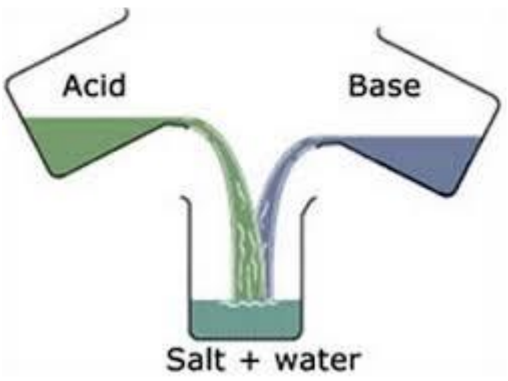
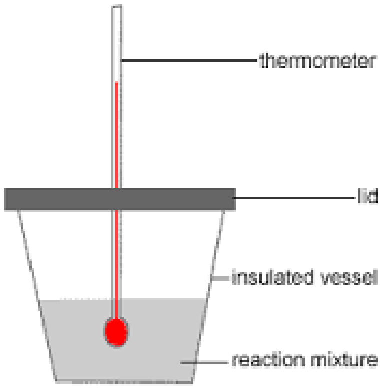
CEAC 104
GENERAL CHEMISTRY

Experiment 4
Heat of Neutralization





Purpose: To calculate enthalpy change of a reaction by using calorimeter and understand the difference between endothermic and exothermic reactions.

Prelaboratory Work

Before the experiment in the laboratory, you should be able to answer these questions.

1. Calculate the volume of solution of 1.50 M HNO_3 required in part (A) of the procedure.

2. Calculate the mass of NH_4NO_3 required in part (B) of the procedure. Show your reasoning.

3. Explain in stepwise fashion (number the steps) how you will determine the ΔH of formation of NH_4NO_3 from your data and information given in the experiment. Use actual numbers whenever possible.

4. How many joules are required to change the temperature of 80.0 g of water from 23.3°C to $38.8\ ^{\circ}$C?

Theory

In chemical reactions, energy change is observed. This energy change is usually in the form of heat and at constant pressure it is defined as **heat of reaction** or **enthalpy change (ΔH).** To form 1 mole of compound from its constituent elements, necessary amount of enthalpy change occurs and this change is defined as **enthalpy of formation**. If heat is released during the reaction, ΔH is shown with negative sign and the reaction is called **exothermic reaction.** If heat is absorbed during the reaction, ΔH is shown with positive sign and the reaction is called **endothermic reaction.**

Direct measurement of enthalpies of formation is difficult experimentally, so indirect methods involving enthalpies of reaction are used. Hess's Law states that the change in a thermodynamic property such as enthalpy depends on the initial and final states and is independent of path followed. An example for Hess's Law is given below.

$\frac{1}{2} N_2 (g) + \frac{3}{2} H_2 \rightarrow NH_3 (g) \qquad \Delta H_{formation} (NH_3(g)) = \Delta H_1$

$NH_3 (g) \rightarrow NH_3 (aq) \qquad \Delta H_{dissolving} = \Delta H_2$

Assume that ΔH_1 and ΔH_2 are known. If first and second reactions are added, net reaction becomes;

$\frac{1}{2} N_2 (g) + \frac{3}{2} H_2 \rightarrow NH_3 (g) \qquad \Delta H_{formation} (NH_3(aq)) = \Delta H_1 + \Delta H_2$

which is also formation reaction of $NH_3(aq)$.

Given that ΔH_1 = - 45.8 kJ/mol and ΔH_2 = - 35.4 kJ/mol, we can calculate the ΔH formation of $NH_3(aq)$ as -81.2 kJ/mol.

The heat is measured experimentally by allowing the reaction to take place in a thermally insulated vessel called as **calorimeter**. If the calorimeter is perfectly insulated, no heat change occurs between system and surrounding and the system is defined as adiabatic (Q=0). Consequently, at constant pressure, ΔH_{system} is also equal to zero. The formulation of enthalpy change of the system, ΔH_{system}, is shown as in Equation (1).

