Electrochemical Cells and the Nernst Equation

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PURPOSE: 1. Measure concentration dependence of voltage output of Ag^+ concentration cell. Plot E_{obs} *vs* log $[Ag^+]$, determine the slope, and compare with the Nernst equation. 2. Determine the solubility product of AgX (X = Cl, Br, and I.) **3.** Determine the standard reduction potential of redox couples involving Zn, Cu, and Pb.

CONCEPTS: oxidation, reduction, redox reactions, electrochemical cells, half-cell, half reaction, half cell potential, salt bridge, Nernst equation, standard hydrogen electrode

BACKGROUND KNOWLEDGE:
Every oxidation-reduction reaction can be written as a combination of two half reactions. In one half-reaction a substance loses electrons (oxidation) and in the other half-reaction the electrons are gained (reduction). We can assign to each half-reaction an electrical potential that indicates the relative driving force for that half-reaction. For many oxidation-reduction reactions, it is possible to set up an electrochemical cell in which the two half reactions are placed in separate compartments called half-cells. The two half-cells are connected by a *salt bridge* which allows for the movement of ions from one half-cell to another. Each half cell has an electrode. The two electrodes are connected with a wire through a voltmeter. Electrons flow *from* the electrode of the half cell in which oxidation takes place via the wire and through a voltmeter *to* the half-cell where reduction takes place. The voltmeter will read the sum of the potentials of the half-cells.

Let $E_{\mathbf{A}}$ be the potential for a half-reaction,

$$A^{\mathbf{m+}} + m\,\mathbf{e\text{-}} \rightarrow A \qquad (\mathbf{e}\text{- stands for electron})$$

and $E_{\mathbf{B}}$ be a potential of a half-reaction,

$$B^{\mathbf{n+}} + n\,\mathbf{e\text{-}} \rightarrow B$$

Then, the potential of the (full) reaction,

$$n\,A^{\mathbf{m+}} + m\,B \rightarrow nA + m\,B^{\mathbf{n+}}$$

Would be $E_{\mathbf{obs}} = E_{\mathbf{A}} + E_B$ (we don't multiply E's by n or m)

The corresponding conventional notation for the electrochemical setup would be

$$A \mid A^{\mathbf{m+}} \parallel B^{\mathbf{n+}} \mid B$$

Where $A \mid A^{\mathbf{m+}}$ and $B^{\mathbf{n+}} \mid B$ are the half cells. If A and B are pure, solid metals, the half-cell potentials at ionic concentrations of A^{m+} or B^{n+} other than 1 M are given by the **Nernst** equation as shown for $A \mid A^{m+}$ and $B^{n+} \mid B$ half cells, for instance,

$$E_A = E_A^0 - (2.303RT/mF) \log (1/[A^{m+}]), \qquad \text{(eq 1)}$$

$$E_B = E_B^o - (2.303RT/nF) \log [B^{n+}] \qquad \text{(eq 2)}$$

Where E_A^0 and E_B^o are the ***standard reduction potentials*** (the potential corresponding to 1 M concentration species) of this redox pair, the log is base 10, and [ ] represent molar concentration. The value of (2.303RT/F) is 0.0592 volts at 25°C.

One can measure a potential difference between two half-cells but not the absolute potentials of individual half-cells. Observed potential difference, E_{obs}, is given by

$$E_{\mathbf{obs}} = E_{\mathbf{unknown}} - E_{\mathbf{reference}} \qquad \text{(eq 3)}$$

$E_{\mathbf{unknown}}$ is determined from a measured $E_{\mathbf{obs}}$ and a "known" $E_{\mathbf{reference}}$. $E_{\mathbf{obs}}$ is obtained by connecting two electrodes of the electrochemical cell to a voltmeter (or more appropriately, a milli-voltmeter). The later should have a sufficiently high input impedance in order not to draw excessive current from the electrochemical set-up.

