

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<sup>7,8</sup> and sound velocity *vs* concentration data at atmospheric pressure for aqueous solutions.<sup>9-11</sup>

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 non-absorbing 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

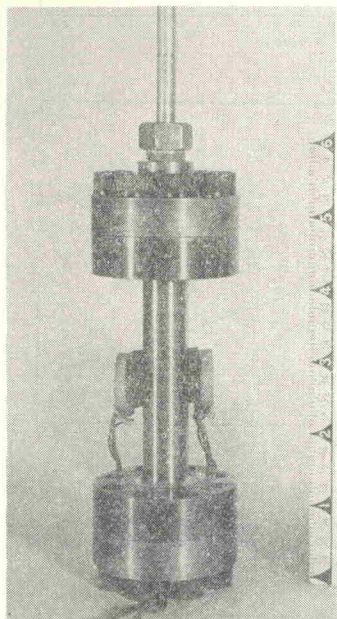


FIG. 3. Small stainless steel resonant cylinder.

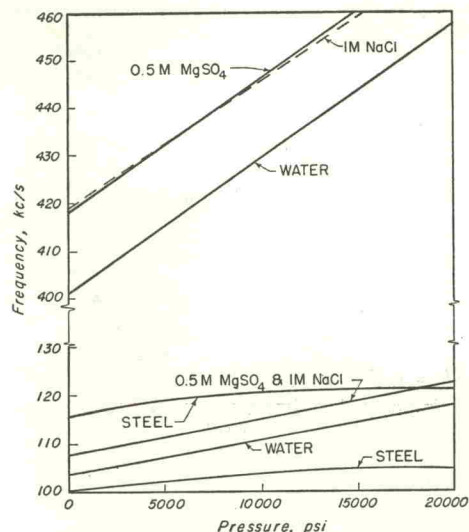


FIG. 4. Typical graph of shift of resonant frequency *vs* pressure for various solutions.

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.

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<sup>†</sup> NaCl solution. These absorption measurements are shown in Fig. 5.

<sup>†</sup> Velocity *vs* concentration data at various temperatures for  $MgSO_4$ <sup>10,11</sup> and NaCl<sup>8,11</sup> were used to compute concentration of NaCl solution which would have same velocity as 0.5 molar  $MgSO_4$  solution.

<sup>9</sup> Romard Barthel, J. Acoust. Soc. Am. 26, 227 (1954).

<sup>10</sup> Schaafs, Z. Physik 105, 658-75 (1937).

<sup>11</sup> A. Weissler and V. A. Del Grosso, J. Acoust. Soc. Am. 23, 222 (1951).

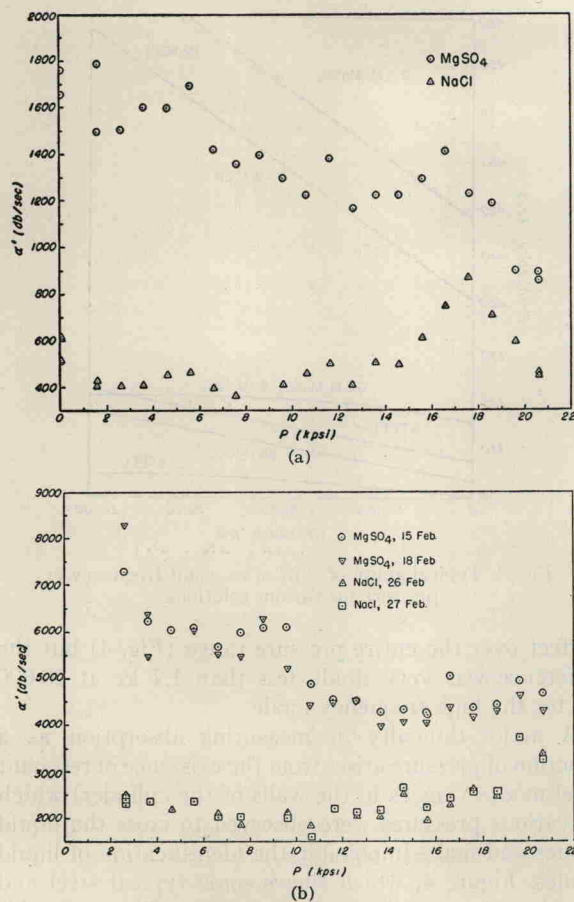


FIG. 5. Raw absorption data, 26°C. (a) Low frequency: Note the absorption peak at 18 000 psi for both solutions where a steel mode crosses the liquid mode. (b) High frequency: The mode for both solutions could not be followed down to atmospheric pressure.

The absorption of the magnesium sulfate was found by subtraction of the NaCl data point-by-point from the MgSO<sub>4</sub> 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<sub>4</sub> 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,  $\pm 10\%$ , there was no change in  $\kappa$ , as the pressure increased; its value was found to be  $1.2 \times 10^6$  rad/sec.

In Fig. 7 this result is compared with those of Wilson and Leonard<sup>6</sup> 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<sup>12</sup>  $(\rho c^2)^{-1}$  for  $\beta_0$  in Eq. (2), one obtains

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

The experiment itself yields sound velocity *vs* pressure; density *vs* pressure at 25°C can be calculated.<sup>13</sup> The

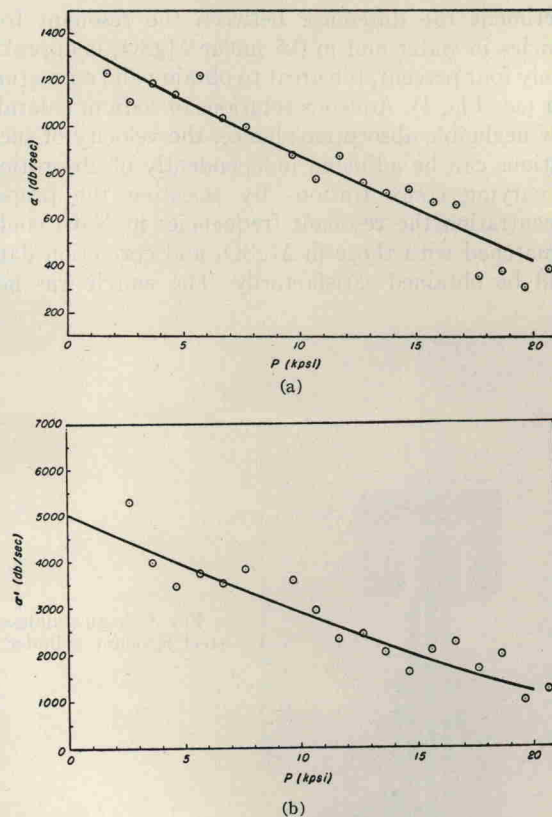


FIG. 6. Absorption of 0.5 molar MgSO<sub>4</sub> solution, 26°C. Note that as the pressure increases the frequency of the resonant mode increases from the atmospheric pressure frequency,  $f_0$ . (a)  $f_0 = 107.7$  kc. (b)  $f_0 = 495.8$  kc.

<sup>12</sup> 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.

<sup>13</sup> Gibson, J. Am. Chem. Soc. **56**: 1, 4 (1934).