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The Effect of Pressure on the Dissociation of Manganese Sulfate

Ion Pairs in Water*

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Conductivity at 25° of aqueous solutions of MnSO_4 and MnCl_2 has been measured as a function of pressure up to 2000 atm. for concentrations from 0.0005 to 0.02 M . The effect of pressure on the molal dissociation constant of MnSO_4 was calculated with the conductance equation used by Davies, Otter, and Prue. Based on a two-state dissociation model, the difference of partial molal volumes between products and reactants, $\Delta \bar{V}^0$, was found to be in agreement with the value calculated on the basis of theory by Fuoss, namely -7.4 cc./mole. Although MnSO_4 and MgSO_4 solutions show reasonable agreement in $\Delta \bar{V}^0$ at atmospheric pressure at the lower concentrations, small differences in the pressure dependence of the equilibrium constant are observed which may be related to the marked differences in acoustic absorption exhibited by these salts.

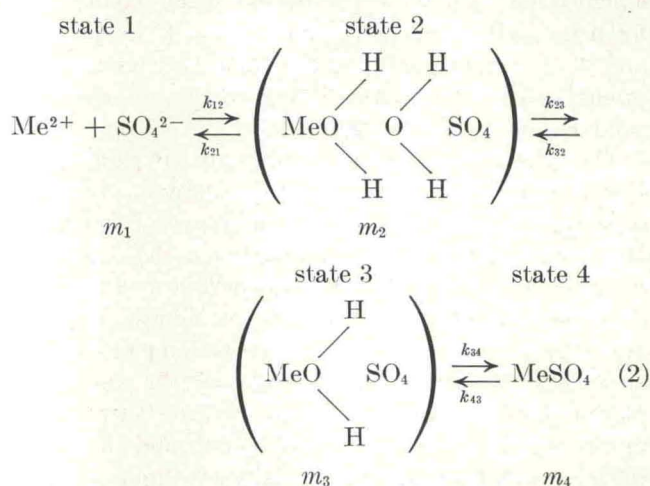
The marked differences in the acoustic absorption exhibited by aqueous solutions of MgSO_4 and MnSO_4 are in sharp contrast to the general similarities between the thermodynamic properties such as equilibrium constants and activity coefficients.

Eigen and Tamm² have proposed a four-state dissociation model to explain the acoustic absorption observed in MgSO_4 aqueous solutions at atmospheric pressure as a function of frequency and concentration. They assign partial molal volume changes and equilibrium constants which lead to a prediction of the pressure dependence of the acoustic absorption as well as electrical conductivity. The predicted behavior as a function of pressure from the four-state model is consistent with acoustic³ as well as conductivity data.⁴ Measurements of conductivity as a function of pressure for MgSO_4 are also in agreement with the theory of Fuoss for the formation of ion pairs as was pointed out by Hamann, Pearce, and Strauss.⁵ The same behavior should be observed for any other 2-2 sulfate on the basis of theory by Fuoss, that is, in the equation

$$\left(\frac{\partial \ln K_m}{\partial p} \right)_{T,m} = - \frac{\Delta \bar{V}^0}{RT} \quad (1)$$

where K_m is the molal equilibrium constant, $\Delta \bar{V}^0$ should be the same for all salts of a given class.

The relation of K_m to the four-state model is seen from eq. 2 where the free hydrated ions in state 1 associate and approach each other more closely as successive water molecules are removed from between the ions until they are in contact with one another. Only state 1 contributes to electrical conduction.



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(1) G. Kurtze and K. Tamm, *Acoustica*, **3**, 33 (1953).

(2) (a) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93 (1962); (b) K. Tamm, "Handbuch der Physik," Vol. XI, Springer-Verlag,

The conventional molal equilibrium constant is

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

where m is the molality of the salt, m_i is the molal concentration of the respective states, α is the degree of dissociation, and $\gamma_{\pm}^2 = \alpha^2 f_{\pm}^2 = \alpha^2 \pi^f$.

