ELECTRICAL CONDUCTANCE

PURPOSE

The purpose is to determine the conductances of solutions of a salt, strong acid, weak acid, and slightly soluble electrolyte.

From the data the ionization constant of the weak acid and solubility product constant of the slightly soluble salt may be calculated.

DISCUSSION

Conductance is defined as the reciprocal of resistance.

$$L = \frac{1}{R}$$

It is expressed as “reciprocal ohms” or “mho” (“ohm” spelled backward). “Specific conductance” is ohm^{-1} cm^{-1}

Specific conductance decreases as the concentration of ions decreases.

“Equivalent conductance”, Λ, is defined as

$$\Lambda = \frac{L}{C}$$

where *C* is the concentration.

The equivalent conductance in a solution in which the ions are far enough apart not to interact (infinite dilution) is known as Λ_0, equivalent conductance at infinite dilution. The ions act independently, and Λ_0 is the sum of the limiting conductances of each ion.

$$\Lambda_0 = \lambda_0^+ + \lambda_0^-$$

(Values of single ion conductances may be found in the <u>CRC Handbook of Chemistry and Physics</u>.

Λ_0 may be determined by plotting Λ vs $\sqrt{c}$ and extrapolating to zero concentration. However, this is not successful for a weak electrolyte because the degree of ionization increases with dilution and the $\Lambda - \sqrt{c}$ curve is not linear.

Λ_0 for acetic acid may be determined from λ_0 of the ions.

$$\Lambda_0 = \lambda_{0,CH_3COO^-} + \lambda_{0,H^+}$$

For a weak electrolyte the degree of dissociation is

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Consider a weak acid:

$$\underset{(1-\alpha)C}{HA} \leftrightarrow \underset{\alpha C}{H^+} + \underset{\alpha C}{A^-}$$

Concentrations:

$$K_a = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C}$$

$$K_a = \frac{(\alpha^2 C)}{(1-\alpha)}$$

For the slightly soluble salt

$$\Lambda_0 = \frac{L}{C}$$

However, since the conductance, *L*, is very small, the conductance of pure water should be subtracted. Thus

$$C = \frac{(L_{soln} - L_{H_2O})}{\Lambda_0}$$

The solubility product constant can then be calculated from the concentration of the salt.

EQUIPMENT AND CHEMICALS

A.C. conductance bridge (YSI or Beckman), conductivity cells, 0.100 *M* NaCl, 0.100 *M* HCL, 1.0 *M* CH_3COOH, saturated solution of $PbSO_4$. (Solution concentrations need not be exactly 0.1000 *M*, but should be known to three significant figures.)

DIRECTIONS

1. Read the instructions for using conductance bridges supplied by the manufacturer. Both instruments are essentially the same. You have a choice of two A.C. frequencies. Multipliers and scale dials are adjusted to give a minimum on the null meter (Beckman) or wide shadow (YSI). At that point the conductivity is equal to

$$L = (\text{dial reading, micromho}) \times (\text{cell constant}) \times (10^{-6})\,\text{mho}$$

2. Extreme care must be made in making solutions and successive dilutions. The strong electrolytes are diluted by one-half so that you have these solutions: 0.025, 0.0125, 0.00625 *M*, 0.00313 *M*. Acetic acid is diluted similarly.

3. Measure conductance of distilled water first. Then measure solution conductances, starting with most dilute solution. After each reading wash the cell with portions of the next solution.

4. Wash some solid $PbSO_4$ with successive portions of distilled water to remove any soluble impurities. Then determine the specific conductance of a saturated $PbSO_4$ solution. For $PbSO_4$, $\Lambda_0 = 149.5\ \text{ohm}^{-1}\ \text{equiv}^{-1}\ \text{cm}^2$

5. Ordinary distilled water is not satisfactory since it has too high a conductance, mostly due to dissolved CO_2. Much better water can be obtained by boiling distilled water to free CO_2 and capping a full bottle while it is hot, It's specific conductance should be $5 \times 10^{-6}\,\text{ohm}^{-1}\text{cm}^{-1}$ or less. (200,00 ohm resistance).

6. Since conductivity is temperature dependent, the experiment may be run in a constant temperature water bath.

UTILIZATION OF DATA

1. For each series of solution graph Λ vs $\sqrt{c}$. If a straight line is obtained use a least squares program on the computer to determine Λ_0 (the intercept). Compare results for strong and weak electrolytes. If the points are scattered make more measurements to define a smooth curve. Compare Λ_0 for each strong electrolyte with accepted values.

2. For CH_3COOH, calculate K_a.

3. For $PbSO_4$ calculate K_{sp}.

SAMPLE CALCULATIONS

Experiment: Exp. 9.4 Electrical Conductance

Data:

conc (mol / L)	Λ $\left(\frac{\text{mho}\cdot\text{cm}^2}{\text{mol}}\right)$
0.05	111.8
0.025	105.6
0.0125	104.0
0.00625	110.4
0.003125	121.4

Calculations:

$$\Lambda = \frac{L}{C} = \frac{\left(0.38\times10^{-3}\,\text{mho}\right)\left(1.0\text{cm}^{-1}\right)}{\left(0.00313\text{mol/dm}^3\right)\left(\frac{1\text{dm}^3}{1000\text{cm}^3}\right)} = 121.4\frac{\text{mho}\cdot\text{cm}^2}{\text{mol}} = 121.4\frac{\Omega^{-1}\cdot\text{cm}^2}{\text{mol}}$$