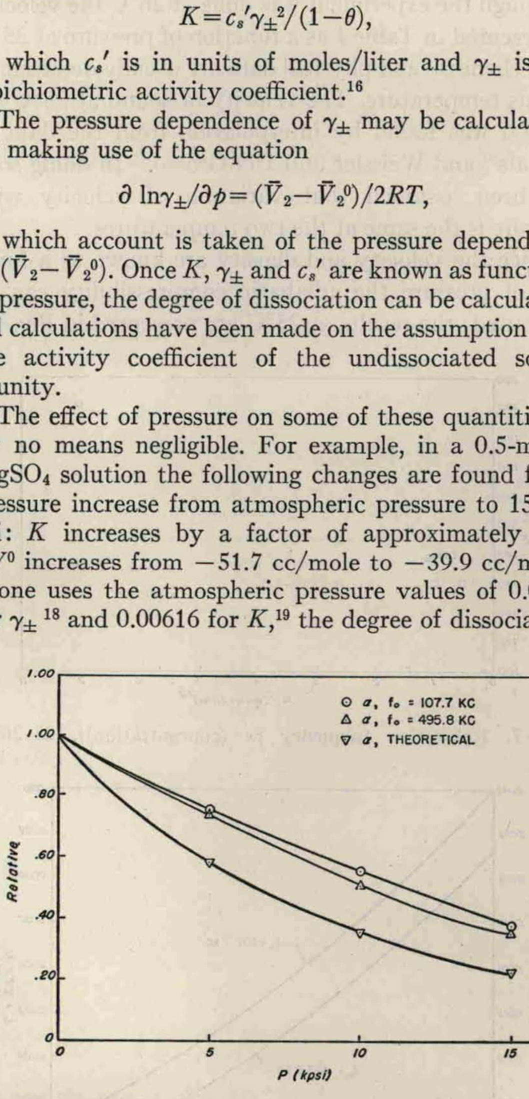

FIG. 11. Comparison of experiment and theory.

Bies[5] incorrectly uses moles/liter.

anes defined $\Delta V'=\partial V/\partial\xi$, where ξ is the degree of advance- the reaction expressed in number of moles of any key t. Taking $\xi=n_2\theta$, where n_2 is the number of moles of t can be shown that $\Delta V'=n_1(\partial\bar{V}_1/\partial\xi)+(\bar{V}_2^m/\theta)+\Delta V^0$, he number of moles of solvent and $\bar{V}_1$ is the partial of the solvent and $\bar{V}_2^m$ the molar volume of the e.

s, Technical Report, No. VI, UCLA Physics (1953).

[16] Robinson and Stokes, *Electrolyte Solutions* (Academic Press, Inc., New York, 1955), p. 403.

[17] Robinson and Harned, Chem. Revs. 28, 419 (1941).

[18] Robinson and Jones, J. Am. Chem. Soc. 58, 961 (1936).

[19] Dunsmore and James, J. Chem. Soc. Pt. 4, 2925 (1951).

if found to increase from 0.37 to 0.84; $(\bar{V}_2-\bar{V}_2^0)$ decreases from 12.9 cc/mole to 9.1 cc/mole. The decrease in $(\bar{V}_2-\bar{V}_2^0)$ has nearly the same pressure dependence as the decrease in the magnitude of ΔV^0, within three percent over the entire range; hence, by Eq. (5), the ratio k_1/κ is nearly independent of pressure. At atmospheric pressure k_1 is calculated to be 0.90×10^6 rad/sec or $k_1/2\pi$ is 143 kc. At infinite dilutions, therefore $f_m=\kappa/2\pi$ is 143 kc which may be compared with the results shown in Fig. 7.

The predicted pressure dependence of sound absorption using Eq. (8) is shown in Fig. 11. The slope of the predicted curve agrees with experiment fairly well from 5000–15 000 psi, but there is a discrepancy between observed and theoretical behavior below 5000 psi. This discrepancy undoubtedly stems from the assumption that $\Delta V'$ is independent of pressure. Unfortunately it is not possible to evaluate this quantity at higher pressures or even at atmospheric pressure with accuracy sufficient to permit quantitative interpretation of results. Until the pressure dependence of $\Delta V'$ is known it will not be possible to discuss this discrepancy more fully. Another source of discrepancy may arise from inaccuracies in the value of θ calculated at atmospheric pressure. Variations as large as 30% in the value of θ might be expected from the reported data.

CONCLUSION

The marked pressure dependence of acoustic absorption in $MgSO_4$ solution offers additional proof that chemical equilibrium in this solution is affected by pressure.

Since κ and the ratio k_1/κ were found to be nearly independent of pressure, it must be concluded that k_1, the specific reaction rate for dissociation, is influenced very little by pressure.

The nature of the pressure-sensitive reaction is still uncertain. It has been shown that the dissociation reaction can be responsible. Other reactions, however, cannot yet be excluded. For example, the variation with pressure of the concentration of the associated ions, $c_s(1-\theta)$, is the major factor in the predicted absorption shown in Fig. 11; the parameters $|\Delta V^0|$ and ρc vary in opposite directions such that their net influence is small. Thus, the quantity $c_s(1-\theta)$ would appear in an analogous manner if a purely monomolecular reaction involving only the associated molecules rather than the dissociation process were responsible.

Owen and Brinkley[14] indicated that ΔV^0, a negative number, becomes more positive with increasing temperature for some electrolytes. If this were true for $MgSO_4$ there may be some temperature at which $\Delta V^0=0$. A crucial test of the theory would be to measure absorption at this temperature to observe whether excess absorption persists.

ACKNOWLEDGMENTS

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