Experiment 446.4

CONDUCTANCE OF SOLUTIONS

Theory

Electrical conduction is a property of ionic solutions. From a macroscopic point of view, conduction of solutions is like conduction of electricity through any object. If the charge transferred is Q, conduction is described by the **current**, I.

$$I = \frac{dQ}{dt} \tag{4.1}$$

Work is done in transporting charge, either on the solution or on the external circuit. If E is the electromotive force (or **voltage**), the electrical work is:

$$w = EQ \ . \tag{4.2}$$

The rate at which work is done is the **power**, P.

$$P = \frac{dw}{dt} = EI \ , \tag{4.3}$$

the last equality assuming a time-independent electromotive force. Average-power expressions can be written down for time-dependent forces, and one frequently sees these in discussions of alternating-current circuits.

Transport Equations

A **transport equation** expresses movement of a quantity, X, from one place to another, e.g. heat or mass or electric charge. In the linear regime, the time derivative of X is proportional to some generalized force, F_X:

$$\frac{dX}{dt} \ \alpha \ F_X \tag{4.4}$$

The ratio of the derivative to the force is a transport parameter, a fundamental property of the material. For electric systems, the force is the electromotive force. The transport parameter is the **electrical conductance**, L, and the transport equation is:

$$\frac{dQ}{dt} = LE \ . \tag{4.5}$$

The unit of conductance is the **siemens**, which in older literature is called the **mho**. Sometimes it is convenient to express this property in terms of the ability to retard movement of charge carriers. The descriptive parameter for this retardation is the **electrical resistance**, $R = 1/L$. The unit of resistance is the **ohm** (= 1 siemens^{-1}). Resistance and conductance describe the same material property. The electricity transport equation [Equation (4.5)] in the linear regime is called **Ohm's Law**.

$$E = IR \tag{4.6}$$

Electrical conductance (or, similarly, resistance) of an object depends on (a) the type of material and (b) the structure of the object (e.g., wires of different sizes of the same material have different resistances). For a simple device of circular cross-section with area *A* and length *l*, the resistance and the intrinsic property, **resistivity** ($\equiv \rho$), are related by:

$$R = \rho \frac{l}{A}. \tag{4.7a}$$

More generally the structural effects are described by some factor, *k*, which depends on the structure of the measuring device:

$$R = \rho k. \tag{4.7b}$$

Resistivity is an intensive property, like molar heat capacity or color. An equivalent parameter, the **conductivity**, κ, is defined as the inverse of the resistivity.

$$\kappa = \frac{1}{\rho} = kL = \frac{k}{R} \tag{4.8}$$

Conduction in Ionic Solution

Movement of charge through solution results from migration of ions from one electrode to another under the influence of a voltage. At the electrode, charge is transferred to the external circuit. One may monitor either resistance or conductance of such a cell. The conductance of the cell is determined as the inverse of the resistance, and *vice versa*.

A mole of ions moving through the solution from one electrode to the other, each with a charge *Ze* (*e* being the fundamental charge, $1.602176462\times10^{-19}$ C, and *Z* being the number of fundamental charges per ion), corresponds to movement of a specific amount of charge between the electrodes.

$$Q = ZN_0e = ZF \tag{4.9}$$

N_0 is Avogadro's number. The parameter N_0e is a fundamental constant, the **Faraday**, *F*, the amount of charge carried by transport of one mole of electrons. This important number is 96,485.3415 C mol^{-1}.

