Electrical Conductivity of Aqueous Solutions

<u>PRE-LAB Reading</u>: Chapter sections 3.3, 3.6, 4.6, 14.5, 15.1 in Olmstead and Williams.

<u>Purpose</u>: The predominate ions in solution are determined during acid-base reactions.

<u>Introduction:</u> The nature of aqueous solutions is investigated by measuring the conductivity of strong and weak electrolytes. Increasing amounts of either acid or base are added to several electrolyte solutions. After each addition the conductivity of the solution is measured. From the conductivity data, you will work to deduce the nature of the chemical reaction that occurred in the experiment. You will work in small groups to decide how best to work up the data. Plotting your data will allow you to follow the chemical reactions that are occurring and the ions that are present.

<u>What is conductivity?</u>
Conductivity is a measure of the concentration of ions in solution. By completing the circuit shown in Figure 1, we can measure the conductivity of the solution in the beaker. The conductivity is proportional to the current that flows between the electrodes. For current to flow, ions must be present in solution to carry the charge from one electrode to another. Increasing the number of ions in solution increases the amount of charge that is carried between electrodes and increases the conductivity. The units microSiemens/cm (µS/cm) and milliSiemens/cm (mS/cm) are most commonly used to describe the conductivity of aqueous solutions.[1]
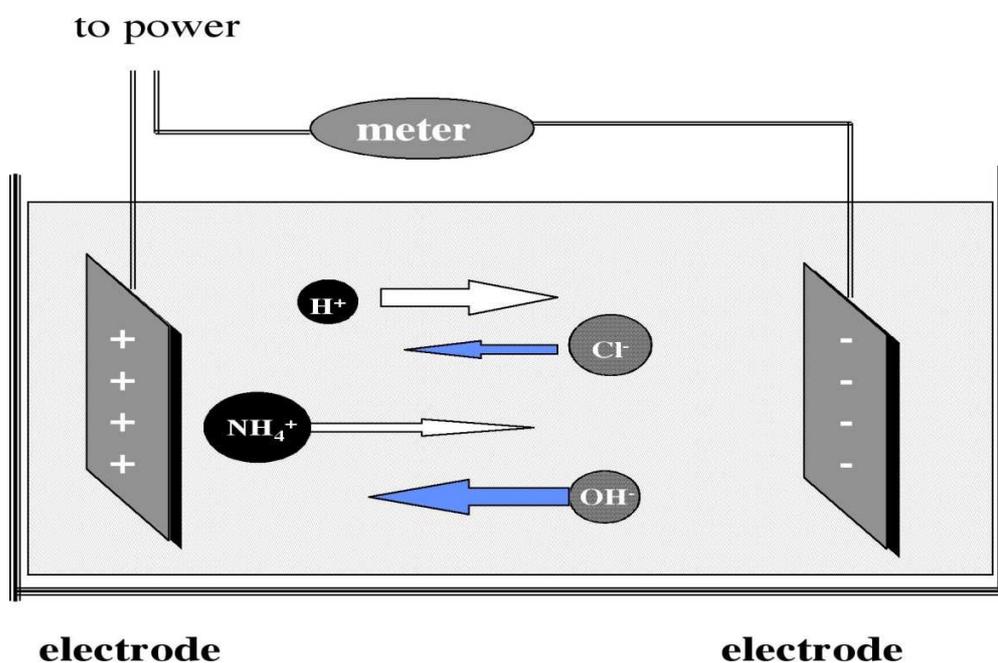

Figure 1. Schematic of a simple conductivity measurement system.

