

Stokes²⁵ used to fit their measured values of the dielectric constant of water under pressure

$$\epsilon_p = A + BP/(1 + CP) \quad (24)$$

can be recast as

$$\frac{1}{\epsilon_p} - \frac{1}{\epsilon_0} = -\frac{B}{A^2} \left[\frac{P}{1 + (C + B/A)P} \right] \quad (25)$$

This expression has the same form as our equations (12) and (22), with $b = C + B/A = 9.46 \times 10^{-5} \text{ bar}^{25}$ at 25°C. It follows that, with the same assumptions as we have made, the expression (25) leads directly to our general equation (21) for free energy changes, with only a slightly different value of b .

Some Linear Relationships in Φ

Finally, we can define a quantity Φ^* as

$$\Phi^* = P/(1 + bP) \quad (26)$$

and rewrite some of El'yanov's linear relationships⁹ in terms of this variable, so that they become analytical functions of the pressure. For this purpose we assume b to be independent of temperature. El'yanov's equation (2) then becomes

$$\Delta G_p - \Delta G_0 = \Delta V_0 \Phi^* \quad (27)$$

and his equations (4), (14), (15) and (16) become

$$\Delta V_p = \Delta V_0 \Phi^{*2}/P^2 \quad (28)$$

$$\Delta S_p = \Delta S_0 - m^* \Phi^* \quad (29)$$

$$\Delta H_p = \Delta H_0 - n^* \Phi^* \quad (30)$$

$$\gamma = n^*/m^* \quad (31)$$

where

$$m^* = \partial \Delta V_0 / \partial T \quad (32)$$

$$n^* = \Delta V_0 - T \partial \Delta V_0 / \partial T \quad (33)$$

The quantities with asterisks differ from the corresponding ones without them⁹ by the factor $R \ln 10$.

Within the approximations of the electrostatic treatment given in the last section, m^* and n^* should each be a simple product of ΔV_0 with a universal function of the temperature. From (19) we have

$$m^* = \frac{\partial \Delta V_0}{\partial T} = \frac{Ne^2 \theta}{2\epsilon_0} \left[\left(\frac{\partial \ln \epsilon}{\partial T} \right)_0 \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 - \frac{\partial}{\partial T} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 \right] \quad (34)$$

$$= \Delta V_0 \left[- \left(\frac{\partial \ln \epsilon}{\partial T} \right)_0 + \frac{\partial}{\partial T} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 \times \left(\frac{\partial P}{\partial \ln \epsilon} \right)_0 \right] \quad (35)$$

and

$$n^* = \Delta V_0 - m^* T \quad (36)$$

²⁵ Dunn, L. A., and Stokes, R. H., *Trans. Faraday Soc.*, 1969, **65**, 2906.

The ratio γ is theoretically independent of ΔV_0 . The term in square brackets in (35) is a universal function of T , only, and can be calculated from the derivatives measured by Owen *et al.*²³ Table 6 compares values of m^* , n^* and γ calculated from (35), (36) and (31) with the experimental values.⁹ The agreement is surprisingly good except in the case of n^* for acetic acid. The reasons for the difference in sign of ΔV_0 (and hence of m^* and n^*) for the two acids in Table 6 is discussed elsewhere.²⁶

Table 6. Experimental and theoretical effects of pressure on ΔH and ΔS for ionization reactions in water at 50°C

ΔV_0 and experimental values are from El'yanov,⁹ calculated values are from equations (34), (36) and (31)

Parameter (units)	Acetic acid	Sulphanilic acid
ΔV_0 (cm ³ mol ⁻¹)	-13.7	+2.15
$m^*_{\text{calc.}}$ (cm ³ mol ⁻¹ K ⁻¹)	-9.6×10^{-2}	$+1.51 \times 10^{-2}$
$m^*_{\text{expt.}}$ (cm ³ mol ⁻¹ K ⁻¹)	-6.4×10^{-2}	$+1.50 \times 10^{-2}$
$n^*_{\text{calc.}}$ (cm ³ mol ⁻¹)	17.3	-2.7
$n^*_{\text{expt.}}$ (cm ³ mol ⁻¹)	7.1	-2.7
$\gamma_{\text{calc.}}$ (K)	180	180
$\gamma_{\text{expt.}}$ (K)	109	180

To summarize, we have presented an empirical relationship which gives a good description of the influence of high pressures on ionization equilibria in aqueous solutions. It is consistent with the simple electrostatic theory of ionic hydration. Combined with the theory, it provides a means for predicting ionization constants over a wide range of pressures and temperatures, simply from the values at atmospheric pressure of K_0 , ΔV_0 and ΔH_0 .

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²⁶ Hamann, S. D., and Linton, M., *J. Chem. Soc., Faraday Trans. 1*, in press.