Virtual Experiment 34

ELECTROCHEMISTRY

Learning Objectives:

Upon completion of this experiment, students will be able to:

1. Identify Redox Reactions
2. Write complete balanced net reaction
3. Determine the cell potential and spontaneity of the net reaction
4. Use the Nernst Equation to determine the equilibrium constant

Discussion

Redox (***red*****uction-*****ox*****idation**) reactions include all chemical reactions in which atoms have their oxidation state changed. This can be either a simple redox process, such as the oxidation of carbon to yield carbon dioxide (CO_2) or the reduction of carbon by hydrogen to yield methane (CH_4), or a complex process such as the oxidation of glucose ($C_6H_{12}O_6$) in the human body through a series of complex electron transfer processes.

Fundamentally, redox reactions are a family of reactions that are concerned with the transfer of electrons between species.

The term comes from the two concepts of reduction and oxidation. It can be explained in simple terms:

- **Oxidation** is the *loss* of electrons or an *increase* in oxidation state by a molecule, atom, or ion.
- **Reduction** is the *gain* of electrons or a *decrease* in oxidation state by a molecule, atom, or ion.

Like acid-base reactions, redox reactions are a matched set, that is, there cannot be an oxidation reaction without a reduction reaction happening simultaneously. The oxidation alone and the reduction alone are each called a half-reaction, because two half-reactions always occur together to form a whole reaction. When writing half-reactions, the gained or lost electrons are typically included to allow the half-reactions to be balanced with respect to the transfer of the same number of electrons or charge.

Oxidation Reduction reactions (Redox) involve the movement of electrons from one species to another species. In learning to balance these chemical reactions, the number of atoms and the number of electrons must be balanced in the chemical reaction. One method of balancing redox reactions involves the use of oxidation and reduction half reactions. A half reaction is the representation of a single movement of electrons to the species who has either lost electrons (oxidation) or the species who has gained electrons (reduction).

Oxidation and reduction properly refer to a change in oxidation state — the actual transfer of electrons may never occur. Thus, oxidation is better defined as an increase in oxidation state, and reduction as a decrease in oxidation state. In practice, the transfer of electrons will always cause a change in oxidation state.

The key terms involved in redox are often confusing to students. For example, an element that is oxidized loses electrons; however, that element is referred to as the reducing agent, because by being oxidized it causes reduction to occur. Likewise, an element that is reduced gains electrons and is referred to as the oxidizing agent. Acronyms or mnemonics are commonly used to help remember what is happening:

- "OIL RIG"—**O**xidation **I**s **L**oss of electrons, **R**eduction **I**s **G**ain of electrons.
- "LEO the lion says GER" — **L**oss of **E**lectrons is **O**xidation, **G**ain of **E**lectrons is **R**eduction.
- "LEORA says GEROA" — **L**oss of **E**lectrons is **O**xidation (**R**educing **A**gent) and **G**ain of **E**lectrons is **R**educed (**O**xidizing **A**gent).

Redox reactions often involve many spectator ions including H^+, OH^{1-} and H_2O. Ionic compounds can be written without the complementary ions such as Mn^{2+} without the anion Cl^{1-} ions to balance the charge or MnO_4^{1-} without a Na^+ or K^+ ion.

To balance a redox reaction:

1. balance atoms generally leaving oxygen and hydrogen unbalanced unless they are being oxidized or reduced;
2. assign oxidation states to all elements individually;
3. determine which species are changing oxidation states and write the half reaction that involves the changes, one for oxidation (loss) and one for reduction (gain);
4. balance the number of electrons needed in each half reaction;
5. balance the number of electrons between the oxidation and reduction half reactions;
6. add H and O atoms to balance the atoms of these elements using water to balance the number of oxygen atoms needed.
7. Complete the process by adding the two half reactions together and canceling any species that are represented on both sides of the total reaction including the electrons which should have equal numbers in the oxidation half reaction and the reduction half reaction.