$\Delta H_{system} = \Delta T$ (heat capacity of calorimeter + heat capacity of contents) (1)

For endothermic reaction in adiabatic system, Equation (1) can be written as below.

$\Delta H_{system} = n\Delta H_{reaction} + C_p\Delta T$

$0 = n\Delta H_{reaction} + C_p\Delta T$

$n\Delta H_{reaction} = - C_p\Delta T$

In a similar manner, for exothermic reaction in an adiabatic system, Equation (1) can be simplified as:

$\Delta H_{system} = -n\Delta H_{reaction} + C_p\Delta T$

$0 = -n\Delta H_{reaction} + C_p\Delta T$

$n\Delta H_{reaction} = C_p\Delta T$

In this experiment, you will determine the heat of formation of various ammonium salts $NH_4X(s)$ where X is Cl, NO_3 or SO_4 by combining measurements of the heat for the neutralization reaction;

$NH_3(aq) + HX(s) \rightarrow NH_4X(aq)$ ΔH_{neut}

And the heat of the dissolution reaction;

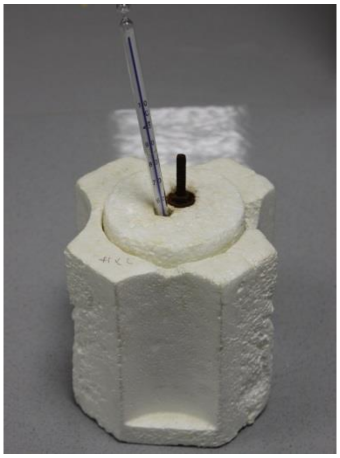
$NH_4X(s) + H_2O \rightarrow NH_4X(aq)$ ΔH_{diss}

with known heats of formation of $NH_3(aq)$ and $HX(aq)$.

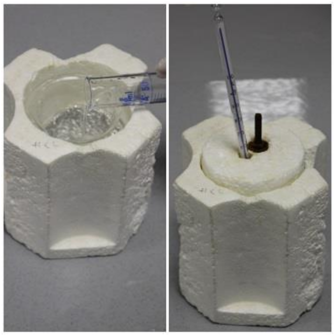
Materials

Nitric acid (HNO_3)	250 mL beaker	Graduated cylinder
Ammonia (NH_3)	Thermometers	
Ammonium nitrate (NH_4NO_3)	Styrofoam cups	

Procedure

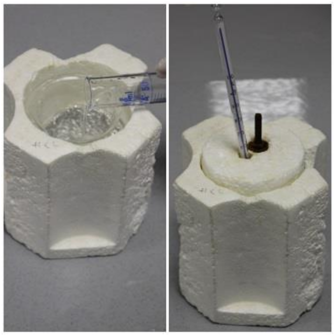
PART A: Heat of Neutralization	
1. Obtain a sytrofoam cup. In the first cup, place 50 mL of 1.5 M NH_3.	
2. Place a thermometer in the cup containing the NH_3 and record temperature at 30 seconds intervals.	

3. Add the acid solution to the NH_3 and swirl to mix. Continue taking temperature data at 30 seconds intervals while swirling the solution occasionally.



PART B: Dissolving

1. Place a volume of distilled water equal to the final volume of solution from part (A) in a Styrofoam cup and record temperature data at 30 seconds intervals.



2. Weigh out that mass of NH_4NO_3 salt into a clean, dry beaker.

3. Immediately, add the weighed amount of salt, swirl to dissolve (use stirring rod if necessary), and continue taking temperature data at 30 seconds intervals.

