

THE THERMODYNAMIC SOLUBILITY PRODUCT CONSTANT BY CONDUCTIVITY MEASUREMENT

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ABSTRACT.—A procedure for correcting solubility product constants to account for effects of activity and concentration dependence of conductivity is presented. This procedure suggests additional treatment of data in the usual conductivity determination of solubility product constants in the undergraduate physical chemistry laboratory.

A common laboratory experiment in an undergraduate course in physical chemistry is the determination of the solubility of a sparingly soluble salt through the measurement of the specific conductivity of a saturated aqueous solution of the salt. In this determination one uses the equation

$$\Lambda_c = \frac{1000 L_s}{c} \quad (1)$$

where L_s is the specific conductivity of the salt in the saturated solution, c is the concentration of the salt in equivalents per liter and Λ_c is the equivalent conductivity of the solution. It is assumed that for dilute solutions, Λ_c , the equivalent conductivity at infinite dilution, may be substituted for Λ_c without introducing any appreciable error. The experimentally determined value of the specific conductivity of the salt in solution and the value of the limiting equivalent conductivity, available in the literature, are introduced into Equation 1 in order to determine the equivalent concentration of the salt and, hence, its solubility product constant.

Using the equations of the Onsager theory of conductivity and the limiting form of the Debye-Hückel Theory, a correction may be applied to the solubility determination outlined above and an estimate made of the thermodynamic solubility product constant.

To illustrate this procedure, the example of lead sulfate will be considered. This salt is a commonly suggested one in laboratory manuals. Because lead sulfate is a 2-2 valent electrolyte, the corrections to be made are quite striking.

A typical student determination yielded a specific conductivity of $4.38 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ for lead sulfate at 25°C . Inserting this value and a value (Robinson and Stokes, 1965, p. 465) of $\Lambda_\infty = 149.5 \text{ ohm}^{-1}$ for the concentration of the saturated solution gives a value of $K_{sp} = 2.10 \times 10^{-8} \text{ mole}^2 \text{ l}^{-2}$.

The value of the concentration so derived may be substituted for the concentration term in the Onsager Limiting Law (Glasstone, 1948, p. 904)

$$\Lambda_c = \Lambda_\infty - (A + B \Lambda_\infty) \sqrt{c} \quad (2)$$

where the terms A and B refer to the electrophoretic effect and the asymmetry effect, respectively. These terms are dependent upon temperature, solvent, ionic charges and the limiting conductance of the ions. The student may now calculate a value of Λ_c from Equation 2 and substitute this value for Λ_c in Equation 1 and obtain a new value for the concentration of lead sulfate. This process is repeated until a consistent value is obtained for the concentration. In this example, four cycles were performed and produced a value of $C = 3.04 \times 10^{-4} \text{ eq l}^{-1}$ and $K_{sp} = 2.32 \times 10^{-8} \text{ mole}^2 \text{ l}^{-2}$.

From the relationship for the thermodynamic solubility product constant (Glasstone, 1948, p. 962)

$$K_a = K_{sp} \gamma^2 \quad (3)$$

and from the Debye-Hückel equation for the mean activity coefficient (Glasstone, 1948, p. 956)

$$\log \gamma = -0.509 Z_+ Z_- \sqrt{\mu} \quad (4)$$

where μ is the ionic strength of the solution calculated from the final concentration for lead sulfate, a value of $K_a = 1.84 \times 10^{-8} \text{ mole}^2 \text{ l}^{-2}$ can be obtained.

Although this series of calculations does not result in any refinements in the value of K_a with regard to those values reported in the literature, it does illustrate to the student the effects of these corrections and the extent to which the approximation for $\gamma_{\pm}$ may be adjusted. By comparing these results with a 1-1 valence type electrolyte, further significance is given to the

influence of charge in the interionic attraction theory.

LITERATURE CITED

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 ROBINSON, R. A. and STOKES, R. H. 1965. Electrolyte Solutions. 2nd ed., Rev., Butterworth and Co., London. 571 pp.

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