A measure of the tendency for a reduction to occur is its ***reduction potential, E,*** measured in units of **volts**. At standard conditions, 25 °C and concentrations of 1.0 *M* for the aqueous ions, the measured voltage of the reduction half-reaction is defined as the ***standard reduction potential, E°.*** Standard reduction potentials have been measured for many half-reactions and they are listed in tables. A short list is also provided below. For the reduction half-reactions in equations (1) and (3), the standard reduction potentials are +1.09 and +1.36 respectively. The more positive (or less negative) the reduction potential, the greater is the tendency for the reduction to occur. So Cl_2 has a greater tendency to be reduced than Br_2. Furthermore, Br_2 has a greater tendency to be oxidized than Cl_2. The values of $E°$ for the oxidation half-reactions are opposite in sign to the reduction potentials. The cell potential can be determined by adding the reduction potential of the reduction half reaction to the oxidation potential of the oxidation half reaction.

$2\,Br^{-1}\,(aq) \rightarrow Br_2\,(aq) + 2e^-$ $E^o_{ox} = -\,1.09$ V (note the change in sign) Cl_2
$(g) + 2e^- \rightarrow 2\,Cl^{1-}\,(aq)$ $E^o_{red} = +\,1.36$ V
$Cl_2\,(g) + 2\,Br^{-1}\,(aq) \rightarrow Br_2\,(aq) + 2\,Cl^{1-}\,(aq)$ $E^o_{cell} = 1.36 - 1.09 = 0.27$ V (4)

A **galvanic cell**, or **voltaic cell**, named after Luigi Galvani, or Alessandro Volta, respectively, is an electrochemical cell that derives electrical energy from

spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or
individual half-cells separated by a porous membrane.

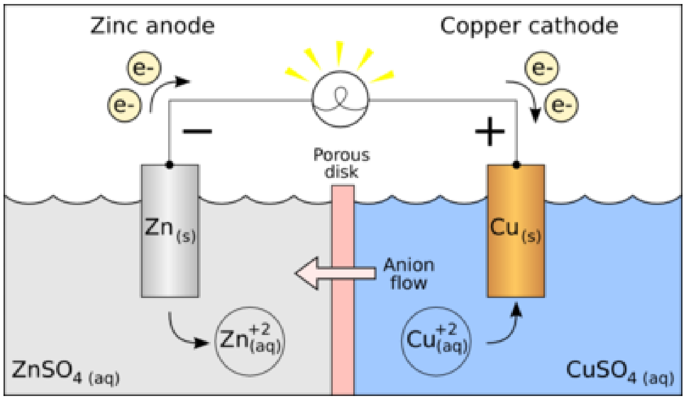


Figure 1. Galvanic cell (or battery) based on the redox reaction.

In order for the transfer of electrons in a redox reaction to produce an electric current and be useful, the electrons are made to pass through an external electrically conducting wire instead of being directly transferred between the oxidizing and reducing agents. The design of a galvanic cell (shown in Figure 1) allows this to occur. In a galvanic cell, two solutions, one containing the ions of the oxidation half-reaction and the other containing the ions of the reduction half-reaction, are placed in separate compartments called *half-cells*. For each half-cell, the metal, which is called an *electrode*, is placed in the solution and connected to an external wire. The electrode at which oxidation occurs is called the *anode* [Zn in Figure 1.] and the electrode at which reduction occurs is called the *cathode* [Cu in Figure 1.] The two half-cells are connected by a *salt-bridge* that allows a "current" of ions from one half-cell to the other to complete the circuit of electron current in the external wires. When the two electrodes are connected to an electric load (such as a light bulb or voltmeter) the circuit is completed, the oxidation-reduction reaction occurs, and electrons move from the anode (−) to the cathode (+), producing an electric current.

Different metals, such as zinc and lead, have different tendencies to oxidize; similarly their ions have different tendencies to undergo reduction. The cell potential of a galvanic cell is due to the difference in tendencies of the two metals to oxidize (lose electrons) or their ions to reduce (gain electrons). Commonly, a reduction potential, which is a tendency to gain electrons, is used to represent the relative tendency for a given metal ion to undergo reduction.

The voltage measured in the cell is the result of the two half-reactions, and the magnitude of the potential depends on the concentrations of the ions, the temperature, and pressure of gases. When all the concentrations in the zinc/lead system are 1 molar and the temperature is 25 °C, the cell voltage is 0.63 volts. It would be a monumental task to assemble a list of all possible cells and report their voltage. Instead we use the potential of the half-reactions. We cannot measure any half-cell potential directly, so we pick one half reaction, call it the standard, construct a cell, measure the cell voltage and report the potential relative to the standard. The standard that has been chosen by convention is:

$$2\,H^+ + 2\,e^- \rightleftarrows H_{2\,(g)} \qquad E\,° = 0.00\ V$$

Here the notation E ° is called the standard electrode potential and is the assigned potential of the standard hydrogen electrode when the concentration of H^+ is 1 *M* and the pressure of the hydrogen gas is one atmosphere. The measured cell voltage using the standard hydrogen electrode is therefore the potential of the other half reaction.