Calculations

1. Plot temperature versus time graph using your data and determine ΔH_{neut} for (a) and ΔH_{diss} for (b).

2. Take ΔH_f of 1.5 M NH_3 as -81.2 kJ/mol and ΔH_f of 1.5 M HCl as -165.1 kJ/mol, calculate the ΔH_f of $NH_4Cl(s)$.

3. Do the same calculations for $NH_4NO_3(s)$ using -206.0 kJ/mol for the ΔH_f of 1.5 M HNO_3.

4. Calculate ΔH_f of $(NH_4)_2SO_4$ using -884.2 kJ/mol for the ΔH_f of 1.5 M H_2SO_4. [Note that all ΔH_f are per mol (not per 1.5 mol)]

DATA SHEET

Heat of Neutralization

Student’s Name : Date:

Laboratory Section/Group No :

Assistant’s Name and Signature :

Prelaboratory Work

1. Volume of 1.5 M HNO_3 solution:

2. Mass of NH_4NO_3:

Time (s)	Temperature of NH_3 solution in °C before adding 1.5 M HNO_3	Temperature of distilled water in °C before NH_4NO_3
0		
30		
60		
90		
120		
150		
180		
Time (s)	Temperature of NH_3 + 1.5 M HNO_3 solution in °C	Temperature of NH_4NO_3 solution in °C
0		
30		
60		
90		
120		
150		
180		

Results

1. Calculate $\Delta H_{neutralization}$:

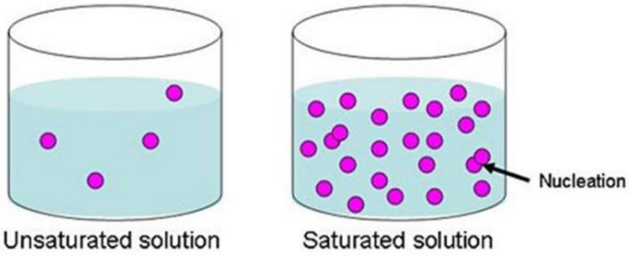
2. Calculate $\Delta H_{dissociation}$:

3. Calculate $\Delta H_{formation}$ of NH_4NO_3:

CEAC 104
GENERAL CHEMISTRY

Experiment 5

The Thermodynamics of Solubility of Potassium Chlorate



Purpose: To observe the effect of temperature on solubility product constant (K_{sp}) and to draw the graph of $\ln K_{sp}$ vs 1/T in order to calculate the standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) via this graph.

APPARATUS AND CHEMICALS:

5 pieces of test tubes	Glass rod	Thermometer
Bunsen burner	Pipet bulb	Distilled water
10-mL pipet	Ring stand	Potassium Chlorate($KClO_3$)

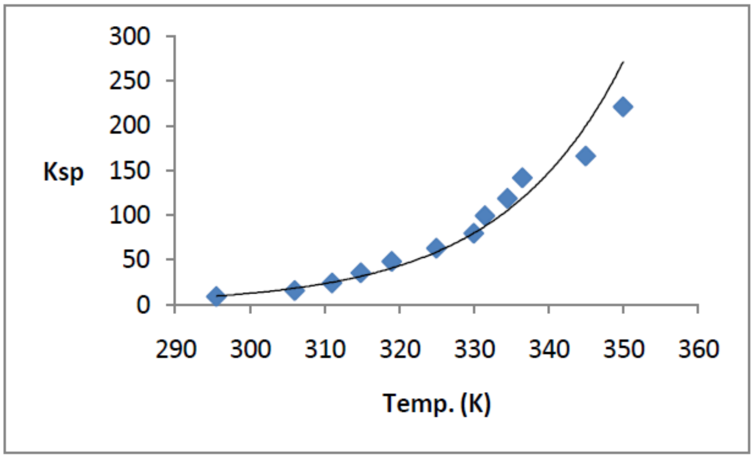
THEORY:

The solubility of $KClO_3$ will be measured at various temperatures. From the molar solubility, s: moles of solute per liter of solvent, a value of the solubility product constant, K_{sp}, can be calculated at various temperatures for the following reaction:

$KClO_{3(s)} \rightleftarrows K^+_{(aq)} + ClO_3^-{}_{(aq)}$

$K_{sp} = [K^+][ClO_3^-] = s^2$

The solubility of a solid is exponential with respect with temperature. A plot of the solubility product constant, Ksp, vs temperature (K) will give an exponential curve.



