

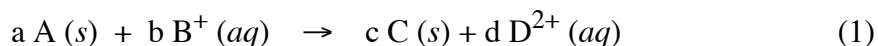
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Applications of the Nernst Equation

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 is important and can be described relatively easily. For the cell reaction at 25 °C:

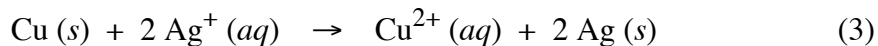


$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257 \text{ V}}{n} \ln \frac{[D^{2+}]^d}{[B^+]^b} \quad (2)$$

where E°_{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 d equals b , if the molarities are simply equal to each other. 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 $\text{Cu}, \text{Cu}^{2+} || \text{Ag}^+, \text{Ag}$ cell as a specific example, the observed cell reaction would be



For this cell, Equation 2 takes the form

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad (4)$$

In the equation n is 2 because in the cell reaction, two electrons are transferred in each of the two half reactions. E° 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 that 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 $[\text{Cu}^{2+}]$. Ordinarily, it is not convenient to change concentrations of an ion by several orders of magnitude, so in general, concentrations effects in cells are relatively small. 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 the experiment we will illustrate this effect by using NH_3 to complex the 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 AgCl . In this case we will surround the Ag electrode in a $\text{Cu}, \text{Cu}^{2+} \parallel \text{Ag}^+, \text{Ag}$ cell with a solution of known Cl^- ion concentration which is saturated with 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 Ag^+ and Cl^- in a solution in equilibrium with $\text{AgCl}(s)$ allows us to find K_{sp} for 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 (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 $\text{Cu}, \text{Cu}^{2+} \parallel \text{Ag}^+, \text{Ag}$ cell, using 10 mL of the CuSO_4 solution in a porous crucible and 10 mL of AgNO_3 in a beaker. Measure and record the potential of the cell. Note which electrode is negative. Take this potential to be E°_{cell} .

While the potential is being measured, add 10 mL of 6 M NH_3 to the 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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad (4)$$

calculate the residual concentration of free 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.

Part II. Solubility Product of AgCl

Procedure for Part II

Remove the crucible from the cell you have just studied and discard the $\text{Cu}(\text{NH}_3)_4^{2+}$. Clean the crucible by drawing a little 6 M NH_3 through it, using the adapter and suction flask. Then draw some distilled water through it. Reassemble the Cu-Ag cell, this time using the beaker for the Cu-CuSO₄ electrode system. Immerse the Ag electrode in the crucible in 1 M KCl; add a drop of AgNO₃ solution to form a little AgCl, so that an equilibrium between Ag⁺ and Cl⁻ can be established. Measure and record the potential of this cell, noting which electrode is negative. In this case conc. Ag⁺ will be very low, which will decrease the potential of the cell to such an extent that its polarity may change from that observed previously.

Calculations for Part II

Using Equation 4, calculate [Ag⁺] in the cell where it is in equilibrium with 1 M Cl⁻ ion. (E°_{cell} in Equation 4 is the *negative* of the measured value if the polarity is not the same as in the standard Cu,Cu²⁺||Ag⁺,Ag cell that you measured in the beginning of Part I.) Assume that [Cu²⁺] is 1 M.

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

$$[\text{Cl}^-]_{\text{original}} = [\text{Cl}^-]_{\text{equilibrium}}$$