The total current is a sum of currents carried by both positive and negative ions. If the solution contains a single salt, then the current consists of two components, the anionic contribution and the cationic contribution:

$$I = I_+ + I_- \tag{4.10}$$

Each component depends on (a) the speed and other properties of the ion, (b) the number of ions, and (c) the structure of the cell (through *k*). The part of the current, I_i, due to an ionic species depends on ion concentration (c_i) and a parameter that describes the electrical and dynamic properties of the ion – the ionic mobility (u_i):

$$I_i = \frac{1}{k} Z_i e c_i u_i E \tag{4.11}$$

By summation and comparison to equation (4.8), one finds an expression for the conductivity, κ, of the cell:

$$\kappa = kL = k\sum_i Z_i e c_i u_i . \tag{4.12}$$

The conductivity of an electrochemical cell, eq. (4.12), can be thought of as a sum of contributions by all ionic species.

$$\kappa = \sum_i \kappa_i \tag{4.13}$$

There is a trivial linear dependence of κ_i on concentration in eq. (4.12). In addition, strong interionic and solvent effects make the ionic mobilities concentration-dependent, as well. To separate these two effects, one defines the **equivalent conductivity**

$$\Lambda = \frac{\kappa}{c_e} \tag{4.14}$$

where c_e is the formal concentration in equivalents [moles of charge] per unit volume.[1] To obtain a concentration-independent parameter characteristic of ionic behavior in solution, chemists extrapolate to infinite dilution where interionic effects are negligible. This process gives a measurement of the properties of ions totally isolated by solvent. The extrapolated quantity is known as the **equivalent conductivity at infinite dilution**, Λ_0.

$$\Lambda_0 = \lim_{c \to 0} \Lambda \tag{4.15}$$

This parameter is a sum of contributions from the ions in solution

$$\Lambda_0 = \sum_i \lambda_{0i}\,, \tag{4.16}$$

where λ_{0i} is a characteristic parameter for a particular ion. Equation (4.16) is known as **Kohlrausch's Law**. Values of λ_{0i} for various ions can be found in texts and reference books, usually reported at 25°C in aqueous solution.[2]

To extrapolate to infinite dilution properly [equation (4.15)] requires knowledge of the expected dependence of equivalent conductivity on concentration. In the early part of the twentieth century, Lars Onsager developed a theory of ionic motion in solution, in which ions are treated as small particles travelling in a dielectric medium, in analogy to the theory of Debye and Hueckel for the equilibrium properties of electrochemical solutions. An important result of his theory is expressed in the simple equation[3]

$$\Lambda = \Lambda_0 - [\theta \Lambda_0 + \sigma]\sqrt{c}\,, \tag{4.17}$$

where θ and σ are collections of fundamental constants and temperature-dependent ionic and solvent properties. From this equation, the expected dependence of equivalent conductivity on concentration, at least at low concentrations, is a linear variation with the square root of concentration. Hence, the appropriate way to extrapolate to infinitely dilute solution is as the square root of concentration.

Conductivity of Weak Electrolytes

The conductivity of weak-electrolyte solutions results from the partial dissociation of a weak electrolyte. One may consider, at least approximately for finite concentrations, that the ionic solution is dilute and obeys Onsager's relation. Consider for example the dissociation of acetic acid, CH_3COOH.

$$CH_3CO_2H \leftrightarrow H^+ + CH_3CO_2^- \tag{4.18}$$

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[1] Because of the plethora of units for parameters, care must be taken in the definition of concentrations. One sees factors of 1000 come and go from equations, for example. These usually reflect a conversion between cm^3 and dm^3.

[2] For example, see J. H. Noggle, *Physical Chemistry,* 3rd Edition, Harper-Collins, New York, 1996, p. 411.

[3] L. Onsager, *Phys. Z., 28,* 277 (1927).

If, at equilibrium, a fraction α of the acetic acid molecules is dissociated, the equivalent conductivity of this 1:1 electrolyte is

$$\Lambda \quad = \quad \alpha F(u_+ + u_-)\,. \tag{4.19}$$

The ratio of this equivalent conductivity to the equivalent conductivity at infinite dilution is

$$\frac{\Lambda}{\Lambda_0} \quad = \quad \alpha\frac{u_+ + u_-}{u_+^o + u_-^0}\,. \tag{4.20}$$

