

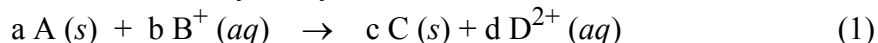
# 15

## Applications of the Nernst Equation

### Introduction

In this experiment, you will make two investigations that involve the effect of concentration on electrochemical cell potential, and therefore, involve the use of the Nernst equation.

The effect of solute ion concentration on the electrochemical cell potential is important and can be described relatively easily. For the cell reaction at 25 °C:

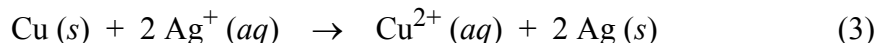


$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592 V}{n} \log \frac{[D^{2+}]^d}{[B^+]^b}. \quad (2)$$

where  $E^{\circ}_{cell}$  is a constant for a given reaction and is called the standard cell potential, and  $n$  is the number of electrons in either electrode reaction.

By equation 2 you can see that the measured cell potential,  $E_{cell}$ , will equal the standard cell potential if the molarities of  $D^{2+}$  and  $B^+$  are both unity, or if the molarities are simply equal to each other in the case when  $d$  equals  $b$ . We will carry out our experiments under such conditions that the cell potentials you observe will be very close to the standard potentials given in the tables in your chemistry text.

Considering the  $Cu, Cu^{2+} || Ag^+, Ag$  cell as a specific example, the observed cell reaction would be



For this cell, Equation 2 takes the form

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592 V}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2} \quad (4)$$

In equation 4,  $n$  is 2 because two electrons are transferred in each of the two half reactions of this cell reaction.  $E^{\circ}$  would be the cell potential when the copper and silver salt solutions are both 1 M, since then the logarithm term is equal to zero.

If we decrease the  $Cu^{2+}$  concentration, keeping the concentration of  $Ag^+$  at 1 M, the potential of the cell will go up by about 0.03 volts for every factor of ten by which we decrease  $[Cu^{2+}]$ . Ordinarily, it is not convenient to change concentrations of an ion by

several orders of magnitude. However, if we should add a complexing or precipitating species to the copper salt solution, the value of  $[\text{Cu}^{2+}]$  would drop drastically, and the voltage change would be appreciable. In this experiment, we will illustrate this effect by using  $\text{NH}_3$  to complex the  $\text{Cu}^{2+}$ . Using Equation 4, we can actually calculate  $[\text{Cu}^{2+}]$  in the solution of its complex ion.

In an analogous experiment, we will determine the solubility product of  $\text{AgCl}$ . In this case we will immerse the  $\text{Ag}$  electrode in a  $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$  cell containing a solution of known  $\text{Cl}^-$  ion concentration saturated with  $\text{AgCl}$ . From the measured cell potential, we can use Equation 4 to calculate the very small value of  $[\text{Ag}^+]$  in the chloride-containing solution. Knowing the concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  in a solution in equilibrium with  $\text{AgCl}(s)$  allows us to find  $K_{\text{sp}}$  for  $\text{AgCl}$ .

**SAFETY PRECAUTIONS:** Wear your SAFETY GOGGLES. Wash your hands and clothing immediately with copious amounts of water, if you spill any of the solutions on them. Remember that silver nitrate ( $\text{AgNO}_3$ ) produces permanent black stains on skin and clothing; these stains gradually appear after exposure to sunlight.

**WASTE DISPOSAL:** Pour all waste solutions from this experiment into the INORGANIC WASTE containers in the fume hood.

## Part I. Complex Ion Formation

### Procedure for Part I

Set up a  $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$  cell, using 10 mL of the 1 M  $\text{CuSO}_4$  solution in a porous crucible and 10 mL of 1 M  $\text{AgNO}_3$  in a beaker. Place the porous crucible containing the  $\text{CuSO}_4$  solution inside the beaker containing the  $\text{AgNO}_3$  solution. Place the copper electrode in the  $\text{CuSO}_4$  solution, and the silver electrode in the  $\text{AgNO}_3$  solution. Connect the copper electrode (anode) to the negative (black) port on the multimeter, and silver electrode (cathode) to the positive (red) port on the multimeter. Set the multimeter to read DC (direct current) voltage. Measure and record the potential of the cell. Take this potential to be  $E^\circ_{\text{cell}}$ . Note which electrode is negative.

While the potential is being measured, add 10 mL of 6 M  $\text{NH}_3$  to the  $\text{CuSO}_4$  solution, stirring carefully with your stirring rod. The complex ion,  $\text{Cu}(\text{NH}_3)_4^{2+}$  will be formed. Measure and record the potential again when it becomes steady. Note which electrode is negative.

## Calculations for Part I

Given Equation 4,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad (4)$$

calculate the residual concentration of free  $\text{Cu}^{2+}$  ion in equilibrium with  $\text{Cu}(\text{NH}_3)_4^{2+}$  in the solution in the crucible. Assume that  $[\text{Ag}^+]$  is 1 M. Now use an ICE table to estimate  $K_f$  for the complex formation reaction:  $\text{Cu}^{2+} + 4 \text{NH}_3 \leftrightarrow \text{Cu}(\text{NH}_3)_4^{2+}$ . You will need to determine initial  $[\text{NH}_3]$  from the dilution rule. How does your calculated  $K_f$  compare with the literature value?

## Part II. Solubility Product of AgCl

### Procedure for Part II

Obtain a fresh clean crucible and reassemble the Cu-Ag cell, this time using the beaker for the Cu- $\text{CuSO}_4$  electrode system. Immerse the Ag electrode in the crucible in 10 mL of 1 M KCl; add a drop of  $\text{AgNO}_3$  solution to form a little AgCl, so that an equilibrium between  $\text{Ag}^+$  and  $\text{Cl}^-$  can be established. The concentration of  $\text{Ag}^+$  will be very low, which will decrease the potential of the cell to such an extent that its polarity may reverse from that observed previously. Measure and record the cell potential.

### Calculations for Part II

Using Equation 4, calculate  $[\text{Ag}^+]$  in the cell where it is in equilibrium with 1 M  $\text{Cl}^-$  ion. Assume that  $[\text{Cu}^{2+}]$  is 1 M.

Since  $\text{Ag}^+$  and  $\text{Cl}^-$  are in equilibrium with AgCl, we can find  $K_{\text{sp}}$  for AgCl from the concentration of  $\text{Ag}^+$  and  $\text{Cl}^-$ , as they exist in the cell. Formulate the expression of  $K_{\text{sp}}$  for AgCl. Calculate  $K_{\text{sp}}$  for AgCl, using your equilibrium value of  $[\text{Ag}^+]$  and the initial  $[\text{Cl}^-]$ . Note: we set up the cell so that there would be a huge excess of  $\text{Cl}^-$ . We added a very small amount of  $\text{Ag}^+$ , so a very small amount of AgCl precipitate was formed. The amount of  $\text{Cl}^-$  used up in forming this small amount of precipitate is negligible, so  $[\text{Cl}^-]_{\text{original}} = [\text{Cl}^-]_{\text{equilibrium}}$ .

### Pre-lab Question

Calculate the  $E^{\circ}_{\text{cell}}$  for reaction (3) using the standard reduction potentials of the half reactions, found in the appendix of your textbook.