A reference electrode could be any which gives a known and reproducible potential. In practice, all electrochemical potentials are quoted relative to the standard hydrogen electrode, the half cell potential of which is zero by definition. There are many choices of reference electrodes, but one seldom uses the standard hydrogen electrode. In our experiment we will use, as reference, an electrode consisting of 0.0100 M Ag^+ and Ag for parts 1 and 2, and, 0.05 M Pb^{2+}/ Pb for part 3.

$$Ag^+ + e^- \rightarrow Ag \quad ; \quad E^0 = +0.80 \text{ V} \quad (@\ 25^0C)$$

$$\begin{aligned} E\,(0.01M\ Ag^+/Ag) &= 0.80 - 0.0592 \log(1/0.01) \\ &= 0.68V \quad (@\ 25^oC) \end{aligned}$$

$$Pb^{2+} + 2e^- \rightarrow Pb \quad ; \quad E^o = -0.13 \text{ V} \quad (@25^oC)$$

$$E\,(1.00M\ Pb^{2+}/Pb) = -0.13 \text{ V} \quad (@\ 25^oC)$$

Thus, if this Ag^+/Ag electrode is used as reference electrode, E_{unk} would be E_{obs} plus 0.68 V (relative to the standard hydrogen electrode). If Pb^{2+}/Pb is the reference, then E_{unk} would be E_{obs} minus 0.13 V (relative to standard hydrogen electrode).

Electrochemical cells in which both half-cells involve the same half reaction, but at different concentrations, are called **concentration cells**. A concentration cell can be shown schematically as:

$$\underbrace{Ag \,|\, [Ag^+] = m_1}_{\text{half cell 1}} \,\|\, \underbrace{[Ag^+] = m_2 \,|\, Ag}_{\text{half cell 2}}$$

and an example, from part 1 below, might be

$$Ag(s) \,|\, Ag\,NO_3\ (1.00 \times 10^{-5}\ M) \,\|\, AgNO_3\ (1.00 \times 10^{-2}\ M) \,|\, Ag\ (s)$$

Figure 1, shows the set up of the cell. The cell voltage of this cell will depend on the relative concentrations in both compartments and the Nernst equation for the cell would be,

$$E_{obs} = 0.0592 \log_{10} ([Ag]_1/[Ag]_2) \qquad \text{(eq 4)}$$

Note that Eq. 4 is derived by combining Nernst equations of the two half cells, similar to eq.1 and eq.2. Subscripts1 and 2 refers to half cells 1 and 2 respectively. For this cell n is 1 and the E^o's of the half reactions cancel because they are the same but of opposite sign.

Electrochemistry is a powerful tool for, among other things, observing equilibrium processes and measuring very low ionic concentrations. One can usually come up with a design of an electrochemical cell for whatever processes and chemical systems one is interested in. Studies of such cells, for example, were and are central to our understanding of the complex chains of electron transfer reactions that provide the energy to all living organism (Oxidative metabolism in all cells, photosynthesis in plants). You will see some examples of such connections between processes/systems and electrochemical cells in this experiment.

CAUTION: a) Ag FORMS UGLY BROWN SPOTS ON CONTACT WITH SKIN.
b) DISCARD ALL Pb, Cu, Zn, and Ag WASTES IN DESIGNATED CONTAINERS.

PART 1:

In this part we will measure E_{obs} of a series of Ag^+ concentration cells. The cells will be made from a Ag-wire inserted in a series of $AgNO_3$ solutions of different concentrations on one side and another (fixed) Ag-wire placed in a 0.0100 M $AgNO_3$ solution as a reference side. The two parts will be connected by a salt bridge made up of a strip of filter paper impregnated with ammonium nitrate solution. As noted above, this constitutes a concentration cell.

According to the **Nernst** equation a plot of E_{obs} against the log of $[Ag^+]$ is expected to be a straight line with a slope equal to - 2.303RT/nF, which is 0.0592/n at 25°C. We will determine the slope of such a plot using a least square fit and compare it with the theoretical value.

