

THE JOURNAL
OF THE
ACOUSTICAL SOCIETY OF AMERICA



Volume 46 Number 3

(Part 2)

SEPTEMBER 1969

10.5

Received 12 March 1968

Effect of Pressure on Ultrasonic Absorption, Multistate Dissociation, and Chemical Equilibrium in MnSO_4 Solutions*

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Measurements were made on the effect of pressure on ultrasonic absorption in a 0.5M aqueous solution of manganese sulfate at 25°C. A cylindrical resonant cavity was used for obtaining absorption in the frequency regions of 300 and 500 kHz, at pressures up to 20 000 psi. Results are similar to those obtained for MgSO_4 , in that absorption decreases by a factor of about 3 for a pressure increase of 15 000 psi. Independent conductivity data show nearly the same behavior for MnSO_4 as for MgSO_4 solutions, namely, an increase of only about 14% in the concentration of dissociated ions for the same pressure increase. These results for MnSO_4 appear to be inconsistent with the model used by Atkinson and Kor to analyze their data. The large effect of pressure on ultrasonic absorption is similar to that observed by Carnevale for 0.1M MnSO_4 at 60°C from 9 to 75 MHz.

INTRODUCTION

The extensive acoustic absorption measurements of Kurtze and Tamm¹ in aqueous solutions of divalent sulfates demonstrated that these electrolytes exhibited pronounced acoustic relaxation frequencies. The high-frequency relaxation was nearly the same ($\nu_1 \cong 200$ MHz) for all the salts but the low relaxation frequency varied over a wide range as the cation varied from Be through Ni, Mg, Co, and Mn ($\nu_{III} = 10^3 - 5 \times 10^6$ Hz). The acoustic properties exhibited by these solutions have been explained by Eigen and Tamm² in terms of a multistate dissociation theory, in which a series of pressure-dependent chemical reactions are coupled together. This theory postulates three forms for an electrically neutral ion pair, in which the successive stepwise addition of water molecules between the ions constitutes the reactions giving rise to the observed acoustic absorption; ultimately, the ion pair dissociates into electrically conducting hydrated ions.

The multistate dissociation theory was developed to account for acoustic absorption at atmospheric pressure, in particular, for solutions of MgSO_4 , the salt that is

responsible for the high sound absorption in sea water below ~ 100 kHz.³ This theory also accounts for the contrasting pressure dependence observed for acoustic absorption and electrical conductivity of MgSO_4 solutions⁴; a pressure increase of 15 000 psi produces a decrease in sound absorption of about 67%, whereas only a 10% increase is observed in electrical conductance.⁵

Because of the large difference (~ 130 kHz vs ~ 5 MHz) in the acoustic relaxation frequency ν_{III} , observed at atmospheric pressure for MgSO_4 and MnSO_4 solutions, a set of experiments was performed in 1958 at the Acoustic Research Laboratory at Harvard in order to compare the effect of pressure on ultrasonic absorption for aqueous solutions of these two salts. Because of the large difference in the relaxation frequency, ν_{III} for MgSO_4 and MnSO_4 , we wished to determine if this difference might have any relation to the pressure dependence of sound absorption.

In 1958, Carnevale⁶ reported pressure data on ultrasonic absorption in aqueous MnSO_4 solutions at 60°

* O. B. Wilson and R. W. Leonard, *J. Acoust. Soc. Amer.* **26**, 223-226 (1954).

† F. H. Fisher, *J. Acoust. Soc. Amer.* **38**, 805-812 (1965).

‡ F. H. Fisher, *J. Phys. Chem.* **66**, 1607-1611 (1962).

§ E. H. Carnevale, "Effect of Pressure on Ultrasonic Relaxation in Electrolytes," PhD thesis, Catholic University of America Press (1958).

* Contribution of Scripps Inst. of Oceanogr., new series.

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¹ G. Kurtze and K. Tamm, *Acustica* **3**, 33-48 (1953).

² M. Eigen and K. Tamm, *Z. Elektrochem.* **66**, 93-121 (1962).

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 TABLE I. Summary of present absorption data of 0.5M $MnSO_4$ at 25°C and atmospheric pressure.^a

		327 kHz	500 kHz
α'	(dB/sec)	2269 ± 231	3991 ± 263
λ	(cm)	0.471	0.308
α	(Np/cm)	1.696×10^{-3}	2.983×10^{-3}
$\alpha\lambda$	(Np)	0.799×10^{-3}	0.919×10^{-3}
$(\alpha/f^2) \times 10^{17}$	(Np cm ⁻¹ · sec ⁻²)	(1590 ± 159)	1190 ± 79
$(Q\lambda) \times 10^{32}$	(m ²)	531 ± 53	610 ± 40

^a $\alpha' = 8.686\alpha c$, $c = 154\,000$ cm/sec, $Q\lambda = 2\alpha\lambda/NA$, where N is concentration in moles/cubic meter and A is Avogadro's number.

over a frequency range from 9.0 to 75 MHz and up to pressures of about 60 000 psi; for a pressure increase of ~15 000 psi, he observed a large decrease in absorption similar to that observed for $MgSO_4$ at 25° and a slight increase, about 15%, in relaxation frequency. However, because of the large temperature difference, it was not possible to compare the results between $MgSO_4$ and $MnSO_4$ solutions.

