FIG. 3. Sound-absorption cross section per wavelength vs frequency for $MnSO_4$ solutions.

TABLE II. Sound absorption and velocity as a function of pressure for $0.5M$ $MnSO_4$ at 25°C.

P (kpsi)	α_{327} Np/cm	α_{500} Np/cm	ρc (g cm^{-2}·sec^{-1})	V (m/sec)
0.015	1.70×10^{-3}	2.98×10^{-3}	1.637×10^{5}	1540
5	1.09	2.03	1.725	1599
10	0.72	1.34	1.810	1657
15	0.42	0.89	1.894	1714

investigators at atmospheric pressure, the data in Table I are expressed in the different units that have been used by various investigators. The pressure dependence of sound absorption and sound speed are indicated in Table II.

The results obtained by Kurtze and Tamm[1] at 20°C are shown in Fig. 3 along with our results at 25°C. The curve is that shown in the paper by Kurtze and Tamm, which overlooks the strong indication of a relaxation in the low-frequency region. The standard deviation of our data is low enough to suggest the existence of another relaxation; however, Bechtler and Tamm[11] have pointed out that, when they interpolate Bechtler's more recent $0.5M$ $MnSO_4$ absorption data to 25°C, there is little evidence to support a low-frequency relaxation below 5 MHz. Because Cartensen's[12] data do not extend to the low frequencies used by Kurtze and Tamm, they are not reproduced here. The sound speed at atmospheric pressure was obtained by matching resonant mode patterns. Comparison of atmospheric-pressure measurements of sound speed are shown in Fig. 4. Bechtler's[11] data appear to be the most reliable. However, dispersion of about 2 m/sec exists between 10-MHz and 500-kHz data for 0.5 molar $MnSO_4$. This difference would mean that Bechtler's data and ours would agree to within 1 m/sec.

Results for chemical compressibility are shown in Table III, in which density data for $MgSO_4$ solutions are used in order to make the calculation according to Eq. 1. The value of β_{III} is sensitive to the value for ν_{III} and results are shown for 25°, where ν_{III} is ~3.5 MHz, according to Atkinson and Kor,[13,14] and ~5 MHz, according to Jackopin and Yeager[15] and Smithson and

Litovitz.[16] According to Tamm,[17] the value of ν_{III} at 25° may actually be higher than 5 MHz for a $0.5M$ solution. However, the conclusions herein would not be altered significantly by a slight adjustment of this lowest relaxation frequency.

II. DISCUSSION

Atkinson and Kor,[9,13] in their studies of ultrasonic absorption in aqueous solutions of $MnSO_4$ at atmospheric pressure, have interpreted their results in terms of the multistate dissociation theory of Eigen and Tamm.[2] The multistate reaction equation is shown below:

$$Mn^{++} + SO_4^{--} \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} \underset{m_2}{\overset{V_2}{MnO_H{}^HO_H{}^HSO_4}}$$

$$\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{m_3}{\overset{V_3}{MnO_H{}^HSO_4}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{m_4}{\overset{V_4}{MnSO_4.}}$$

Here, the V_i are partial molal volumes; k_{ij}, reaction rates; and m_i, the concentrations of the various states i. It is seen that the dissociated ions in electrically conducting State 1 associate, forming various ion pairs in which successive water molecules are removed from between the ions until a contact ion pair is formed. The ultrasonic relaxation spectra exhibited by $MnSO_4$ solutions can be related to the various reactions in the multistate model.

From the values assigned by Atkinson and Kor to the reaction rates and equilibrium constants, which are

TABLE III. Chemical compressibility β_{III} as a function of pressure for $0.5M$ $MnSO_4$ and $0.5M$ $MgSO_4$ at 25°C.

