FIG. 5. Sound absorption per wavelength vs pressure for $0.1M$ MnSO$_4$ aqueous solution at 60°C.

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

volume change, $\Delta V_{23} = 18$ cm^3/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] $\Delta V_{12} \simeq 5$ cm^3/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's[6] 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 1.79×10^{-14} cm^2/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-

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 Heidelberg[22] 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. Tamm[22] 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

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

[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.

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 MnSO₄ 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}. Tamm[22] has indicated that a model for MnSO₄, 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 MnSO₄ solutions at 25°C, in the frequency

region of 5–100 MHz, it should be possible to decide upon a multistate model for MnSO₄.

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