Experimental:

Silver Nitrate Solutions:

You will be provided with 1.0×10^{-1}, 1.0×10^{-2}, 1.0×10^{-3}, 1.0×10^{-4}, and 1.0×10^{-5} M $AgNO_3$ solutions in the lab.

Set-up and Calibration of pH/voltmeter:

Connect two clean dry silver metal electrodes using marked alligator clips to "**INPUT**" and "**REF**" jacks on the back of a pH-meter (for some of the meters these go to the center pin and ground connectors, respectively, of a BNC connector; for the others these are the red and black terminals, respectively). Set the pH-meter for voltage measurement.

Proper connection is needed to know how to interpret the sign of the voltmeter reading. A positive milli-volt reading means that electrons are flowing from the "ref" electrode, through the wire to the voltmeter, and out to the "input" electrode, which is thus positive with respect to the "ref" electrode. Reduction is occurring at the "input" electrode. Here, electrons are being furnished to reduce Ag^+(aq)species to metallic Ag. Corresponding, oxidation is occurring at the "ref" electrode: Ag metal is losing electrons and dissolving as Ag^+ (aq).

To calibrate the pH meter, take 5 mL of 0.0100 M $AgNO_3$ in a clean 10 mL beaker. Measure and record the temperature of the solution. Place both Ag electrodes in the beaker, and read voltage. If the meter does not read 0 mV, adjust **STANDARDIZE** knob until it reads zero.

Measurement of E_{obs}:

Set up first electrochemical cell as shown in the figure below.

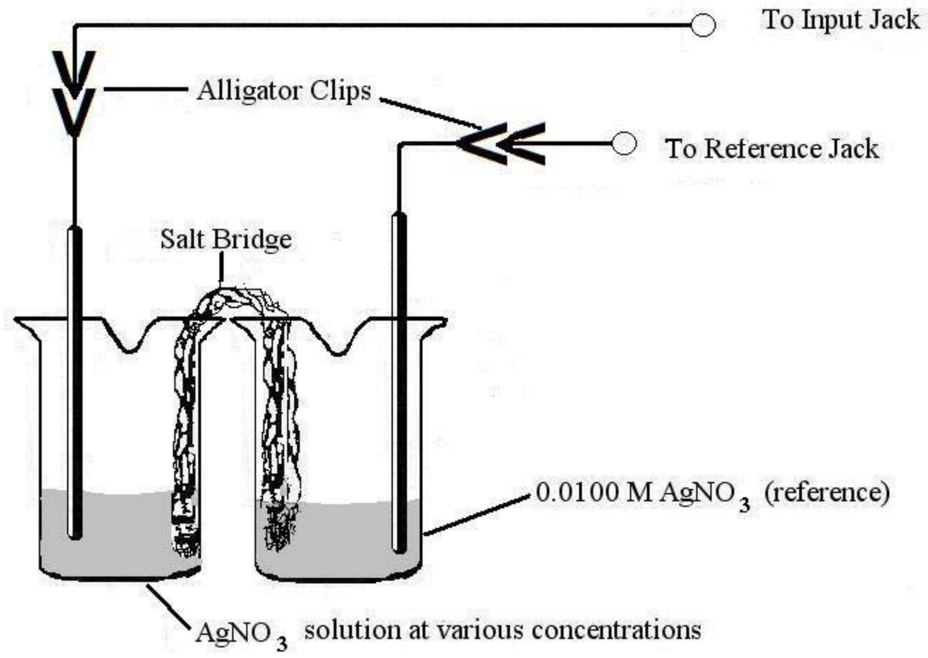

Fig 1

Barely dampen a filter paper strip with NH_4NO_3 solution. Dip one end of the filter paper strip (salt bridge) in 0.0100 M $AgNO_3$ solution in a 10-mL beaker and the other end in 10^{-5} M $AgNO_3$ solution in another 10-mL beaker. Make sure that the both ends of filter paper strip are plastered against the inner walls of the beakers.