P (kpsi)	$\beta_{III} \times 10^{14}$ (cm^2/dyn)[a] $MnSO_4$				
	A	B	C	D	$MgSO_4$
0.015	11.7	8.3	15.5	10.9	4.4
5.0	7.6	5.4	9.4	6.6	3.0
10.0	4.8	3.4	6.0	4.2	2.1
15.0	3.0	2.1	3.3	2.4	1.6

[a] A. $f = 500$ kHz, $\nu_{III} = 5.0$ MHz. B. $f = 500$ kHz, $\nu_{III} = 3.5$ MHz. C. $f = 327$ kHz, $\nu_{III} = 5.0$ MHz. D. $f = 327$ kHz, $\nu_{III} = 3.5$ MHz.

[11] K. Tamm (private communication).
[12] E. L. Carstensen, J. Acoust. Soc. Amer. **26**, 862–864 (1954).
[13] G. Atkinson and S. K. Kor, J. Phys. Chem. **69**, 128–133 (1965).
[14] G. Atkinson and S. K. Kor, J. Phys. Chem. **70**, 314 (1966).
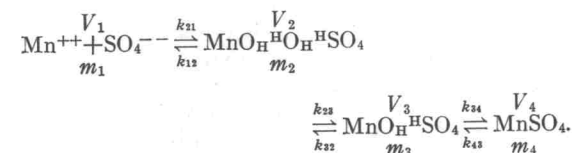[15] L. G. Jackopin and E. Yeager, J. Phys. Chem. **70**, 313 (1966).

[16] J. R. Smithson and T. A. Litovitz, J. Acoust. Soc. Amer. **28**, 462–468 (1956).
[17] K. Tamm (private communication).

TABLE IV. Rate and equilibrium constants for aqueous MnSO$_4$ at 25°C (Atkinson and Kor).

$$K_m = 1/139 = 0.00720$$
$$k_{12} = 4.2 \times 10^{10} \text{ C}^{-1} \text{ sec}^{-1}$$
$$k_{21} = 8.0 \times 10^{8} \text{ sec}^{-1}$$
$$K_{12} = 0.0192 \text{ mole/liter}$$
$$k_{23} = 6.9 \times 10^{7} \text{ sec}^{-1}$$
$$k_{32} = 1.9 \times 10^{8} \text{ sec}^{-1}$$
$$K_{23} = m_2/m_3 = 2.8$$
$$k_{34} = 4.8 \times 10^{7} \text{ sec}^{-1}$$
$$k_{43} = 1.4 \times 10^{7} \text{ sec}^{-1}$$
$$K_{34} = m_3/m_4 = 0.29$$

shown in Table IV, it is possible to calculate the concentrations of the various states. The equation for the over-all dissociation constant K_m is

$$K_m = \frac{m\gamma_\pm^2}{1-\theta} = \frac{m\theta^2 f_\pm^2}{1-\theta} = \frac{m_1^2 \pi^f}{m_2+m_3+m_4}, \quad (3)$$

where θ is the degree of dissociation and the m_i, the concentration in molal units. The method of calculation is identical to that used for MgSO$_4$ solutions.[4] For a $0.5M$[18] solution, the activity coefficient $\gamma_\pm = \theta f_\pm = 0.0640$ (Ref. 19), π^f is the activity-coefficient product and is equal to $f_\pm^2$ when the activity coefficient of an uncharged ion pair is taken to be unity. The results are shown in Table V and are compared with those calculated earlier[4] for MgSO$_4$ on the basis of parameter values assigned by Eigen and Tamm[2] for MnSO$_4$; it is seen that the concentration of the contact ion pair is about 14%, over 20 times greater than the corresponding value for MgSO$_4$.