At the time this work was performed, no quantitative model had been proposed for $MnSO_4$, and the multistate dissociation theory had not yet appeared in detail, although its basic features had been outlined.⁷ The results for the pressure dependence of sound absorption in $MnSO_4$ solutions were similar to but less accurate than those obtained in $MgSO_4$ solutions. Results for the pressure dependence of electrical conductivity for $MnSO_4$ solutions⁸ were also nearly the same as for $MgSO_4$.⁵ The recent work of Atkinson and Kor⁹ on $MnSO_4$, as well as the work of Bechtler at Tamm's laboratory, stimulated the reexamination of these 10-year-old data.

The present experimental results are discussed in relation to a critical test of a multistate dissociation model proposed by Atkinson and Kor⁹ for $MnSO_4$ solutions at 25°.

I. EXPERIMENTAL MEASUREMENTS AND RESULTS

Measurements of ultrasonic absorption were made in two frequency regions, using the resonant-cavity technique described in relation to the $MgSO_4$ work.⁴ The results were converted to single-frequency data as a function of pressure¹⁰ by means of Eq. 1,

$$2\alpha = \beta_{III}\rho c [2\pi\nu_{III}f^2 / (f^2 + \nu_{III}^2)], \quad (1)$$

where α is absorption in nepers/centimeter; β_{III} , the chemical compressibility in square centimeters/dyne; ρ , the density in grams/cubic centimeter; c , the sound speed in centimeters/second; f , the acoustic frequency

⁷ M. Eigen, *Discussions Faraday Soc.* **24**, 25-36 (1957).

⁸ F. H. Fisher and D. F. Davis, *J. Phys. Chem.* **69**, 2595-2598 (1965).

⁹ G. Atkinson and S. K. Kor, *J. Phys. Chem.* **71**, 673-677 (1967).

¹⁰ The resonant mode frequency varies with pressure, owing to changes in sound velocity and cavity dimensions.

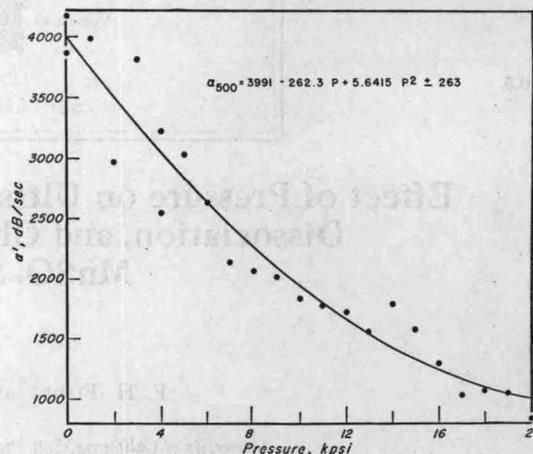


FIG. 1. Sound absorption at 327 kHz vs pressure for 0.5M $MnSO_4$ aqueous solution at 25°C.

in hertz; and ν_{III} , the relaxation frequency. At a given pressure ν_{III} , β_{III} , ρ , and c are constant, so

$$\frac{\alpha_1}{\alpha_2} = \left(\frac{f_1}{f_2}\right)^2 \left(\frac{f_2^2 + \nu_{III}^2}{f_1^2 + \nu_{III}^2}\right). \quad (2)$$

If ν_{III} is known, then absorption at frequency f_1 can be converted to that at f_2 with this equation. Since data in this work were obtained at frequencies well below the low relaxation frequency reported in the literature, it makes little difference for this conversion which value of ν_{III} is used. Because of the negligible pressure dependence observed for ν_{III} in $MgSO_4$ solutions at this concentration,⁴ ν_{III} was assumed to be pressure independent for $MnSO_4$. This assumption for 25° is not in substantial disagreement with Carnevale's work, in which he calculated a slight change of 15% for a pressure increase of about 15 000 psi.

The absorption results, reduced to fixed frequency through use of Eq. 2, are shown in Figs. 1 and 2. To facilitate comparison of these results with those of other

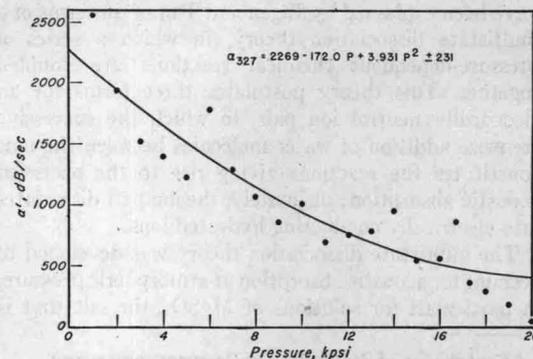


FIG. 2. Sound absorption at 500 kHz vs pressure for 0.5M $MnSO_4$ aqueous solution at 25°C.

