[Reprinted from the Journal of Physical Chemistry, **69**, 2595 (1965).]

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.

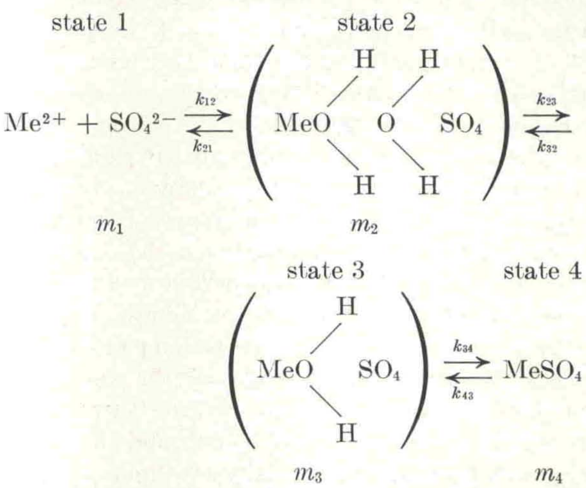
The marked differences in the acoustic absorption exhibited by aqueous solutions of $MgSO_4$ and $MnSO_4$[1] are in sharp contrast to the general similarities between the thermodynamic properties such as equilibrium constants and activity coefficients.

Eigen and Tamm[2] 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 acoustic[3] 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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* This paper represents results of research sponsored by the Office of Naval Research.

(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 Tamm[2] 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 Kor[6] 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°

		P, atm.			
	$C \times 10^{4a}$	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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(4) F. H. Fisher, *J. Phys. Chem.*, **69**, 695 (1965).

(5) S. D. Hamann, P. J. Pearce, and W. Strauss, *ibid.*, **68**, 375 (1964).

(6) G. Atkinson and S. K. Kor, *ibid.*, **69**, 128 (1965).

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

Table II: Λ_p for Aqueous $MnSO_4$ Solutions at 25°

$C \times 10^4$ [a]	P, atm. 1	500	1000	1500	2000
0	133.2[b]	135.0	135.3	134.5	133.0
5	116.3[b]	118.7	120.3	120.3	119.6
10	108.7[b]	111.6	113.3	113.8	113.4
20	99.7[b]	103.3	105.4	106.2	106.3
100	75.2[c]	79.6	82.6	84.5	85.4
200	65.9[c]	70.4	73.7	75.8	77.0

[a] *C* is atmospheric pressure concentration in moles/liter. [b] C. J. Hallada and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 3759 (1961). [c] Measured this experiment.

Table III: Degree of Association $(1 - \alpha)$ for Aqueous $MnSO_4$ at 25°

$C \times 10^4$ [a]	P, atm. 1	500	1000	1500	2000
5	0.070	0.065	0.055	0.050	0.046
10	0.115	0.105	0.094	0.085	0.079
20	0.172	0.155	0.140	0.129	0.119
100	0.345	0.316	0.292	0.271	0.255
200	0.415	0.383	0.355	0.332	0.314

[a] *C* is atmospheric pressure concentration in moles/liter.

Table IV: Molal Dissociation Constant (K_m) and $\Delta \bar{V}^0$ for Aqueous $MnSO_4$ at 25°

P, atm.	C, atm. press. concn., M 0.0005	0.001	0.002	0.01	0.02
1	0.0044	0.0044	0.0046	0.0052	0.0060
500	0.0048	0.0050	0.0053	0.0063	0.0073
1000	0.0059	0.0057	0.0062	0.0073	0.0086
1500	0.0066	0.0065	0.0069	0.0084	0.0099
2000	0.0073	0.0072	0.0077	0.0094	0.0111
	$\Delta \bar{V}^0$, cc./mole[a]				
1	−7.4	−7.1	−8.0	−9.3	−10.0
2000	−5.3	−5.0	−4.8	−5.0	−5.0

[a] $\Delta \bar{V}^0$ was calculated by a least-squares fit of log *K* to a quadratic curve.