The relationship between ΔH^o and the K_{sp} comes from the free energy equations

(1) $\Delta G^o = - RT \ln K$, where R = the gas constant, 8.3143 Joule/mol K
and T = absolute temperature in degrees Kelvin.

(2) $\Delta G^o = \Delta H^o - T\Delta S^o$, where ΔH^o is the standard enthalpy change
and ΔS^o is the standard entropy change.

From (1) and (2) comes the equation

(3) $- RT \ln K = \Delta H^o - T\Delta S^o$,

Both the molal heat of solution ΔH^o and the entropy ΔS^o values can be obtained for the reaction by solving the equation relating the slope of the graph with ΔH^o and the y- intercept with ΔS^o. The plot of ln K vs 1/T in K^{-1} will give the following equation of a straight line:

Each group will be assigned a different composition of solution to measure. The data from each group will be combined and plotted.

SAFETY PRECAUTIONS

- $KClO_3$ is flammable and strong oxidizing agent. Therefore, dispose of all wastes by flushing them down the sink with plenty of running water.
- Avoid any contact between the $KClO_3$ and paper.

REVIEW QUESTIONS:

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. Suppose a reaction has negative $\Delta H°$ and negative $\Delta S°$. Will more or less product be present at equilibrium as the temperature is raised?
2. Fisherman know that on hot summer days, the largest fish will be found in deep sinks in lake bottoms, where the water is coolest. What is the reason of it, think about the temperature dependence of oxygen solubility in water?
3. Nitrogen dioxide reacts with water to produce nitric acid according to following reaction:

   $$3\ NO_2(g) + H_2O(l) \longrightarrow 2\ HNO_3\ (l) + NO\ (g)$$

   Predict the sign of $\Delta S°$ for this reaction
4. Suggest a reason why the value of ΔH_{soln} for a gas such as CO_2 , dissolving in water, is negative.

PROCEDURE:

1.In a test tube, weigh a sample of $KClO_3$ to the nearest 0.01g. The amount of sample will range from 1 to 5 grams in 1 gram increments.

2. Pipet 10 mL of distilled water into the test tubes. Stir the mixture with a glass rod.

3. Gently warm the mixture until the crystals dissolve. For high sample amounts, an evaporating dish can be used as a water bath to transfer heat more evenly. Insert thermomer into test tube and try to note the temperature at which the last crystals go into solution. Then allow the solution to cool until crystals reappear and again note the temperature.

4. Record the saturation temperature you have just determined and enter your values in your data sheet.

CALCULATIONS:

A. Ksp values.

1. Write the equation for the equilibrium between solid $KClO_3$ and its ions in solution and the expression for the K_{sp} of $KClO_3$.

2. From the weight-volume data, calculate the molar concentration of $KClO_3$ for each composition. This is the molar solubility at the saturation temperature measured.

3. Calculate the solubility product of $KClO_3$ for each trial. Use the concentrations found in step 1.

4. Tabulate the resulting values of solubility, K_{sp}, and temperature in your lab datasheet.

5. Using Excel, graph temperature (Kelvin) on the horizontal axis (x-axis) versus Ksp on the vertical axis (y-axis).

B. Molar heat of solution of $KClO_3$.

1. Using excel calculate values of 1/T, the reciprocal of the absolute temperature, and ln K_{sp} for each of the points graphed in part A.

2. Make a new graph with ln K_{sp} on the vertical axis and 1/T (K^{-1}) on the horizontal axis. Use the linear curve fit option in excel to obtain the best fit linear fit.

3. From the slope of your graph calculate ΔH^o, the heat of solution for $KClO_3$ Also determine $\Delta S°$ from the y-intercept.

Tabulate data for the written report and include the curve fit equation with the graph of lnKsp vs 1/T.

