

constant, $D = 4.9$, pressure, P , approximately 220 bars,⁶ while $-\log K_d = 0.97$ at $d = 0.70$ g/ml, and $P \approx 1000$ bars.⁶

Marshall and Quist found that, at constant temperature, plots of $\log K_d$ vs. $\log C_{H_2O}$ are linear. C_{H_2O} is the molar concentration of water. They concluded that water should be included explicitly in a "complete equilibrium"



with the equilibrium constant given by

$$K^\circ = a_M a_X / a_{MX} a_{H_2O}^k = K_d / a_{H_2O}^k \quad (3)$$

Marshall and Quist then set the activity of water in the infinitely dilute salt solution to be equal to the molar concentration of water. Their statement regarding the choice of standard state that leads to this is, in one instance,^{2b} "... a_{H_2O} is replaced by the molar concentration of water (C_{H_2O}) with a hypothetical standard state of unit molarity at the particular density (or pressure), ...". I submit that this is incorrect if one is concerned with the changes in the activity of the water solvent as the density (pressure) changes. The activity of a substance is defined by the relation

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (4)$$

where μ_i is the chemical potential (partial molar free energy) of component i and μ_i° is the chemical potential in some chosen standard state at the temperature T . If the effects of changes in activity (concentration) of water solvent at different densities on a chemical reaction are to be investigated, the standard state chosen should *not* change with solvent density or pressure. A suitable choice here would be any invariant state of water (constant T and P). Now

$$d\mu_i = \bar{V}_i dP - \bar{S}_i dT \quad (5)$$

where \bar{V}_i is the partial molar volume of i and \bar{S}_i is the partial molar entropy of i . At constant temperature, this becomes

$$d\mu_i = \bar{V}_i dP$$

and thus

$$d\mu_i^\circ + RT d \ln a_i = \bar{V}_i dP$$

at constant T . The only variable here is the pressure. I take as a suitable standard state, water at one particular density, say 0.300 g/ml, at the temperature T . Then $d\mu_i^\circ = 0$ and

$$d \ln a_i = \bar{V}_i dP / RT$$

or

$$\log a_{H_2O} = (1/2.303RT) \int_{P^\circ}^P \bar{V}_{H_2O} dP \quad (6)$$

where P° is the pressure corresponding to the density in the standard state at T , and P is the pressure corre-

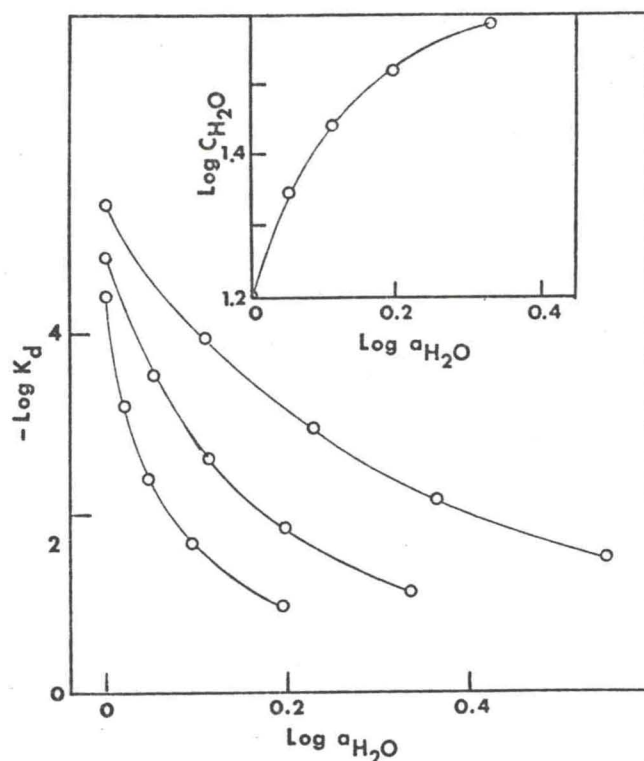


Figure 1. The water concentration, C_{H_2O} , in the insert, and the ion-pair dissociation constants for NaCl at 400, 500, and 700° as a function of the water activity, a_{H_2O} . The standard state for the water solvent at all temperatures was taken to be pure water at a pressure producing a density of 0.300 g/ml.

sponding to the density of water whose activity is a_{H_2O} . Values of $\log a_{H_2O}$ were calculated from eq 6 at 400, 500, and 700° using available specific volume (or density)-pressure data⁷ referenced by Quist and Marshall.^{2b} These values at 500° at densities of 0.4, 0.5, 0.6, and 0.7 g/ml are plotted vs. $\log C_{H_2O}$ in the insert, Figure 1. It can be seen that the activity of water increases at a greater rate with increasing pressure than does the concentration. It might be noted here that the pressure at a density of 0.30 g/ml is 550 bars, while at the highest density here, 0.70 g/ml, the pressure is 2000 bars, at 500°.

I have plotted values of $\log K_d$ for NaCl vs. these values of $\log a_{H_2O}$ at the corresponding densities at 400, 500, and 700°, Figure 1, to emphasize the fact that if equation 3 is correct, then the "complete" constant K° certainly is *not* constant as the density of solvent water changes. Marshall and Quist concluded on the basis of the linearity of isothermal $\log K_d$ vs. $\log C_{H_2O}$ plots that the complete equilibrium constant was independent of changes in the solvent dielectric constant. I conclude that the conclusions of Marshall and Quist are

(6) Interpolated from data compiled by A. W. Lawson and A. J. Hughes in "High Pressure Physics and Chemistry," Vol. I, R. S. Bradely, Ed., Academic Press, Inc., New York, N. Y., 1963, p 209.

(7) (a) W. T. Holser and G. C. Kennedy, *Am. J. Sci.*, 257, 71 (1959); (b) S. Maier and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, 70, 639 (1966).