The ionic mobilities at infinite dilution are indicated by a superscript ^{0}. In solutions approaching infinite dilution,

$$\lim_{c\to 0}\frac{\Lambda}{\Lambda_0} \quad = \quad \alpha \tag{4.21}$$

Usually, as a practical matter, one defines an **apparent degree of dissociation**, α', from the equivalent conductivity at finite concentration:

$$\alpha' \quad = \quad \frac{\Lambda}{\Lambda_0}, \tag{4.22}$$

from which one calculates an **apparent equilibrium constant**, K_C, for a 1:1 electrolyte.

$$K_C \quad = \quad \frac{\alpha'^2}{1-\alpha'}c \tag{4.23}$$

Extrapolation of K_C to infinite dilution (versus the square root of concentration) gives the true equilibrium constant, K_a, as the intercept. With knowledge of K_a, one can subsequently calculate activity coefficients at any finite concentration from the ratio of the apparent equilibrium constant to the true equilibrium constant.

In this experiment, you measure the conductances of a series of solutions. These data are then analyzed to obtain the equilibrium constant for the dissociation of a weak acid.

Experimental Procedure

The experiment requires care in measuring the conductivity of the solutions. The experimental method is based on the use of a commercially available conductance meter that is calibrated to read the conductivity directly. The meter has several setting for measuring solutions of different conductivity. Settings A-C give values in 10^{-6} siemens. Settings D-F give values in 10^{-3} siemens. Check the calibration of the conductivity meter using range D and the Amber Science calibration solution.[4] (Be sure to read details of how to make the measurement or you will be wasting your time and getting erroneous results.)

Conductivity Cell

Conductivity measurements are carried out with a dip cell. When not in use, place the dip cell in the tube filled with deionized water to ensure it is safely stowed. To use the dip cell, you **must** follow a regimen that ensures you are measuring a representative solution. Here's how – the **fill-stir-empty-refill** protocol:

1. Fill the test tube with solution and immerse the dip cell in the solution. Ensure there is enough solution to cover both electrodes and make certain there are no bubbles in the interior of the dip cell.

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[4] The typical calibration solution is 0.0500 N KCl. It has a conductivity of 718 x 10^{-6} S/cm at 25°C. The conductance meter can be adjusted to read directly the conductivity. If the calibration solution is of some other concentration, you must look up the conductivity of that solution.

2. Mix the solution thoroughly by lowering and raising the dip cell in and out of the solution at least ten times. (This procedure is necessary because the rough platinum surface of the electrode is very slow to rinse; rinsing surfaces of the electrodes that face each other is essential. This requires repeated mechanical exchange of solution.)
3. Pour out the solution, let the dip cell and test tube drain for a minute, and refill with fresh solution, again mixing the contents thoroughly by lowering and raising the dip cell ten times. If this is done carefully, a single fill-stir-empty-refill cycle may be sufficient to give accurate values. However, if you have enough solution, do this again. (NOTE: It is essential that the test tube and cell have a representative concentration to have a proper measurement. Any carry-over from a previous solution will affect the concentration and introduce error into the measurement. So take great care in this part of the experiment.)

Always allow time for the solutions to equilibrate in the constant-temperature bath before using them. (This takes time so wait **for several minutes** after you place the solution in the bath before taking a reading.)

Conductivity Water

Ordinary distilled water is not suitable for use in this experiment since it has a high conductance, usually because of dissolved CO_2 gas from the air.[5] In the laboratory, we remove CO_2 and other ions by passing the water through an ion-exchange resin to "deionize" it. The water for this experiment is to be taken from the deionizer mounted to the right of the distilled water tap.[6] Allow ~ 1 L of water to flow before collecting water for use in this experiment to ensure that you are getting equilibrated water.

Check the reliability of the deionized water by measuring its conductance. It should have conductance of less than 5×10^{-6} siemens. If it shows higher conductance, the water is not sufficiently deionized; consult your TA if you find there is a problem with the water.