QUESTIONS:

1. When a certain solid dissolves in water, the solution becomes cold. Is ΔH_{soln} for this solute positive or negative? Is the solubility of this substance likely to increase or decrease with increasing temperature?
2. What is the value of equilibrium constant for a reaction for which $\Delta G° = 0$? What will happen to the composition of the system if we begin the reaction with the products?
3. The solubility of ZnS at 25°C is 3.5×10^{-12} M. What is the K_{sp} for ZnS? What is $\Delta G°$ at 25°C?

DATA SHEET

The Thermodynamics of Solubility of Potassium Chlorate

Student's Name : Date:
Laboratory Section/Group No :
Assistant's Name and Signature :

A. K_{sp} Values

1. Write the reaction equation and the solubility product expression for $KClO_3$.

2.

Amount of $KClO_3$ (g)	**Molar Concentration of $KClO_3$ (mol/L)**	**Ksp**	**T (°C)**	**T (K)**

3. Draw K_{sp} vs Temperature (K) graph using Excel.

B. Molal Heat of Solution of $KClO_3$

1.

1/T (K^{-1})	**ln Ksp**

2. Draw ln Ksp vs 1/T graph using Excel and calculate ΔH° from the slope and ΔS° from y-intercept.

ΔH° =

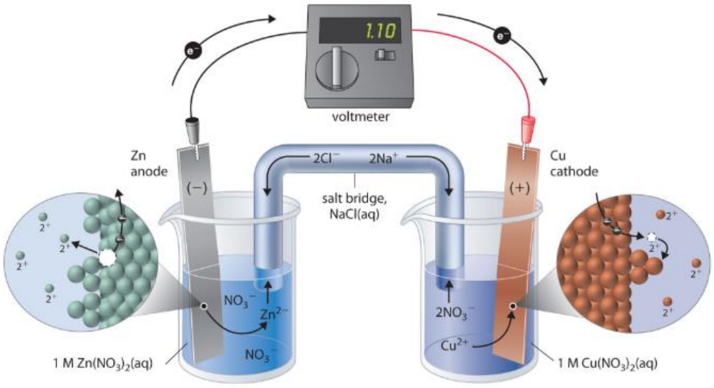
ΔS° =

CEAC 104

GENERAL CHEMISTRY

Experiment 6

Electrochemical Cells and Thermodynamics



Purpose: To examine the correlation between the reactions of metals and their ions (half cells), and to measure the voltages produced at various concentrations when two half cells are combined to form electrochemical (voltaic) cells. The voltage of the redox reactions will be calculated theoretically via Nernst equation.

Apparatus and Chemicals:

Copper strips or wire	Cotton	Ring stand, iron ring and wire
KNO_3	Agar-agar	Zinc strips or wire
$ZnSO_4$ solution	Wires	$CuSO_4$ solution
DC voltmeter or potentiometer	250-mL beaker	HCl solution
Glass U-tubes	Emery cloth	2 sets clips
Thermometer	Clamps	

THEORY:

Electrochemistry is that area of chemistry that deals with the relations between chemical changes and electrical energy. It is primarily concerned with oxidation-reduction phenomena. Chemical reactions can be used to produce electrical energy in cells that are referred to as ***voltaic***, or galvanic, cells. Electrical energy, on the other hand, can be used to bring about chemical changes in what are termed ***electrolytic*** cells. In this experiment you will investigate some of the properties of voltaic cells.

Oxidation-reduction reactions are those that involve the transfer of electrons from one substance to another. The substance that loses electrons is said to be oxidized, while the one gaining electrons is reduced. Thus if a piece of zinc metal were immersed into a solution containing copper (II) ions, zinc would be oxidized by copper (II) ions. Zinc loses electrons and is oxidized, and the copper (II) ions gain electrons anda re reduced. We can conveniently express these processes by the following two half-reactions, which add to give the overall reaction:

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Reduction: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

[1]

Net reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In principle, any spontaneous redox reaction can be used to produce electrical energy- that is, the reaction can be used as the basis of a voltaic cell. The trick is to seperate the two half reactions so that electrons will flow through an external circuit. A voltaic cell that is based upon the reaction in Equation [1] and that uses a salt bridge is shown in Figure 6.1.