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[*] The Siemen, was formerly called mho (pronounced "mo") which was derived as a unit of conductivity by reversing the letters in "ohm," the unit of resistance.
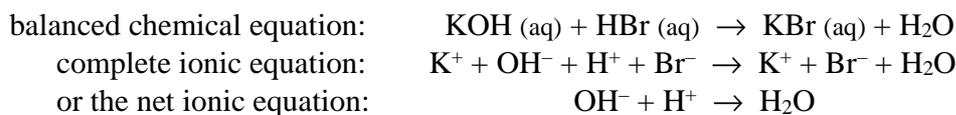
Another factor in conductivity measurements is that not all ions carry charge (conduct electricity) equally. H^+ and OH^- are unique and move through solution very rapidly and are very good charge carriers. Ions such as NH_4^+ and Cl^- move through solution at a slower rate and therefore do not conduct electricity as well. Uncharged species in solution do not carry any charge. Table 1 lists the molar conductivity of the ions in this exercise. The molar conductivity is the conductivity of a solution of the ion containing one mole of charge per liter. Note that the molar conductivity of H^+ ions is 5-7 times the conductivity of other small cations. The molar conductivity of OH^- is 3-5 times the conductivity of other small anions. To calculate the conductivity of a solution, multiply the concentration of each ion in solution by the product of the molar conductivity and charge, then add these values for all ions in solution: $\kappa_{total} = \Sigma\, c_i z_i \Lambda_i$.

Table 1. Molar Conductivity of Selected Ions (Λ_i)

	Ion	Molar Conductivity $(S\ L\ mol^{-1}cm^{-1})$
Cations:	H^+	0.34982
	Na^+	0.05011
	NH_4^+	0.0735
	K^+	0.0735
Anions:	OH^-	0.1986
	Cl^-	0.07635
	$C_2H_3O_2^-$	0.0409
	Br^-	0.0781

$C_2H_3O_2^-$ (acetate) is often written as CH_3COO^-.

How can we use conductivity to study solutions? Substances that completely dissociate into ions (strong electrolytes) produce solutions with high conductivity. Substances that partially dissociate (weak electrolytes) produce solutions with low conductivity. Substances that dissolve but do not dissociate produce solutions that have the very low conductivity of pure water. How can we use conductivity to study chemical reactions? Since conductivity is a function of both the concentration and the composition of the solution being measured, we can use conductivity to follow chemical reactions. Consider an acid-base titration of a solution of KOH with HBr:

balanced chemical equation: $KOH_{(aq)} + HBr_{(aq)} \rightarrow KBr_{(aq)} + H_2O$
complete ionic equation: $K^+ + OH^- + H^+ + Br^- \rightarrow K^+ + Br^- + H_2O$
or the net ionic equation: $OH^- + H^+ \rightarrow H_2O$

During the course of the titration, OH^- is consumed, Figure 2. The **equivalence point** is reached when the number of moles of H^+ added is equal to the number of moles of OH^- in the starting solution. After the equivalence point, the moles of H^+ increase, because they are no longer consumed by reaction with OH^-. For the spectator ions, the number of moles of K^+ remains constant and the number of moles of Br^- increases as the titrant is added. How will these ion concentrations be reflected in the conductivity of the solution?