Tables of standard half-reaction potentials have been computed. The reactions by convention are written as reductions and hence the tables are called tables of standard reduction potentials. A brief example follows below in an excerpt from a Standard Reduction Potentials table.

The *cell potential*, E_{cell}, which is a measure of the voltage that the battery can provide, is calculated from the half-cell reduction potentials:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

At standard conditions, indicated by the superscript °, the *standard cell potential*, $E°_{\text{cell}}$, is based upon the standard reduction potentials, as shown in equation (5).

$$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} \tag{5}$$

The positive voltage for $E°_{\text{cell}}$ indicates that at standard conditions the reaction is spontaneous. Recall that $\Delta G° = -nFE°_{\text{cell}}$, so that a positive $E°_{\text{cell}}$ results in a negative $\Delta G°$. Thus the redox reaction would produce an electric current when set up as a galvanic cell.

When conditions are not standard, the *Nernst equation,* equation (6), is used to calculate the potential of a cell.

$$E_{cell} = E^0_{cell} - \left(\frac{RT}{nF}\right) lnQ \tag{6}$$

In the above equation, R is the gas constant (8.314 J / mole K), T is the temperature (Kelvin), F is Faraday's constant (96,485 coulombs/mole), n is the number or electrons transferred in the balanced oxidation/reduction reaction, and Q is the reaction quotient, or ([products]/[reactants]). If the reactions are carried out at room temperature (25 °C), the Nernst equation becomes

$$E_{cell} = E^0_{cell} - \left(\frac{0.0591}{n}\right) logQ$$

For our equation (4) example, $Cl_2\,(g) + 2\,Br^{-1}\,(aq) \rightarrow Br_2\,(aq) + 2\,Cl^{1-}\,(aq)$,

$$Q = \frac{[Cl^{1-}]^2[Cl_2]}{[Br^{1-}]^2[Br_2]}$$

Procedure

Part I - Redox Equations:

For all the reactions in this part of the experiment, observe the reaction and record your observations.

Reactions	Add first and record appearance	Then add…..
A	1 mL of 0.1 M $CuSO_4$ plus 6 drops of 6 M H_2SO_4	A small piece of zinc metal
B	1 mL of 3 M HCl	A small piece of zinc metal
C	1 mL of 3 M HCl	A small piece of copper metal
D	1 mL of 0.1 M $FeCl_3$ and 6 drops of 6 M HCl	1 mL of 0.1 M KI
E	1 mL of 0.1 M $FeCl_3$	1 mL of 0.1 M KBr
E"	1 mL of 0.1 M $FeCl_3$	1 mL of 2.0 M KBr
F	1 mL of 0.1 M KI	1 mL of 0.1 M $CuSO_4$
G	1 mL of 0.1 M KI	1 mL of 0.1 M KIO_3
H	Add 1 mL of 3 M HCl to the reaction in G	

Chemical Substance	Appearance
CO_2 (g)	Colorless non flammable gas – a splint test extinguishes
H_2 (g)	Colorless gas – split test causes explosion
O_2 (g)	Colorless gas – split test ignites
$C_2O_4^{2-}$ (aq)	Colorless in aqueous solution
Cu (s)	"copper-colored" to a blackish metal when precipitated
Cu^{2+} (aq)	Varies from blue to green in solution
MnO_4^- (aq)	Purple in aqueous solution
MnO_2 (s)	Muddy black precipitate
Mn^{2+} (aq)	Light pink to colorless in aqueous solution
I_2 (s)	Brown to purple solid, violet vapor, yellow to brown in solution
I_3^{1-}	Ion is colorless in solution
I^- (aq), Br^- (aq), Cl^- (aq)	Colorless in aqueous solution
Fe^{3+} (aq)	Yellow to Reddish -brown in solution
Fe^{2+} (aq)	colorless in aqueous solution
Cl_2	Light green gas

Part II. The Nernst Equation

In this part of the experiment, you will examine the effect of solution concentration on the cell voltage for the reaction:

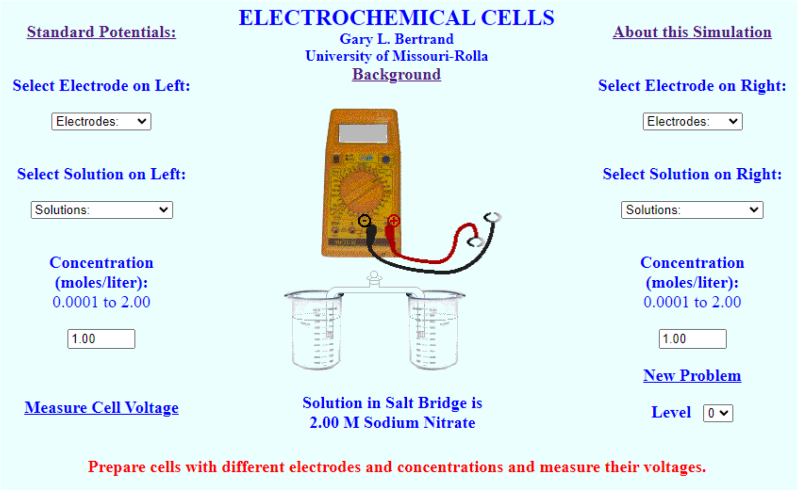
$$Cu^{2+}{}_{(aq)} + Zn_{(s)} \rightleftarrows Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

The Nernst Equation allows you to calculate $E°_{\mathbf{cell}}$ as a function of the reactant and product concentrations. For the above reaction at 25 °C, the Nernst Equation becomes:

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{2}\, log(\frac{[Zn^{2+}]}{[Cu^{2+}]})$$

Remember, solids and pure liquids are not included in the Q expression. Theoretically, $E°_{\mathbf{cell}}$ for the above reaction is 1.10 V. Thus, the value for $E_{\mathbf{cell}}$ can be calculated, knowing $[Zn^{2+}]$ and $[Cu^{2+}]$.

Using the simulation, determine the cell voltage of the Copper/Zinc cell at various concentrations: https://web.mst.edu/~gbert/Electro/Electrochem.html



ELECTROCHEMICAL CELLS
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Concentration (moles/liter): 0.0001 to 2.00 — 1.00

Concentration (moles/liter): 0.0001 to 2.00 — 1.00

Level 0

Solution in Salt Bridge is 2.00 M Sodium Nitrate

Prepare cells with different electrodes and concentrations and measure their voltages.

Choose the metal on the left, the anode (black) as Zinc with a 1.00 M solution of Zinc nitrate. Choose the metal on the right, the cathode (red) as copper and the solution concentration of 2.00 M of a copper (II) nitrate solution. Click the "Measure Cell Voltage" to determine the voltage of the system. Change the concentration of the copper(II) nitrate solution and "measure cell voltage" for each of the different concentrations.

Cell	$[Cu^{2+}]$	$[Zn^{2+}]$
1	2.0 M	1.0 M
2	1.0 M	1.0 M
3	0.10 M	1.0 M
4	0.010 M	1.0 M
5	0.0010 M	1.0 M
6	1.0 M	2.0 M

Calculations:

Determine $E_{\mathbf{cell}}$ for an unknown Cu^{2+} concentration. Using the Potential, E° measured above for the 1 M concentrations and the temperature of the room is 25 °C, *calculate* E for each of the above. Create a graph of $E_{\mathbf{cell}}$ (measured) versus log [Cu^{2+}]. Explain how this graph of $E_{\mathbf{cell}}$ versus log [Cu^{2+}], could be used to determine the unknown copper ion concentration in the solution.

Cell	[Cu^{2+}]	[Zn^{2+}]	Measured potential, E	Calculated potential, E
1	2.0 M	1.0 M		
2	1.0 M	1.0 M		E^{o}
3	0.10 M	1.0 M		
4	0.010 M	1.0 M		
5	0.0010 M	1.0 M		
6	1.0 M	2.0 M		

Table 1. Standard Reduction Potentials.