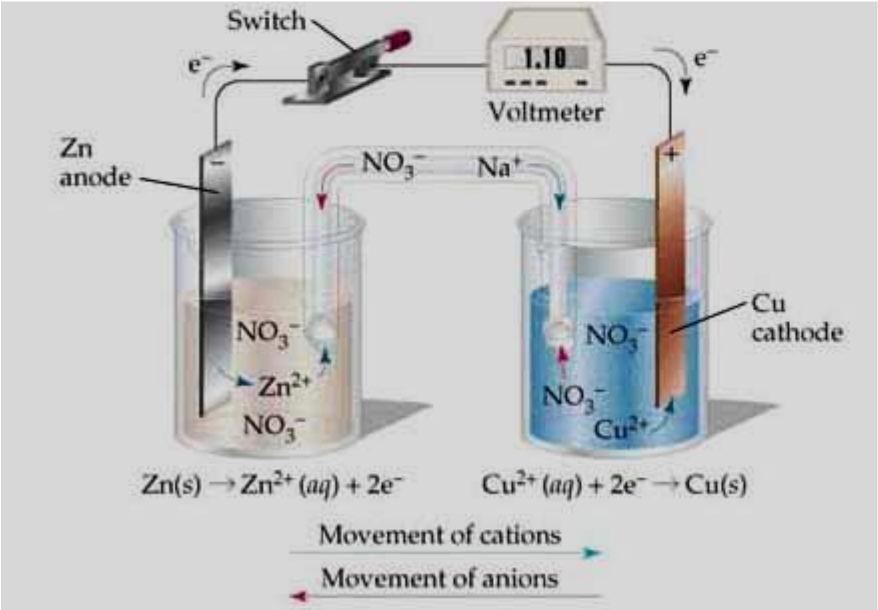


Figure 6.1 Complete and functioning voltaic cell using a salt bridge to complete the electrical circuit.

The cell voltage, or electromotive force (abbreviated emf), is indicated on the voltmeter in units of volts. The cell emf is also called the cell potential. The magnitude of teh emf is a quantitative measure of the driving force or thermodynamic tendency for the reaction to occur. In general, the emf of a voltaic cell depends upon the substances that make up the cell as well as on their concentrations. Hence, it is common practice to compare ***Standard cell potentials,*** symbolized by E^0_{cell}. These potentials correspond to cell voltages under Standard state conditions-gases at 1 atm pressure, solutions at 1 M concentration and temperature at 25^0C.

Just as the overall cell reaction may be regarded as the sum of two half-reactions the overall cell emf can be thought of as the sum of two half-cell potentials, that is, the sum of the voltage of the oxidation half-reaction (E_{ox}) and the voltage of the reduction half-reaction (E_{red}):

$E_{cell} = E_{ox} + E_{red}$

Because it is impossible to measure directly the potential of an isolated half-cell, the Standard hydrogen half-reaction has been selected as a reference and has been assigned a standar reduction potential of exactly 0.000 V:

$2H^+(1M) + 2e^- \rightarrow H_2(1atm) \qquad E^0_{red} = 0.000V$

To demonstrate the consequence of this, let us consider a voltaic cell that utilizes the following reaction:

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

The corresponding half-cell reactions are as follows:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^0_{ox} = 0.76\ V$

$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^0_{red} = 0.000\ V$

The Standard cell emf of this cell is 0.76 V (that is, E^0_{cell} = 0.76 V). Because the Standard reduction potential of H^+ is 0.000 V, it is possible to calculate the Standard oxidation potential, E^0_{ox}, of Zn:

$$E^0_{cell} = E^0_{red} + E^0_{ox}$$

$$0.76\ V = 0.000 + E^0_{ox} \qquad [2]$$

Thus the Standard oxidation potential of 0.76 V can be assigned to Zn. By measuring other Standard-cell emf values, we can establish a series of Standard potentials for other half-reactions. It is important to note that the half cell potential for any oxidation is equal in magnitude but opposite in sign to that of the reverse reduction. Hence,

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^0_{red} = -0.76\ V$

It is customary today to tabulate half-cell potentials as Standard reduction potentials and also to refer to them as Standard electrode potentials.