Initially the solution conductivity is high, because OH^- has a large molar conductivity. However, as OH^- is neutralized the conductivity falls. After all the OH^- is neutralized the H^+ concentration increases and the conductivity again rises steeply. However, remember that the conductivity includes contributions from all ions in solution, not just H^+ and OH^-.
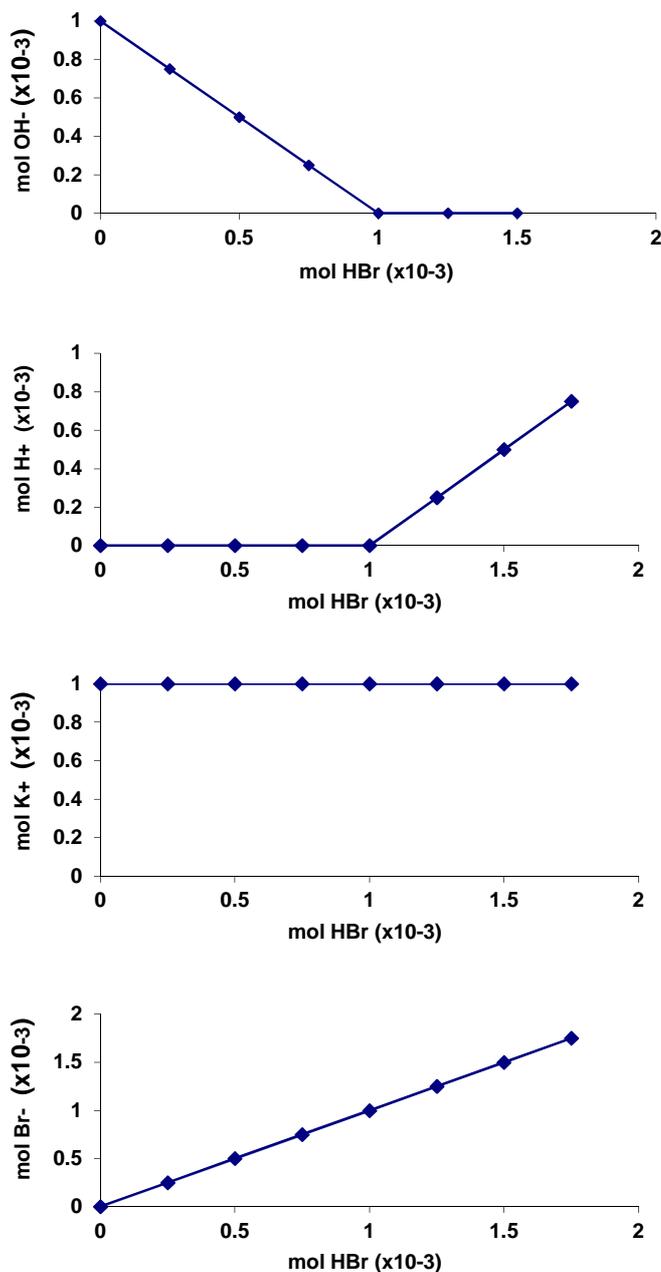
Figure 2. Titration of 150 mL of 0.00667 M KOH with 0.02 M HBr. **Note the expanded scale for Br⁻.**

Procedure:

Overview: For this experiment you will work in pairs and perform conductivity titrations on three different solutions. Every pair will perform a titration of NaOH with HCl. Half of the class will also titrate NH_3 with HCl and NH_4Cl with NaOH. The other half of the class will titrate acetic acid (CH_3COOH) with NaOH and sodium acetate ($NaCH_3COO$) with HCl, Table 2. At the end of class you will work in groups of four to analyze your data so that each group has all the titrations. The data for all five titrations is plotted using Excel in a similar fashion as Figure 2.

You will use this conductivity data to determine the ionic composition of your test solutions before, during, and after the titrations.

Measuring conductivity: You will be using a pH meter in conductivity mode (model: AR20) with a conductivity electrode to analyze your solutions. The meter will be setup for conductivity measurement, so that you will not need to press any buttons on the meter. The electrode will be standardized prior to lab time. When using the electrode, the level of aqueous solution should be in, but not over, the "circular white zone." The "white zone" allows the solution to be accurately measured (the solution must cover the "hole" in the electrode body so that sample can reach the electrode); while keeping the electronics dry. The electrode can be easily raised and lowered to keep the solution in this zone. Read the conductivity on the display when the meter reads "stable." Remember to record the unit of conductivity that the meter is displaying, as the meter will automatically change from μS/cm to mS/cm. For low conductivity solutions, 1 μS/cm = 1×10^{-3} mS/cm. When not in use, the electrode is stored in a small beaker of distilled water.

Rinse the electrode with distilled water and dry gently with a Kim Wipe before each use. This rinse cleans the electrode and minimizes contamination between solutions. Use the "waste beaker" to collect the rinse water. This rinse and all other solutions may be poured down the drain (but not the stir bar!).

You and your partner will be performing three titrations together. Table 2 outlines the starting solution and titrant for each group. Notice that there are two different concentrations of NaOH present in the lab; be careful to use the correct one for your titrations.

