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Multistate Dissociation and the Effect of Pressure on the Equilibrium on Magnesium Sulfate[1]

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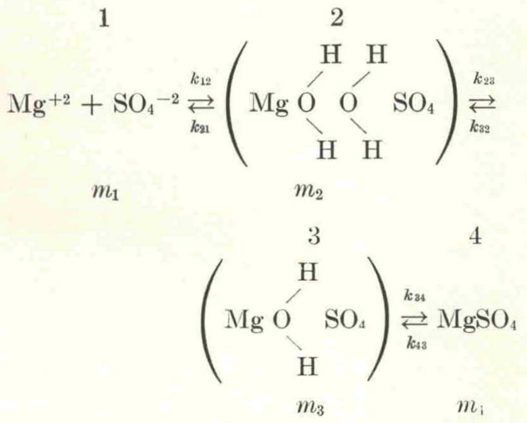
Eigen and Tamm[2] have proposed a four-state model for the dissociation of $MgSO_4$ in order to explain ultrasonic absorption in aqueous solutions of this salt. The model is shown in eq. 1, where the free ions which would affect the electrical conductivity of solutions are those in state 1.



(1)

The conventional molal equilibrium constant is

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

where m is the molality of the salt, m_i is the molal concentrations 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[2b] proposed two sets of parameters to describe the four-state model. Work on the effect of pressure on sound absorption in $MgSO_4$ solutions favors one of the sets of parameters and these values are set forth below

$$K_{12} = 0.04 = \frac{m_1{}^2\pi^f}{m_2} = \frac{k_{21}}{k_{12}}, \quad \Delta V^0{}_{12} = 0 \tag{3}$$

$$K_{23} = 1 = \frac{m_2}{m_3} = \frac{k_{32}}{k_{23}}, \quad \Delta V_{23} = -18 \text{ cc./mole} \tag{4}$$

$$K_{34} = 9 = \frac{m_3}{m_4} = \frac{k_{43}}{k_{34}}, \quad \Delta V_{34} = -3 \text{ cc./mole} \tag{5}$$

Calculation

Using eq. 2, 3, 4, and 5, it is possible to show

$$K_m = \frac{K_{12}K_{23}K_{34}}{1 + K_{34} + K_{23}K_{34}} \tag{6}$$

From the Van't Hoff equation

$$\left(\frac{\partial \ln K_{ij}}{\partial p}\right)_{T,m} = -\frac{\Delta V_{ij}}{RT} \tag{7}$$

the effect of pressure on the K_{ij} can be calculated using the above parameters. The effect of pressure on π^f is negligible at low concentrations. Using the equation

$$\left(\frac{\partial \ln f_{\pm}{}^2}{\partial p}\right) = \frac{\Delta V^*}{RT} \tag{8}$$

the value of ΔV^* is of the order of 0.2 cc./mole at $m = 0.02$.[3] Values of the parameters as a function of pressure are given in Table I. This is carried up to only the pressures at which ultrasonic absorption has been measured.[4]

In conductivity experiments and in the Fuoss theory of ion association, only a two-state model has been used to calculate the effects of pressure on equilibrium according to the equation

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(2) (a) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93 (1962); (b) *ibid.*, **66**, 107 (1962).

(3) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962).

(4) F. H. Fisher, *J. Acoust. Soc. Am.*, to be published.

$$\left(\frac{\partial \ln K_m}{\partial p}\right)_{T,m} = \frac{-\Delta V^0}{RT} \qquad (9)$$

where ΔV^0 represents the difference in partial molal volumes between products and reactants. However, from eq. 6 it is seen that ΔV^0 is a composite of all volume changes involved in the four-state model; that is

$$-\frac{\Delta V^0}{RT} = \left(\frac{\partial \ln K_m}{\partial p}\right)_{T,m} = \frac{\partial \ln\left[\frac{K_{12}K_{23}K_{34}}{1 + K_{34} + K_{23}K_{34}}\right]}{\partial p} \qquad (10)$$

From a plot of $RT \log K_m$ (calculated from the Eigen and Tamm model) *vs.* pressure, the slope of this curve $\Delta V^0 = -7.7$ cc./mole. This is in excellent agreement with the experimental value of $\Delta V^0 = -7.3$ cc./mole

Table I: Pressure Dependence of Equilibrium Constants of $MgSO_4$ Based on Four-State Eigen and Tamm Model

P, p.s.i.	K_m	K_{12}	K_{23}	K_{34}
14.7	0.019	0.04	1	9.0
5,000	0.021	0.04	1.28	9.4
10,000	0.024	0.04	1.65	9.8
15,000	0.026	0.04	2.13	10.24

obtained by Fisher[3] from conductivity experiments and with the value $\Delta V^0 = -7.4$ cc./mole calculated by Hamann[5] from the ion association theory of Fuoss.

Discussion

From the close agreement of the values evaluated by three independent methods, it appears that acoustic and conductivity data on aqueous solutions of $MgSO_4$ can be interpreted in a quantitative manner on the basis of a four-state dissociation model. It is seen how different values of the ΔV_{ij} describing each step of the dissociation reaction must be considered in order to relate the multistate model to conductivity measurements.

As Eigen and Tamm point out, their values of the K_{ij} are only known to within $\pm 50\%$ and the ΔV_{ij} to within $\pm 20\%$ based on their ultrasonic experiments at atmospheric pressure. Eigen and Tamm show that adiabatic and isothermal ΔV_{ij} can be taken as numerically equal in aqueous solutions since the enthalpy correction term is negligible. It is seen that one of their four-state models is consistent with both acoustic and conductivity data as a function of pressure.

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(5) S. D. Hamann, *J. ~~Acoust. Soc. Am.~~*, Phys. Chem., **68**, 375 (1964).