EXAMPLE 1:

The cell in Figure 6.1 may be represented by the following notation:

$Zn|Zn^{2+}||Cu^{2+}|Cu$

The double bar represents the salt bridge. Given that E^0_{cell} for this cell is 1.10 V and that E_{ox} is 0.76 V for zinc (see Equation [2]), find the Standard electrode potential, E^0_{red}, for the reduction of copper ($Cu^{2+} + 2e^- \rightarrow Cu$).

Solution 1:

$$E^0_{cell} = E^0_{red} + E^0_{ox}$$

$$1.10\ V = 0.76\ V + E^0_{red}$$

$$E^0_{red} = 1.10\ V - 0.76\ V \qquad E^0_{red} = 0.34\ V$$

The free-energy change, ΔG, associated with a chemical reaction is a measure of the driving force or spontaneity of the process. If the free-energy change of a process is negative, the reaction will ocur spontaneously in the direction indicated by the chemical equation.

The cell potential of a redox process is related to the free-energy change as follows:

$$\Delta G = -nFE \qquad [3]$$

In this equation, F; is Faraday's constant, the electrical charge on 1 mol of electrons:

$$1\text{F} = 96.500\ \text{C/mol e}^- = 96500\ \text{J/V mol e}^-$$

and *n* represents the number of moles of electrons transferred in the reaction. For the case when both reactants and products are in their standard states, Equation [3] takes the following form:

$$\text{w}_{\text{max}} = \Delta\text{G} = -\text{nFE}^0 \qquad [4]$$

The maximum amount of work that can be obtained from a galvanic cell is equal to the free energy change, ΔG, for the process.

The standard free-energy change of a chemical reaction is also related to the equilibrium constant for the reaction as follows:

$$\Delta\text{G}^\circ = -\text{RT In K} \qquad [5]$$

where R is the gas-law constant (8.314 J/K mol) and T is the temperature in Kelvin. Consequently, E° is also related to the equilibrium constant. From Equations [4] and [5] it follows that

$$-\text{nFE}^\circ = -\text{RTlnK}$$

$$\text{E}^\circ = \frac{\text{RT}}{\text{nF}}\ \text{InK} \qquad [6]$$

When T = 298 K, In K is converted to log K, and the appropriate values of R and 9; are substituted, Equation [6] becomes

$$E^0 = \frac{0.0591}{n} logK \qquad [7]$$

We can see from this relation that the larger K is, the larger the standard-cell potential will be.

In practice, most voltaic cells are not likely to be operating under standard-state conditions. It is possible, however, to calculate the cell emf, E, under non-standard-state conditions from a knowledge of E°, temperature, and concentrations of reactants and products:

$$\mathrm{E} = \mathrm{E}^0 - \frac{0.0591}{\mathrm{n}} \mathrm{logQ} \qquad [8]$$

Q is called the reaction quotient; it has the form of an equilibrium-constant expression, but the concentrations used to calculate Q are not necessarily equilibrium concentrations. The relationship given in Equation [8] is referred to as the Nernst equation).

Let us consider the operation of the cell shown in Figure 1 in more detail. Earlier we saw that the reaction

$$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$$

is spontaneous. Consequently, it has a positive electrochemical potential (E° = 1.10 V) and a negative free energy ($\Delta G° = - nFE°$). As this reaction occurs, Cu^{2+} will be reduced and deposited as copper metal onto the copper electrode. The electrode at which reduction occurs is called the cathode. Simultaneously, zinc metal from the zinc electrode will be oxidized and go into solution as Zn^{2+}. The electrode at which oxidation occurs is called the anode. Effectively, then, electrons will flow in the external wire from the zinc electrode through the voltmeter to the copper electrode and be given up to copper ions in solution. These copper ions will be reduced to copper metal and plate out on the copper electrode. Concurrently, zinc metal will give up electrons to become Zn^{2+} ions in solution. These Zn^{2+} ions will diffuse through the salt bridge into the copper solution and replace the Cu^{2+} ions that are being removed.