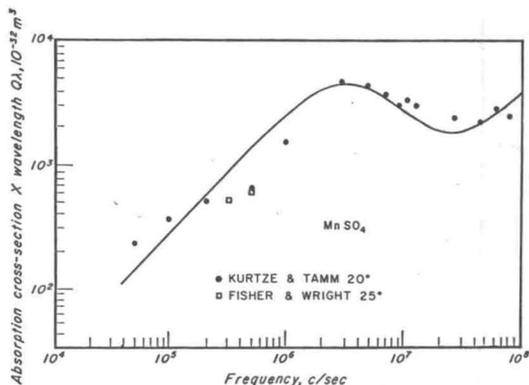


Fig. 3. Sound-absorption cross section per wavelength vs frequency for MnSO_4 solutions.

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 Tamm¹ 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 Tamm¹¹ 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's¹² 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's¹¹ 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 Yeager¹⁵ and Smithson and

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).

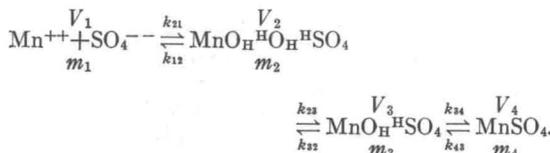
TABLE II. Sound absorption and velocity as a function of pressure for 0.5M MnSO_4 at 25°C.

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}	1.637×10^6	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

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:



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)	$\beta_{\text{III}} \times 10^{14}$ (cm ² /dyn) ^a MnSO ₄				MgSO ₄
	A	B	C	D	
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, $\nu_{\text{III}} = 5.0$ MHz. B. $f = 500$ kHz, $\nu_{\text{III}} = 3.5$ MHz. C. $f = 327$ kHz, $\nu_{\text{III}} = 5.0$ MHz. D. $f = 327$ kHz, $\nu_{\text{III}} = 3.5$ MHz.

¹⁶ J. R. Smithson and T. A. Litovitz, *J. Acoust. Soc. Amer.* **28**, 462-468 (1956).

¹⁷ K. Tamm (private communication).

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 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 0.5M¹⁸ 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 earlier⁴ for $MgSO_4$ on the basis of parameter values assigned by Eigen and Tamm² 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 below²:

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

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.

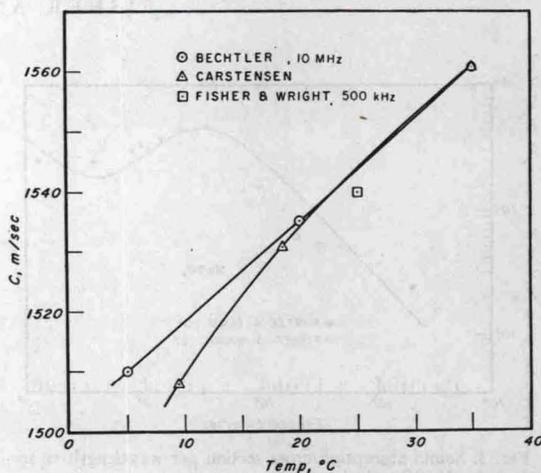


Fig. 4. Sound velocity vs temperature for 0.5M $MnSO_4$ solutions.

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):

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

Using the value of $(\alpha\lambda)_{III\max} = 1.8 \times 10^{-3}$ given by Atkinson and Kor⁹ for 0.1M $MnSO_4$ at 25°C, and assuming $c = 1.51 \times 10^5 \text{ cm}^3/\text{sec}$, we find $\beta_{III} \cong 2.85 \times 10^{-14} \text{ cm}^2/\text{dyn}$. Therefore, since $m\Gamma_{III}^* \cong 0.06 \times 10^{-3} \text{ moles/cm}^3$ (Ref. 20) ($\Delta V_{III})^2 \cong 50$, and $\Delta V_{III} \cong 7 \text{ cm}^3/\text{mole}$.

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 $MgSO_4$, $\Delta V_{III} \cong 19 \text{ cm}^3/\text{mole}$, 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.