Now, dip the Ag-electrodes in the solutions. Keep the silver wire of the electrode as far away from the filter paper salt bridge as possible. Record the voltage on data sheet.

Proceed to next higher concentration. The reference side remains the same. For each solution rinse the Ag-wire with distilled water and dry it with a towel. Use a new salt bridge for each solution.

Collect the data in your notebook. Plot voltage against log of molarity of the $AgNO_3$ solution. Calculate slope and comment on the slope. What are the units of the slope?

PART 2: DETERMINATION OF SOLUBILITY PRODCT OF A SILVER HALIDE.

Electrochemical cells can be used to determine the concentration of an ion in a solution by comparison with a half cell where the ion is of known concentration. If the ion is in equilibrium with an insoluble salt containing the ion, the electrochemical concentration cell can be used to measure the solubility product (**K_{sp}**) constant, of the insoluble salt. Read the CHE 132 text book to learn more about K_{sp}

In this part you will be provided with an unknown solution of potassium halide (KX; where X = Cl, Br, or I) of 0.0500 M concentration and you will mix it with a known volume of 0.0100 M $AgNO_3$ to produce solid AgX. The procedure is as follows:

To a clean dry 10-mL beaker, add 5.00 mL of 0.0100 M $AgNO_3$ solution. To a second clean, dry 10-mL beaker add 5.00 mL of 0.0100 M $AgNO_3$ solution and 5.00 mL of 0.0500 M unknown potassium halide solution. Swirl; a precipitate forms. Connect two solutions by using a newly prepared salt bridge as in part 1. Dip silver wire electrodes as in part 1 and record the initial voltage (**E_{obs}**) since it will drop slowly.

Calculations:

reaction: $Ag^{+} + X^{-} \leftrightarrow AgX\ (\text{solid})$

$$K_{sp} = [Ag^{+}]\,[X^{-}]$$

Initial Concentration of Ag+ = 0.0100 M
volume of Ag^{+} used = 5.00 mL
mmoles of Ag^{+} used = 0.0100 x 5.00 = 0.0500
initial concentration of X^{-} = 0.0500 M
volume of X^{-} used = 5.00 mL
mmoles of X^{-} used = 0.0500 x 5.00 = 0.250
Final volume in the reaction cell = 10.00 mL

mmoles of X^- remaining after = 0.250 – 0.0500 = 0.200
Molarity of X- at equilibrium, $[X^-] = 0.200/10.00 = 0.0200M$

$$K_{sp} = [Ag^+][0.0200]$$

The concentration of $[Ag^+]$, shown as m, can be calculated from measured E_{obs} by using Nernst equation (eq 4) as follows:

$$E_{obs} = 0.0592 \log_{10}[0.0100/m]$$

$$E_{obs} = 0.0592 (\log_{10} 0.0100 - \log_{10}[m])$$

$$E_{obs} = (-2)(0.0592) - 0.0592 \log_{10}[m]$$

$$\log_{10}[m] = (E_{obs} + 0.118)/-0.0592$$

$$[m] = \text{antilog}_{10}\ (E_{obs}+0.118)/-0.0592) = 10^{-(E_{obs}+0.118)/-0.0592)}$$

Finally,

$$K_{sp} = [m][0.0200]$$

PART 3: STANDARD REDOX POTENTIALS FOR VARIOUS HALF CELL

In this part you will prepare three $M(s)\,|\,M^{2+}(aq)$ half cells, where M = Zn, Pb, and Cu, and $M(NO_3)_2$ is at 0.05 M. Then you will determine the voltage for complete cell system with the permutations Zn/Cu, Zn/Pb, and Pb/Cu. With a knowledge of one half cell potential and the measured cell potentials, you will calculate other half-cell potentials. The procedure to set up Zn/Cu cell is as follows.