Procedure

1. Obtain 50 mL of stock solution of HCl and CH_3COOH from the carboys in the lab. Prepare about 50 mL of KCl stock solution from the solid KCl.[7] You need to know the **concentrations of these materials**, so record these. They are listed on the carboys.
2. From each stock solution, prepare four or more solutions by dilution of the stock solution for each of the compounds, using volumetric flasks. First add the appropriate volume of stock solution, which is then diluted with conductivity water to volume. These should span a range from perhaps 1% up to 20% of the concentration of the stock solution. Be sure to do this very carefully, and record all pertinent information to allow you to determine the concentrations of the solutions you make. The more different solutions you have, the more accurately you should be able to do the extrapolations necessary in reducing data. Make each dilution separately; do not do serial dilutions!

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[5] Experiments on the rate of uptake of CO_2 by deionized water show that it can increase the conductance from 10^{-6} siemens to 1.7×10^{-6} siemens in 20 minutes, and to 2×10^{-6} siemens in 2 hours. **Keep your containers of solutions closed to avoid this source of error.**

[6] The deionizer has valves around it, so these must be open for water to flow, but at other times they should be shut.

[7] The stock solution should be of such a concentration that it is roughly comparable to the concentrations of the HCl and acetic acid solutions of highest concentration. You have to decide what this concentration should be, and the detail of this calculation should be in your notebook.

3. Use a first aliquot of a solution for rinsing the electrode: dip, stir, and shake off excess solution (gently) as described above. (This ensures a representative concentration at the electrode.) Then empty and refill the test tube with solution (or use the second aliquot in the other tube). Repeat the dip-stir-shake routine. Measure the conductivity after this sequence. Repeat the sequence, followed by a measurement. Continue the measurement until you get a stable reading.

Calculations

1. Report the conductivity, κ, of each solution as measured with the conductivity meter. Include uncertainties based on an uncertainty analysis of the multiple readings for each solution.
2. Using Eq. (4.14), calculate the equivalent conductivity, Λ, of each solution in siemens-m^2 mole^{-1}.
3. Plot Λ versus $\sqrt{c}$ according to the Onsager relation for KCl and for HCl, and obtain Λ_0 for each of these materials.[8] Report these results and compare them to literature values.
4. Combine your value of Λ_0 for KCl and HCl with a value for KAc (gotten from the literature, being sure to reference your source) to obtain Λ_0 for acetic acid.
5. For each dilution of acetic acid, calculate α' from the equivalent conductivity. Using this value, calculate the apparent equilibrium constant K_C at each concentration. Present these results in a tabular form in the RESULTS section of your report. (If your values of Λ_0 for KCl and for HCl differ significantly from the values given in the literature, do these calculations using your data **and** the literature values separately.)
6. Make a plot of $\ln K_C$ versus $(\alpha' c)^{1/2}$. Extrapolate this plot to zero concentration to obtain a value for K_a for acetic acid. Be sure to include proper estimates of uncertainty for this quantity.
7. Using your value of K_a, and the values of K_C at each concentration, calculate the mean activity coefficient, $\gamma_\pm$, as a function of concentration in the acetic acid solutions.

Discussion Questions

1. Why is the equivalent conductivity at infinite dilution, Λ_0, of HCl so large?
2. How do the slopes of your plots of Λ versus $c^{1/2}$ compare with values determined from Onsager theory? (You can find a discussion in most physical chemistry texts.)
3. Discuss sources of experimental error, other than the possible contamination of the conductivity of water with ions.
4. Estimate the errors in the concentrations of KCl from the uncertainty of the initial solution, and comment on their effects on the overall results.
5. Referring to the plot, do your data for $\ln K_C$ deviate from $\ln K_a$ in a manner that is expected and reasonable? Given your estimates of error in K_C? Explain.
6. What is the limiting factor in determining K_C?
7. Compare your result for the equilibrium constant with values from the literature. Are they comparable, within uncertainty? Explain you answer in a couple of sentences.

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[8] As with every measurement, you should determine the uncertainty in these values and report that.