Eigen and Tamm² proposed two sets of parameters for the four-state model within which they can account for the acoustic effects at atmospheric pressure. The accuracy of their values of equilibrium constants for the steps in eq. 2 are claimed to be within $\pm 50\%$ and the partial molal volumes to be within $\pm 20\%$. Work on the effect of pressure on sound absorption and electrical conductivity in MgSO_4 solutions favors one of the sets of parameters

$$K_{12} = 0.04 = \frac{m_1^2 \pi^f}{m_2} = \frac{k_{21}}{k_{12}}, \Delta V_{12}^0 = 0 \quad (4)$$

$$K_{23} = 1 = \frac{m_2}{m_3} = \frac{k_{32}}{k_{23}}, \Delta V_{23} = -18 \text{ cc./mole} \quad (5)$$

$$K_{34} = 9 = \frac{m_3}{m_4} = \frac{k_{43}}{k_{34}}, \Delta V_{34} = -3 \text{ cc./mole} \quad (6)$$

From these equations it is seen that

$$K_m = \frac{K_{12} K_{23} K_{34}}{1 + K_{34} + K_{23} K_{34}} \quad (7)$$

Decided differences between MgSO_4 and MnSO_4 multistate models exist; Atkinson and Kor⁶ have published values for the equilibrium constants but have assigned no values for the partial molal volume differences. Their values are $K_{12} = 0.0192$, $K_{23} = 2.8$, and $K_{34} = 0.29$. Until ΔV_{ij} values are assigned, a prediction of the pressure dependence of electrical conductivity cannot be made.

The observed acoustic effects are attributed by Eigen and Tamm to transitions between different sorts of intermediate hydrate complexes or ion pairs. Hamann, Pearce, and Strauss point out that the small value of $-\Delta \bar{V}^0$ (less than half the partial molal volume of water) suggests that the ions are almost fully hydrated in the ion-pair state and that an ion pair contains at least one water molecule between the ions. For MgSO_4 there appears to be no conflict between the multistate theory of Eigen and Tamm and the Fuoss theory, for both lead to essentially the same value of $\Delta \bar{V}^0$ although the interpretation of $\Delta \bar{V}^0$ in the Fuoss theory does not consider different species of ion pairs. In the multistate theory $\Delta \bar{V}^0$ is a composite of the volume changes and the equilibrium constants associated with the different species of ion pairs.⁴

Any differences in multistate models to explain sound absorption for MnSO_4 and MgSO_4 solutions might show up in the pressure dependence of the equilibrium constant of these salts.

Experimental

Measurements of electrical conductivity of aqueous solutions of MnSO_4 were made in essentially the same manner as described for MgSO_4 solutions.⁷ The results were obtained using the same equations as for MgSO_4 .

The ratios of equivalent conductivity Λ_p/Λ_1 for MnSO_4 , K_2SO_4 , MnCl_2 , and KCl as a function of concentration are shown in Table I. The equivalent conductivity Λ_p of MnSO_4 is shown in Table II. The degree of association $(1 - \alpha)$ and molal dissociation constant K_m are shown in Tables III and IV.

Table I: Λ_p/Λ_1 for Aqueous Solutions at 25°

	$C \times 10^{10}$ ^a	P , atm.			
		500	1000	1500	2000
MnSO_4	5	1.021	1.034	1.034	1.028
	10	1.027	1.042	1.047	1.043
	20	1.036	1.057	1.065	1.066
	100	1.059	1.098	1.124	1.136
	200	1.068	1.118	1.150	1.169
K_2SO_4	5	1.010	1.011	1.006	0.995
	20	1.010	1.012	1.008	0.998
	200	1.016	1.025	1.025	1.017
MnCl_2	5	1.015	1.021	1.016	1.004
	20	1.015	1.020	1.015	1.005
	200	1.020	1.030	1.023	1.019
KCl	5	1.012	1.015	1.009	0.996
	10	1.011	1.015	1.008	0.996
	20	1.012	1.015	1.009	0.998
	100	1.012	1.015	1.009	0.998
	200	1.013	1.016	1.010	0.999

^a C is atmospheric pressure concentration in moles/liter.

In contrast to the $\Delta \bar{V}^0$ values for MgSO_4 which were obtained with a straight line to fit to $\log K_m$ vs. pressure, the MnSO_4 data clearly showed a quadratic behavior. Accordingly, $\Delta \bar{V}^0$ is a function of pressure, and values are listed for $\Delta \bar{V}^0$ at atmospheric pressure and 2000 atm. in Table IV.

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(3) F. H. Fisher, to be submitted to *J. Acoust. Soc. Am.*

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(7) F. H. Fisher, *ibid.*, **66**, 1607 (1962).