



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}
$k_{32}/(k_{23}' + k_{32})$	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 $(\alpha\lambda)_{\text{II}}$ 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.

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difference in ν_{III} , there are no significant differences in the pressure dependence of the $(\alpha\lambda)_{III}$ absorption peak. However, Carnevale's work indicates that the $(\alpha\lambda)_{II}$ peak may prove to be significant in evaluating differences in acoustic absorption as a function of pressure.

The similarity of these pressure-dependent properties of $MnSO_4$ solutions must be accounted for by multistate dissociation models. In this paper, we conclude that parameters assigned to the model by Atkinson and Kor^{9,13} cannot account for the observed pressure dependence of ultrasonic absorption unless there is a reversal of sign for ΔV_{23} and ΔV_{34} . Tamm²² has indicated that a model for $MnSO_4$, based on ultrasonic work by Bechtler in his laboratory (the parameters of which differ from those of Atkinson and Kor), can account qualitatively for the observed pressure dependence. By measuring the pressure dependence of ultrasonic absorption in $MnSO_4$ solutions at 25°C, in the frequency

region of 5–100 MHz, it should be possible to decide upon a multistate model for $MnSO_4$.

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The concentration of $MnSO_4$ in the solutions was determined by NMR experimental work in which it was concluded that the water molecules are rapidly upon formation of the complex ion $MnSO_4 \cdot 6H_2O$ in the stock solutions. It has been postulated that the water molecules are in the complex ion and not in a separate ion as suggested by Atkinson and Kor.⁹

A most quantitative model for $MnSO_4$ was which different investigators can give upon it, in some cases using Tamm's parameters for $MnSO_4$ and $MnSO_4 \cdot 6H_2O$ values of multistate parameters for $MnSO_4$ and $MnSO_4 \cdot 6H_2O$ which are in qualitative agreement with the previous reports in the literature. The present paper is intended to point out that the new NMR values are in qualitative agreement with the data of Atkinson and Kor⁹ and the $MnSO_4$ values from the work of Atkinson and Kor⁹ in the region of the model by Atkinson and Kor⁹ is in qualitative agreement with the present data for the pressure dependence of ultrasonic absorption. It only one aspect of the problem is treated in the present paper, a detailed description of multistate dissociation for $MnSO_4$.

III. SUMMARY

The over-all features of the pressure dependence of acoustic absorption for $MnSO_4$ solutions have been described very clearly. This and agrees with the pressure dependence of electrical conductivity in $MnSO_4$ solutions. Despite the difference in concentration of the complex ion pair (state 4) as treated here and the large

values of ΔV_{23} and ΔV_{34} which are assigned by Atkinson and Kor⁹ to the transition between states 2 and 3, the predicted absorption peaks are in good agreement with the experimental data for $MnSO_4$.

As noted in the introduction, the maximum difference in sound absorption at 1500 Hz can only be about 10% in the case of the 10% solution—according to Atkinson and Kor⁹ ΔV_{23} and ΔV_{34} are in the order of 1000 cm³ mole⁻¹. From the equation for ΔV_{23} we see that the value of ΔV_{23} cannot be great enough to account for the observed dependence of acoustic absorption on pressure of opposite sign. It therefore seems that the present model is not in agreement with the experimental data. The present model, however, predicts that the pressure dependence of sound absorption will increase with increasing concentration of state 4, which is in qualitative agreement with the data of Atkinson and Kor⁹ and the $MnSO_4$ values from the work of Atkinson and Kor⁹ in the region of the model by Atkinson and Kor⁹ is in qualitative agreement with the present data for the pressure dependence of ultrasonic absorption. It only one aspect of the problem is treated in the present paper, a detailed description of multistate dissociation for $MnSO_4$.

TABLE I. Calculated values of $(\alpha\lambda)_{II}$ and $(\alpha\lambda)_{III}$ for $MnSO_4$ solutions at 25°C.

State	$(\alpha\lambda)_{II}$	$(\alpha\lambda)_{III}$
1	0.000	0.000
2	0.000	0.000
3	0.000	0.000
4	0.000	0.000
5	0.000	0.000
6	0.000	0.000