

Some Quantitative Relationships for Ionization Reactions at High Pressures

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Abstract

A simple formula is proposed to describe the pressure dependence of the variable Φ in El'yanov and Gonikberg's linear free energy relationship for ionization reactions in solution at high pressure.

The expression, given in equations (10) and (12), provides a good description of the influence of pressure on ionization equilibria in aqueous solutions. It permits El'yanov's general linear relationships between Φ and ionization free energies, enthalpies and entropies, pH and Hammett's ρ parameter, to be expressed in terms of the pressure in convenient analytical forms.

The formula is shown to be consistent with the simple electrostatic theory of ion hydration, allowing for the effect of pressure on the dielectric constant of water. Combined with the theory, it provides a general means of predicting ionization constants over a wide range of pressures and temperatures simply from knowledge of the changes in molar volume, enthalpy and entropy which accompany the reactions at atmospheric pressure.

Introduction

The thermodynamic relationship¹ which expresses the influence of pressure P on the molal ionization constant K of a weak electrolyte in solution is

$$\partial RT \ln K / \partial P = -\Delta V \quad (1)$$

where ΔV denotes the molar volume change accompanying the reaction (if K is the 'thermodynamic' ionization constant expressed as a product of activities, ΔV is then the volume change at infinite dilution²), R is the gas constant and T is the absolute temperature. This relationship can be integrated to give

$$RT \ln(K_p/K_0) = -\Delta V_0 P + \frac{1}{2} \Delta \kappa_0 P^2 + \frac{1}{6} \Delta \lambda_0 P^3 + \dots \quad (2)$$

where the subscripts ₀ and _p denote values at atmospheric pressure and at a relative pressure P (the symbol P denotes the absolute pressure minus atmospheric pressure), and

$$\Delta \kappa = -\partial \Delta V / \partial P \quad (3)$$

$$\Delta \lambda = \partial \Delta \kappa / \partial P \quad (4)$$

¹ Planck, M., *Ann. Phys. Chem.*, 1887, **30**, 250.

² Hamann, S. D., in 'High Pressure Physics and Chemistry' (Ed. R. S. Bradley) Vol. 2, p. 132 (Academic Press: New York 1963); also in 'Modern Aspects of Electrochemistry' (Eds J. O'M. Bockris and B. E. Conway) Vol. 9, p. 78 (Plenum Press: New York 1974).

Although ΔV_0 can often be measured by density methods at atmospheric pressure, the values of $\Delta\kappa_0$, $\Delta\lambda_0$, ... can only be obtained from measurements made over a range of moderate or high pressures.

There have been several attempts to replace the series (2) by simpler, and general, expressions. They are summarized below in chronological order.

Owen and Brinkley³ assumed that the pressure dependence of $\Delta\kappa$ could be represented by the Tait equation of state, and on that basis derived the relationship

$$RT \ln(K_P/K_0) = -\Delta V_0 P + \Delta\kappa_0 [BP - B^2 \ln(1 + P/B)] \quad (5)$$

where B is a parameter characteristic of the solvent. To apply this equation at high pressures it is necessary to know both ΔV_0 and $\Delta\kappa_0$, which requires measurements of both the densities and the compressibilities of related solutions of strong electrolytes. Kearns⁴ applied it in that way to the self-ionization of water and obtained fair agreement with Hamann's⁵ measured values of K_P/K_0 to a maximum pressure of 2 kbar (1 kbar = 10^3 bar = 10^8 Pa \equiv 986.92 atm). However, the equation fails to fit the more recent results of Linov and Kryukov⁶ at higher pressures—it departs by a factor of 2 at 8 kbar (see the dotted curve of Fig. 2 below).

El'yanov and Gonikberg⁷ found that the ionization constants of weak acids and bases in water, over the pressure range 0–3 kbar, can be fitted closely by the relationship

$$\log(K_P/K_0) = -\Phi \Delta V_0 / T \quad (6)$$

where Φ is a function of P only and has almost the same value, within $\pm 5\%$, for seven different acids and bases. They tabulated average values of Φ at 1, 2 and 3 kbar, and later⁸ showed that these values give a good description of the behaviour of 24 other weak electrolytes at pressures up to 3 kbar. Using values of Φ calculated from the ionization constants of ammonium hydroxide in water and piperidine in methanol at pressures up to 12 kbar, they showed that (6) describes the self-ionization constant K_w of water very well over the pressure range 0–8 kbar. Recently, El'yanov⁹ has found that (6) also gives a good fit of the ionization constants of acetic and sulphanilic acids over the same pressure range. He pointed out⁹ that it is a 'linear free energy relationship' for the influence of pressure; he analysed its properties and showed that similar linear dependences upon Φ must hold for enthalpy changes ΔH , entropy changes ΔS , and Hammett's ρ parameter in ionization reactions, as well as for the pH of buffer solutions. He also showed that the coefficients in the linear relationships should be calculable from data measured at atmospheric pressure. These conclusions were checked and confirmed by comparison with experiment.⁹

Lown *et al.*¹⁰ truncated the series (2) to the terms in ΔV_0 and $\Delta\kappa_0$ and concluded that it then describes the experimental data well up to 2 kbar, but fails at higher

³ Owen, B. B., and Brinkley, S. R., *Chem. Rev.*, 1941, **29**, 461.

⁴ Kearns, E. R., Dissertation, Yale University, 1966.

⁵ Hamann, S. D., *J. Phys. Chem.*, 1963, **67**, 2233.

⁶ Linov, E. D., and Kryukov, P. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1972, **4**, 10.

⁷ El'yanov, B. S., and Gonikberg, M. G., *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1967, 1044; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, 1007.

⁸ El'yanov, B. S., and Gonikberg, M. G., *Zh. Fiz. Khim.*, 1972, **46**, 1494; *Russ. J. Phys. Chem.*, 1972, **46**, 856.

⁹ El'yanov, B. S., *Aust. J. Chem.*, 1975, **28**, 933.

¹⁰ Lown, D. A., Thirsk, H. R., and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1968, **64**, 2073.