In the above reaction scheme, the chemical compressibility associated with the reactions between States 3 and 4 is designed as β_{III} and is related to the volume changes, concentration, and reaction rates as shown below[2]:

$$\beta_{III} = m\Gamma_{III}{}^*(\Delta V_{III})^2/RT, \quad (4)$$

where

$$\Delta V_{III} = V_4 - V_3 + k_{32}/(k_{23}'+k_{32})$$
$$\times [(V_3-V_2)+[k_{21}/(k_{12}'+k_{21})](V_2-V_1)]; \quad (5)$$

$$k_{23}' = [k_{12}'/(k_{12}'+k_{21})]k_{23}; \quad (6)$$

$$k_{12}' = k_{12}{}^0\theta m\pi^f[2+(\partial \ln\pi^f/\partial \ln\theta)_c]; \quad (7)$$

and

$$m\Gamma_{III}{}^* = (m_1'+m_2+m_3)m_4/(m_1'+m_2+m_3+m_4). \quad (8)$$

[18] The difference between molar and molal is neglected.
[19] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths Scientific Publications Ltd., London, 1959), 2nd ed., p. 502.
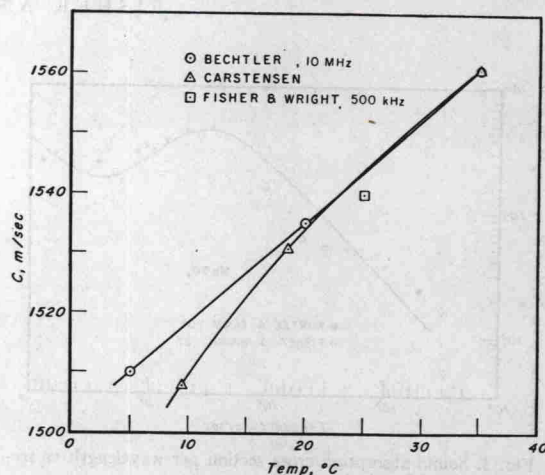

FIG. 4. Sound velocity vs temperature for $0.5M$ MnSO$_4$ solutions.

We let $m_1' \cong c_1'$, where $1/c_1' = 2/c_1 + (\partial \ln\pi^f/\partial c_1)_c$; c denotes molar concentration. The rate constant $k_{12}{}^0$ is the diffusion-controlled reaction rate for recombination of ions at infinite dilution.

To relate the results of Atkinson and Kor to the observed effect of pressure on sound absorption, let us examine in detail the parameters they assign to MnSO$_4$. In particular, to evaluate ΔV_{III} in Eq. 4, we need to know k_{12}' in addition to k_{32} and k_{21} in Table IV. The relevant equations are Eq. 9 below,

$$2\pi\nu_{III} = k_{43} + [k_{23}'/(k_{23}'+k_{32})]k_{34} = k_{43} + k_{34}', \quad (9)$$

and Eq. 7. Using their values of the observed relaxation frequency, we arrive at the results shown in Table VI.

The chemical compressibility is related to the maximum value of $(\alpha\lambda)$ as follows (i.e., when $f = \nu_{III}$ in Eq. 1):

$$\beta_{III} = 2(\alpha\lambda)_{IIImax}/\pi\rho c^2. \quad (10)$$

Using the value of $(\alpha\lambda)_{IIImax} = 1.8 \times 10^{-3}$ given by Atkinson and Kor[9] for $0.1M$ MnSO$_4$ at 25°C, and assuming $c = 1.51 \times 10^5$ cm/sec, we find $\beta_{III} \cong 2.85 \times 10^{-14}$ cm^2/dyn. Therefore, since $m\Gamma_{III}{}^* \cong 0.06 \times 10^{-3}$ moles/cm^3 (Ref. 20) $(\Delta V_{III})^2 \cong 50$, and $\Delta V_{III} \cong 7$ cm^3/mole.

For MgSO$_4$, it was shown that β_{III} decreases with pressure because of a decrease in concentration of m_4 owing to the effect of pressure on the equilibrium constants K_{ij}, as given by the van't Hoff equation,

$$(\partial \ln K_{ij}/\partial p) = -\Delta V_{ij}/RT. \quad (11)$$

For MgSO$_4$, $\Delta V_{III} \cong 19$ cm^3/mole, and it was the large

[20] It is important to note that the units of concentration have to be moles/cubic centimeter in order to calculate compressibility correctly.