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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 $\pm 10\%$. 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 researchers¹⁻⁶ in the general problem of sound absorption in solutions. In treating this phenomenon Liebermann¹ 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.

Liebermann¹ 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

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

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 equation¹:

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

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 Leonard⁶ 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

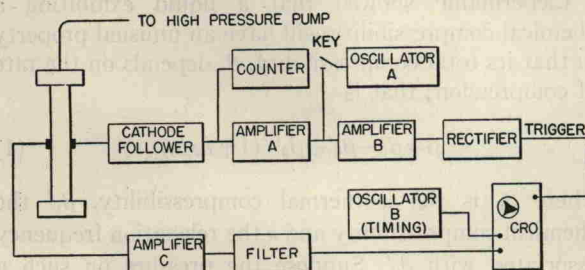


FIG. 1. Block diagram of apparatus.

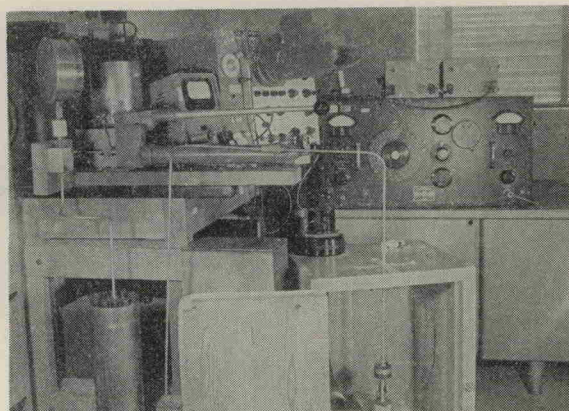


FIG. 2. High pressure absorption apparatus.

or salt solutions, and yet have thin walls to minimize absorption losses.

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 $26 \pm 0.5^\circ\text{C}$.

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

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

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