Table 2. Solutions to be titrated:

Group	Starting Solution	Titrant
everyone	150 mL of 0.00667 M NaOH	0.02 M HCl
group 1	150 mL of 0.00667 M $NaC_2H_3O_2$	0.02 M HCl
group 1	150 mL of 0.00667 M $HC_2H_3O_2$	0.02 M NaOH
group 2	150 mL of 0.00667 M NH_3	0.02 M HCl
group 2	150 mL of 0.00667 M NH_4Cl	0.02 M NaOH

Titration procedures for this lab: Place 150 mL of the starting solution in a clean 250-mL beaker. The graduations on your beaker are of sufficient accuracy to measure the solution volume for this experiment. Add a stir bar to the beaker and stir the solution slowly using a magnetic stirrer. Do not allow the stir bar to hit the conductivity electrode. Measure the conductivity of the starting solution.

Titrate the starting solution by adding 10.0-mL increments of the titrant to the solution. Use a graduated cylinder to measure the titrant volume. Adjust the probe height to ensure that the liquid surface is within the probe's white zone. Allow the solution to mix for a few seconds after each addition before measuring the conductivity. Record your results in your lab book. Add a total of 90 mL of titrant to the beaker. Rinse your beaker and electrode well with distilled water before the next titration. **Do not leave the probe exposed to air. The probe should always be immersed in liquid.**

Data analysis: To analyze data for all 5 titrations, you and your partner will need to share data with another student pair. If you collected Group 1 data, you'll need to get together with some other pair that collected Group 2 data, and *vice versa*. Make a suitable plot of the conductivity during each titration. Each group should make its own graph of the five titrations. To help with

your explanations, you should use plots similar to Figure 2 to help you follow the concentration of each species during each titration

What Should be in Your Laboratory Notebook?:
- Keep track of all measurements and appropriate units in your lab notebook.
- Record all observations in your lab notebook as they occur.
- The names of all students who contributed data for your group
- A balanced complete ionic equation for each titration should be given.
- Make and complete a table similar to the Experiment Supplemental Report Sheet.
- Explain the shape of **EACH** graph. State why the conductivity increases or decreases.

Laboratory Report:
Your report must include a completed **Report Form** (on the lab Web site) and the **Supplemental Report Sheet** (below).

1. For each titration, provide one clear statement identifying each of the five starting solutions as being strong or weak electrolytes.

2. Explain why the conductivity of the solutions during the titrations never reaches zero (this explanation need only be stated once).

3. The remainder of the report will consist of five short paragraphs, one for each titration. Explain the shape of EACH titration graph in a separate paragraph. Use the following parameters as a guide for your comments:
- Before the titration, what is the magnitude of the starting conductivity (small, intermediate, or large) and why?
- Chemically, why does the conductivity increase or decrease upon initial addition of titrant?
- An inflection point occurs on each graph. What is the stoichiometric relationship between reactants at the inflection point?
- Chemically, why is the slope increasing or decreasing after the inflection point?

What Should be Attached to Your Lab Report?
- All five final graphs (one per titration) or one graph of all 5 titrations.
- The Excel spreadsheet data that was used to make your graph(s) of all 5 titrations.
- The data that you acquired should be labeled with your name.
- A balanced complete ionic equation for each of the 5 titrations, including states of matter (i.e. (aq)) and ionic charges.
- The completed Supplemental Report Sheet.

Endnote: 1. The electrical current, I, increases with the cross sectional area of the electrodes, A, and decreases with the distance between the electrodes, L. The electrical current also increases with the voltage applied to the electrodes, V. To make a fair comparison between different electrodes and different meters, the conductivity, κ, is defined as:

$$\kappa = \frac{I\,L}{V\,A}$$

The conductivity only depends on the properties of the solution and not the electrodes or meter used.

CONDUCTIVITY   SUPPLEMENTAL REPORT SHEET
In each block fill in all the chemical species present.

Starting Solution, Titrant	0 mL titrant added	50 mL titrant added	80 mL titrant added
NaOH, HCl			
NaC$_2$H$_3$O$_2$, HCl			
HC$_2$H$_3$O$_2$, NaOH			
NH$_3$, HCl			
NH$_4$Cl, NaOH			