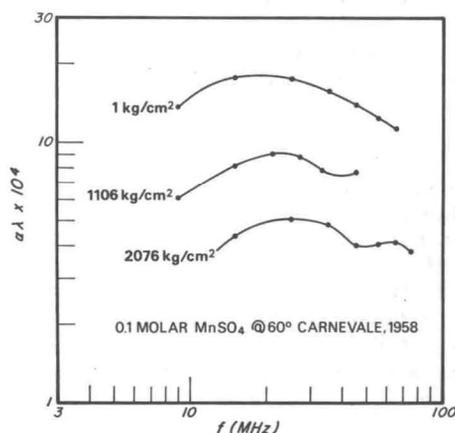


FIG. 5. Sound absorption per wavelength vs pressure for 0.1M MnSO_4 aqueous solution at 60°C.

volume change, $\Delta V_{23} = 18 \text{ cm}^3/\text{mole}$, assigned by Eigen and Tamm to the transition between States 2 and 3, that produced the principal pressure effect on sound absorption.

According to the value of ΔV_{III} , obtained for MnSO_4 from the Atkinson and Kor parameters, the maximum decrease in sound absorption at 15 000 psi can only be around 20% instead of the 70% observed—according to Atkinson and Kor,¹⁴ $\Delta V_{12} \approx 5 \text{ cm}^3/\text{mole}$. Therefore, from the equation for ΔV_{III} , we see that the values of ΔV_{34} and ΔV_{23} cannot be great enough to account for the observed dependence of acoustic absorption unless they are of opposite sign. If they are, then the implication would be that the absorption associated with the middle relaxation frequency must increase with pressure because the concentration of State 3 would increase.

Now, according to Carnevale's⁶ analysis of his absorption data at 60° from 9 to 75 MHz, there does not appear to be a significant increase in a middle peak as pressure increases. He treats the data in terms of two relaxation frequencies, the upper one being diffusion controlled. From his data, he calculates that β_{III} decreases from 4.55×10^{-14} to $1.79 \times 10^{-14} \text{ cm}^2/\text{dyn}$ for a pressure increase of about 15 000 psi, a decrease very similar to that reported here. However, as we re-examine Carnevale's data, a plot of absorption per wavelength recalculated from his raw data and cor-

TABLE V. Concentrations of states in 0.5M MnSO_4 compared to those in 0.5M MgSO_4 .

State	MnSO_4	MgSO_4
m_1	0.36 moles/liter	0.44 moles/liter
m_2	0.55	0.027
m_3	0.020	0.027
m_4	0.068	0.003

TABLE VI. Modified reaction rates and ratios for MnSO_4 at 25°C predicted by Atkinson and Kor.

C (moles/liter)	0.01	0.1
ν_{III} (MHz)	2.7	3.3
k_{12}'	0.22 k_{21}	0.81 k_{21}
k_{23}'	0.066 k_{32}	0.16 k_{32}
$k_{22}/(k_{23}' + k_{32})$	0.95	0.86
$k_{21}/(k_{12}' + k_{21})$	0.82	0.55

rected only for water absorption is most interesting, as we see in Fig. 5; the data at 15 720 and 28 800 psi appear to indicate the existence of a third middle relaxation frequency. These limited data indicate the possibility of an initial increase, with pressure, of a middle ($\alpha\lambda$)_{II} peak; further increase of pressure appears to diminish this peak. Additional data with more extensive frequency coverage and at closer pressure intervals appear to be most desirable and useful, preferably at 25°C.

The concentration of State 4 deduced by Atkinson and Kor appears to be confirmed by NMR experimental work,²¹ in which it was concluded that two water molecules are replaced upon formation of the contact ion pair. Furthermore, in the work at Heidelberg²² it has been postulated that a reversal of sign does take place in the volume changes but not in a manner that is consistent with Atkinson and Kor.

A final quantitative model for MnSO_4 , one which different investigators can agree upon, may be some time in coming. Tamm²² has presented new quantitative values of multistate parameters for MnSO_4 and MgSO_4 solutions that indicate qualitative agreement with the pressure dependence of the ultrasonic absorption reported here. It should be noted that the newer MgSO_4 values differ considerably from those in the paper by Eigen and Tamm,² and the MnSO_4 values differ from those of Atkinson and Kor.^{9,13} The criticism in this paper of the model by Atkinson and Kor—namely, its failure to account for the pressure dependence of ultrasonic absorption—is only one aspect of the problem of arriving at an undisputed description of multistate dissociation for MnSO_4 .

III. SUMMARY

The over-all features of the pressure dependence of acoustic absorption for MnSO_4 resemble those of MgSO_4 very closely. This also applies to the pressure dependence of electrical conductance in MnSO_4 solutions.⁸ Despite the differences in concentration of the contact ion pair (State 4) as treated here and the large

²¹ L. S. Frankel, T. R. Stengle, and C. H. Langford, J. Inorg. Nucl. Chem. **29**, 243-246 (1967).

²² K. Tamm "Acoustical Measurements of Chemical Relaxation in Electrolytical Solutions," paper delivered at Int. Congr. Acoust., 6th, Tokyo, Japan, 21-28 Aug. 1968.