Oxidant		**Reductant**	**E° (V)**
$Li^+ + e^-$	⇄	$Li(s)$	−3.0401
$K^+ + e^-$	⇄	$K(s)$	−2.931
$Ba^{2+} + 2\ e^-$	⇄	$Ba(s)$	−2.912
$Sr^{2+} + 2\ e^-$	⇄	$Sr(s)$	−2.899
$Ca^{2+} + 2\ e^-$	⇄	$Ca(s)$	−2.868
$Na^+ + e^-$	⇄	$Na(s)$	−2.71
$Mg^{2+} + 2\ e^-$	⇄	$Mg(s)$	−2.372
$Al^{3+} + 3\ e^-$	⇄	$Al(s)$	−1.662
$2H_2O + 2\ e^-$	⇄	$H_2(g) + 2OH^-$	−0.8277
$Zn^{2+} + 2\ e^-$	⇄	$Zn(s)$	−0.7618
$Fe^{2+} + 2\ e^-$	⇄	$Fe(s)$	−0.44
$Cu_2O(s) + H_2O + 2e^-$	⇄	$2Cu(s) + 2OH^-$	−0.360
$PbSO_4(s) + 2\ e^-$	⇄	$Pb(s) + SO_4^{2-}$	−0.3588
$Sn^{2+} + 2e^-$	⇄	$Sn(s)$	−0.13
$Pb^{2+} + 2\ e^-$	⇄	$Pb(s)$	−0.13
$Fe^{3+} + 3e^-$	⇄	$Fe(s)$	−0.04
$2H^+ + 2\ e^-$	⇄	**$H_2(g)$**	**0.0000**
$Sn^{4+} + 2e^-$	⇄	Sn^{2+}	+0.15
$Cu^{2+} + e^-$	⇄	Cu^+	+0.159
$Cu^{2+} + 2e^-$	⇄	$Cu(s)$	+0.340
$O_2(g) + 2H_2O + 4\ e^-$	⇄	$4OH^-(aq)$	+0.401
$Cu^+ + e^-$	⇄	$Cu(s)$	+0.520
$I_3^- + 2e^-$	⇄	$3I^-$	+0.53
$I_2(s) + 2\ e^-$	⇄	$2I^-$	+0.54
$MnO_4^- + 2H_2O + 3\ e^-$	⇄	$MnO_2(s) + 4OH^-$	+0.59
$O_2(g) + 2H^+ + 2\ e^-$	⇄	$H_2O_2(aq)$	+0.70
$Fe^{3+} + e^-$	⇄	Fe^{2+}	+0.77
$Ag^+ + e^-$	⇄	$Ag(s)$	+0.7996
$Cu^{2+} + I^- + e^-$	⇄	$CuI\ (s)$	+0.86
$Br_2(aq) + 2e^-$	⇄	$2Br^-$	+1.0873
$2IO_3^- + 12H^+ + 10\ e^-$	⇄	$I_2(s) + 6H_2O$	+1.20
$O_2(g) + 4H^+ + 4\ e^-$	⇄	$2H_2O$	+1.229
$Cr_2O_7^{2-} + 14H^+ + 6\ e^-$	⇄	$2Cr^{3+} + 7H_2O$	+1.33
$Cl_2(g) + 2e^-$	⇄	$2Cl^-$	+1.36
$HClO(aq) + H^+ + 2\ e^-$	⇄	$Cl^-(aq) + H_2O$	+1.49
$MnO_4^- + 8H^+ + 5\ e^-$	⇄	$Mn^{2+} + 4H_2O$	+1.51
$Pb^{4+} + 2e^-$	⇄	Pb^{2+}	+1.69
$H_2O_2(aq) + 2H^+ + 2e^-$	⇄	$2H_2O$	+1.78
$Ag^{2+} + e^-$	⇄	Ag^+	+1.98
$S_2O_8^{2-} + 2\ e^-$	⇄	$2SO_4^{2-}$	+2.010
$F_2(g) + 2\ e^-$	⇄	$2F^-$	+2.87

Experiment 34

Name __________________________________

Pre Laboratory Problems

1. Give the oxidation numbers for the underlined element in each of the following molecules or ions.

a. $\underline{Mn}O_4^{1-}$ ________________________

b. $H_2\underline{O}_2$ ________________________

c. $K\underline{I}O_3$ ________________________

d. $\underline{Fe}_3O_4$ ________________________

2. Consider the following unbalanced net ionic redox equation:

$$Mg\ (s) + Al^{3+}\ (aq) \rightleftarrows Mg^{2+}\ (aq) + Al$$

Determine the Cell potential for the following reactions, using the reduction potentials given above.

a. Which atom is being oxidized? Which atom is being reduced? Which species is the reducing agent? Which is the oxidizing agent?

b. Which reaction occurs at the anode, which at the cathode?

c. What is the cell potential?