Table V: Comparison of $K_m(P = 2000)/K_m(P = 1)$ for $MgSO_4$ and $MnSO_4$ Aqueous Solutions at 25°

C, M	$MgSO_4$	$MnSO_4$
0.0005	1.9	1.7
0.001	1.8	1.6
0.002	1.7	1.7
0.01	1.8	1.8
0.02	1.7	1.9

It is seen that at atmospheric pressure the value of $\Delta \bar{V}^0$, as concentration decreases, approaches that predicted from the Fuoss theory, namely, −7.4 cc./mole. There appears to be a concentration dependence of $\Delta \bar{V}^0$ at atmospheric pressure but not at 2000 atm.

A comparison in Table V of the ratios of the equilibrium constants at 2000 and 1 atm. indicates that a

Table VI: Comparison of $\Delta \bar{V}^0$ for $MgSO_4$ and $MnSO_4$ Aqueous Solutions at 25° and 1 Atm.

C, M	$\Delta \bar{V}^0$, cc./mole $MgSO_4$	$MnSO_4$
0.0005	−8.5	−7.4
0.001	−7.0	−7.1
0.002	−7.0	−8.0
0.01	−7.3	−9.3
0.02	−6.9	−10.0

Table VII: Cell Constants[a]

Cell constants at atm. press. Concn., M	L_1	Press. dependence of cell constant P, atm.	L^*_p
0.0005	0.808	500	0.991
0.001	0.811	1000	0.986
0.002	0.812	1500	0.982
0.01	0.824	2000	0.979
0.02	0.829		

[a] To find cell constant L_p at pressure *P* multiply atmospheric pressure value L_1 by L^*_p.

Table VIII: Copy of Original Conductivity Data Measured for Electrolytes at 25° in Aqueous Solutions (Teflon Cell without Glass Bar)

	P, atm. 1	500	1000	1500	2000	1[a]
0.02 *M* KCl, mmhos	3.338	3.484	3.582	3.639	3.670	3.322
$MnSO_4$	3.118	3.436	3.681	3.868	4.008	3.104
K_2SO_4	5.769	6.046	6.245	6.381	6.456	5.742
$MnCl_2$	4.941	5.197	5.374	5.482	5.539	4.934
0.01 *M* KCl, mmhos	1.715	1.790	1.840	1.871	1.886	1.709
$MnSO_4$	1.812	1.977	2.101	2.196	2.264	1.802
0.002 *M* KCl, μmhos	359.7	375.0	385.4	391.6	394.8	358.7
$MnSO_4$	486.7	519.9	543.8	560.3	571.5	484.5
K_2SO_4	684.4	712.6	732.3	744.6	751.4	681.2
$MnCl_2$	575.6	602.6	620.3	631.5	637.1	573.2
0.001 *M* KCl, μmhos	181.8	189.9	195.0	198.2	199.9	181.3
$MnSO_4$	267.5	283.4	295.0	302.6	307.6	266.5
0.0005 *M* KCl, μmhos	92.0	96.1	99.0	100.4	101.4	91.3
$MnSO_4$	144.2	152.0	157.9	161.5	163.8	144.0
K_2SO_4	181.8	189.5	194.5	197.8	199.6	181.3
$MnCl_2$	153.4	160.7	165.7	168.8	170.3	152.9
Water, μmhos	0.5	0.7	0.9	1.1	1.3	0.8
Series lead resistance, ohms	0.134	0.134	0.134	0.134	0.134	

[a] The readings in this column were obtained the day after the pressure run was made.

different trend as a function of concentration exists between $MgSO_4$ and $MnSO_4$ solutions.

At atmospheric pressure and at the lower concentrations the values of $\Delta \bar{V}^0$ for both $MnSO_4$ and $MgSO_4$ agree with the value predicted by the Fuoss theory. For $MnSO_4$ there appears to be a dependence of $\Delta \bar{V}^0$ on pressure which was not observed for $MgSO_4$. Furthermore, there is a more noticeable concentration dependence of $\Delta \bar{V}^0$ at atmospheric pressure for $MnSO_4$ and in the opposite direction to that exhibited by $MgSO_4$, as shown in Table VI. The change in $\Delta \bar{V}^0$ is greater than would be accounted for assuming errors in Λ_p/Λ_1 to be as great as $\pm 0.5\%$.

The differences in the pressure behavior of these two salts may, in fact, be due to differences in the various ion-pair species which can be related to the differences in acoustic behavior. However, a multistate model cannot be deduced from conductivity data; these results can only provide a check for consistency of any multistate models which may be proposed.