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.
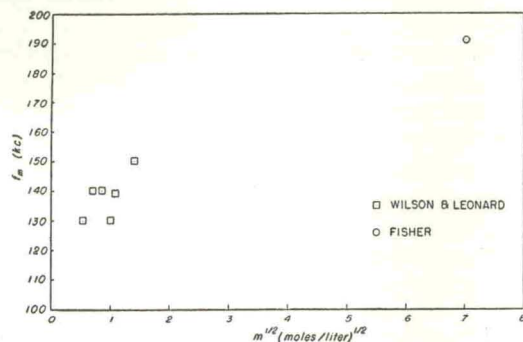

FIG. 7. Relaxation frequency vs (concentration)$^{\frac{1}{2}}$, 23–26°C.
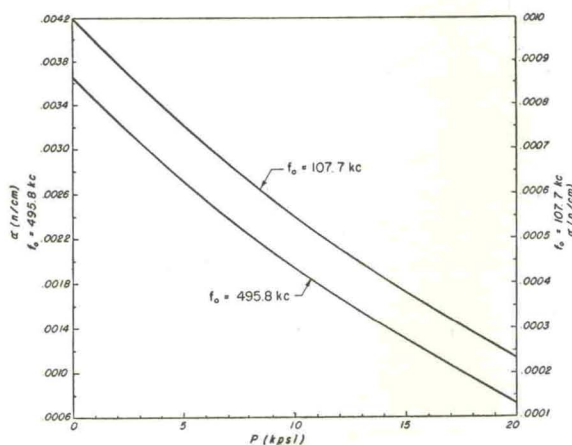

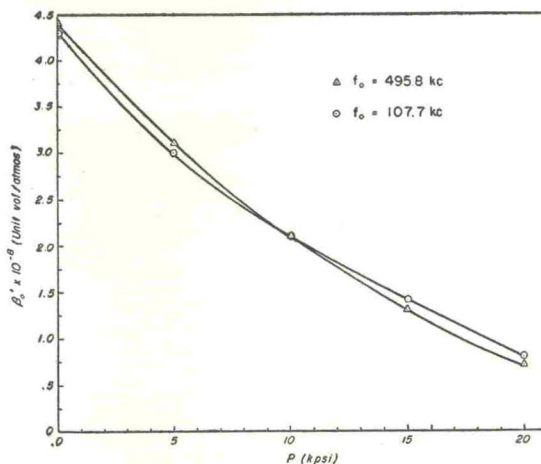FIG. 8. Absorption of 0.5 molar MgSO$_4$ solution at 26°C.

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

[14] Owen and Brinkley, Chem. Revs. **29**, 461 (1941). A detailed discussion is given of Eq. (4).
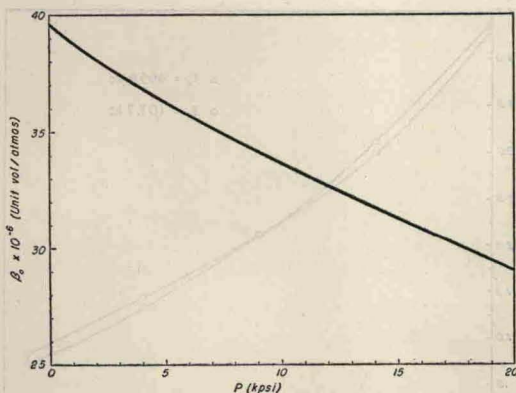
Fig. 10. Adiabatic compressibility *vs* pressure, 25°C.

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;

Bies[5] incorrectly uses moles/liter.

Manes defined $\Delta V' = \partial V / \partial \xi$, where ξ is the degree of advancement of the reaction expressed in number of moles of any key constituent. Taking $\xi = n_2\theta$, where n_2 is the number of moles of solute it can be shown that $\Delta V' = n_1(\partial \bar{V}_1 / \partial \xi) + (\bar{V}_2^m / \theta) + \Delta V^0$, where n_1 is the number of moles of solvent and $\bar{V}_1$ is the partial molal volume of the solvent and $\bar{V}_2^m$ the molar volume of the solute.

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

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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
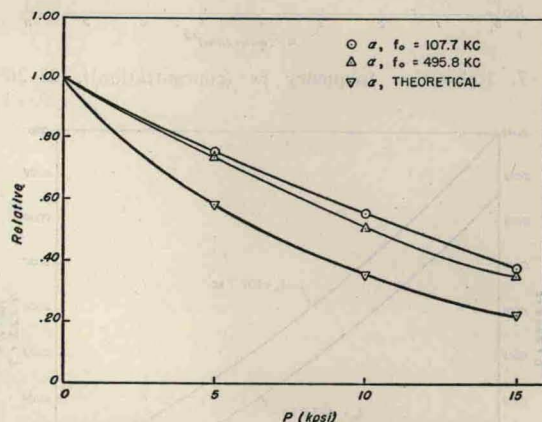

Fig. 11. Comparison of experiment and theory.

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[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).