Oxidation half reaction ______________________________ E^o = ____________

Reduction half reaction ______________________________ E^o = ____________

Net Reaction ______________________________________ E^o = ____________

d. Determine the Free Energy, ΔG^o, for the reaction in 4 under standard conditions.

e. Is the above reaction spontaneous? Explain.

f. If the concentrations of the ions are not at standard 1 M concentration but we begin the reaction with 0.30 M Mg^{2+} and 0.20 M Al^{3+}, determine the cell potential using the Nernst equation.

Experiment 34

Name ______________________________

Data, Results and Discussion

Part I: Redox Equations

A. Reaction**:** **Zn with 0.1 M $CuSO_4$**

Oxidation half reaction: ______________________________ E° = __________

Reduction half reaction: ______________________________ E° = __________

Final reaction: ______________________________ E° = __________

Is the reaction expected to be spontaneous or non-spontaneous? ______________

Expected Observations	**Experimental Observations**

B. Reaction**:** **3 M HCl + Zn**

Oxidation half reaction: ______________________________ E° = __________

Reduction half reaction: ______________________________ E° = __________

Final reaction: ______________________________ E° = __________

Is the reaction expected to be spontaneous or non-spontaneous? ______________

Expected Observations	**Experimental Observations**

C. Reaction: 3 M HCl + Copper

Oxidation half reaction: ______________________________ E° = __________

Reduction half reaction: ______________________________ E° = __________

Final reaction: ______________________________ E° = __________

Is the reaction expected to be spontaneous or non-spontaneous? ______________

Expected Observations	**Experimental Observations**

D. Reaction: **0.1 M KI + 0.1 M $FeCl_3$**

Oxidation half reaction: ________________________________ E° = ______________

Reduction half reaction: ________________________________ E° = ______________

Balanced net reaction: ________________________________ E° = ______________

Is the reaction expected to be spontaneous or non-spontaneous? __________________

Expected Observations	**Experimental Observations**

E. Reaction: **0.1 M Iron (III) chloride + 0.1 M potassium Bromide**

Oxidation half reaction: ________________________________ E° = ______________

Reduction half reaction: ________________________________ E° = ______________

Balanced net reaction: ________________________________ E° = ______________

Is the reaction expected to be spontaneous or non-spontaneous? __________________

Expected Observations	**Experimental Observations**

F. Reaction**:** **0.10 M KI + 0.10 M $CuSO_4$**

Oxidation half reaction: ________________________________ E° = ______________

Reduction half reaction: ________________________________ E° = ______________

Balanced net reaction: ________________________________ E° = ______________

Is the reaction expected to be spontaneous or non-spontaneous? __________________

Expected Observations	**Experimental Observations**

1. Using the Nernst Equation, determine the Cell Potential for this reaction under nonstandard conditions.

G. Reaction: **0.10 M KI + 0.10 M KIO_3**

Oxidation half reaction: ____________________________________ E° = _______________

Reduction half reaction: ____________________________________ E° = _______________

Balanced net reaction: ____________________________________ E° = _______________

Is the reaction expected to be spontaneous or non-spontaneous? ____________________

Expected Observations	**Experimental Observations**

H. Add 1 mL of 3 M HCl to the solution. What is the experimental observation?

2. Why did this reaction not occur until after the acid was added?

3. Using the Nernst Equation, determine the Cell Potential for this reaction under nonstandard conditions.

Part II: Nernst Equation

Zn / 1.0 M Zn^{2+} solution vs.

1. Write the cell reaction for $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

2. Table of Cell Potentials for copper (II) ion and Zn.

Cell	$[Cu^{2+}]$	$[Zn^{2+}]$	Potential (V) measured	Potential (V) calculated
1	2.0 M	1.0 M		
2	1.0 M	1.0 M		
3	0.10 M	1.0 M		
4	0.010 M	1.0 M		
5	0.0010 M	1.0 M		
6	1.0 M	2.0 M		

3. Calculate the cell potential using the Nernst Equation for the 0.0010 M copper (II) solution.

4. Graph of Log concentration of copper (II) ion vs Cell potential

5. Explain how the graph above can be used to determine the copper (II) ion concentration of an unknown solution.