Clean copper and zinc metal strips with sandpaper or steel wool to remove oxide layer. Take 5 mL of $Cu(NO_3)_2$ solution in a 10 mL beaker and 5 mL of $Zn(NO_3)_2$ in another 10 mL beaker. Insert the copper and lead strip in their respective solutions. Connect two half cells by a salt bridge as explained under procedure of part 1. Connect leads from the pH-meter to copper and zinc strips using alligator clips. Read the voltage. If your measured potential is negative, reverse the wire connection. Record the highest potential observed if the reading on voltmeter drifts.

Similarly, construct Zn/Pb and Cu/Pb cells and measure their voltages. From the measured voltages, calculate the half cell potentials for the copper and zinc half Cells. In these calculations write down the exact balanced equation for each half reaction and combine with the half reaction for the $Pb^{2+}\,|\,Pb$ couple for which $E^0 = -0.13$ V. Write the reference half-reaction as an oxidation and all other half reactions as reduction.

Note that it is alright to combine the value of the standard reduction potential of Pb^{+2}/Pb with the E_{obs}, in spite of the fact that the concentration of solutions are 0.05M not 1.0M. This happens to be all right on considering Eq 1, and 2, where 2.303RT/nF are equal for all cells since n = 2 and furthermore, all solutions used are 0.05M so that the log terms of all half cell are equal: and cancel out for all full cells. The only non-vanishing terms are those of the standard reduction potential. Thus, $E_{obs} = E^o_A - E^o_B$

Notebook Grade: _____	
Safety Grade:	_____

DATA SHEET – SUSB-056
ELECTROCHEMISTRY AND THE NERNST EQUATION

NAME:________________________________ **SEC:_______**

PART 1: Concentration Cells

[Ag^+]	**E_{obs} Volts**

Temperature:_____________ ^{0}K

Slope Observed:________________ Slope calculated:____________

Part 2: Solubility products of unknown AgX (X = Cl, Br, or I)

.E_{obs} of the cell __________________ V

Ag| AgX(s) | Ag^+ (m) ‖ Ag^+(0.010 M)| Ag

Molarity (m) of (Ag^+) in the above cell __________________ V

Molarity of X^- in the cell __________________ V

K_{sp} of unknown halide (AgX) __________________ V

Part 3: Standard Reduction Potentials:

Electrochemical Cell	**E_{obs} (V)**	**E^0** of the half cells
Cu^{2+}/ Cu and Pb^{2+}/ Pb		Cu^{2+}/ Cu =
Pb^{2+}/ Pb and Zn^{2+}/ Zn		Zn^{2+}/ Zn =
Cu^{2+}/ Cu and Zn^{2+}/ Zn		Cu^{2+}/Cu =

SUSB-056 PRE-LAB ASSIGNMENT

Name:________________________________ **SEC:_________**

1) You know that Mg(s) dissolves in dilute HCl but Cu(s) does not. What would happen if you dipped the Cu(s) electrode into 0.1 M $Mg(NO_3)_2$ solution?

What would happen if you dipped the Mg(s) electrode into 0.1 M $Cu(NO_3)_2$ solution?

Show by an arrow which way the electrons would flow in the cell below:

$$\text{Mg(s)} \mid 0.1\text{M } Mg(NO_3)_2 \parallel 0.1\text{M } Cu(NO_3)_2 \mid \text{Cu(s)}$$

2) Given that the value of (2.303RT/mF) is 0.0592 at 25°C , what would be the voltage reading for the concentration cell 0.01 M Cu^{2+} /Cu and 1.0 M Cu^{2+} / Cu.

$$\text{Cu(s) “input”} \mid Cu^{+2} \text{ (1.0 M)} \parallel Cu^{+2} \text{ (0.01 M)} \mid \text{Cu(s) “ref”}$$

3) A student followed the procedure of part 3 for an unknown potassium halide and recorded the initial voltage reading as 0.xx Volt (xx is the last two digits of your S.S. #). Calculate K_{sp} of the unknown halide.