EXAMPLE 2:

Calculate the cell potential for the following cell:

$Zn \mid Zn^{2+}$ (0.6 M) $\parallel$ Cu^{2+} (0.2 M) Cu

given the following:

$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ E°=1.10V

(HINT: Recall that Q includes expressions for species in solution but not for pure solids.)

Solution 2:

$$E = E^0 - \frac{0.059}{n} log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10\ V - \frac{0.059}{2} log \frac{[0.6]}{[0.2]}$$

$$= 1.10 - 0.014$$

$$= 1.086$$

$$= 1.09\ V$$

You can see that small changes in concentrations have small effects on the cell emf.

A list of the properties of electrochemical cells and some definitions of related terms are given in Table 6.1.

TABLE 6.1 Summary of Properties of Electrochemical Cells and Some Definitions

Voltaic cells: $E > 0$, $\Delta G < 0$: reaction spontaneous, K large (greater than 1)

Electrolytic cells: $E < 0$, $\Delta G > 0$; reaction nonspontaneous, K small (less than 1)

Anode electrode at which oxidation occurs

Cathode electrode at which reduction occurs

Oxidizing agent-species accepting electrons to become reduced

Reducing agent-species donating electrons to become oxidized

Chemists have developed a shorthand notation for electrochemical cells, as seen in Example 1. The notation for the Cu-Zn cell that explicitly shows concentrations is as follows:

$Zn \mid Zn^{2+}(xM) \parallel Cu^{2+}(yM) \mid Cu$

Anode Cathode

(oxidation) (reduction)

In this notation, the anode (oxidation half-cell) is written on the left and the cathode (reduction half-cell) is written on the right.

Your objective in this experiment is to construct a set of three electrochemical cells and to measure their cell potentials. With a knowledge of two half-cell potentials and the cell potentials obtained from your measurements, you will calculate the other half-cell potentials and the equilibrium constants for the reactions. By measuring the cell potential as a function of temperature, you may also determine the thermodynamic constants, ΔG, ΔH, and ΔS, for the reactions. This can be done with the aid of Equation [9]:

$$\Delta G = \Delta H - T\Delta S \qquad [9]$$

ΔG may be obtained directly from measurements of the cell potential using the relationship

$$\Delta G = -nFE$$

A plot of ΔG versus temperature in degrees Kelvin will give -ΔS as the slope and AH as the intercept. A more accurate measure of ΔH can be obtained, however, by substituting ΔG and ΔS back into Equation [9] and calculating ΔH.

REVIEW QUESTIONS:

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1.Define the following: faraday, salt bridge, anode, cathode, voltaic cell, electrolytic cell.

2.Write a chemical equation for the reaction that occurs in the following cell:

$Ag \mid Ag^{+} \parallel Cu^{2+} \mid Cu$.

3. Given the following E°'s, calculate the standard-cell potential for the cell in question 2.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ E° = +0.34 V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ E° = +0.80 V

4. Calculate the voltage of the following cell:

$$Zn \mid Zn^{2+} (0.10\ M) \parallel Cu^{2+} (0.40\ M) \mid Cu$$

5. Calculate the cell potential, the equilibrium constant, and the free energy for the following cell:

$$Ba(s) + Mn^{2+}(aq)(1\ M) \rightarrow Ba^{2+}(aq)(1\ M) + Mn(s)$$

given the following E° values:

$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$ E° = -2.90 V

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ E° = -1.18 V

6. Would you normally expect ΔH^0 to be positive or negative for a voltaic cell? Justify your answer.

7. Predict whether the following reactions are spontaneous or not.

$Pd^{2+} + H_2 \rightarrow Pd + 2H^+$ $Pd^{2+} + 2e^- \rightarrow Pd$ E° = 0.987 V

$Sn^{4+} + H_2 \rightarrow Sn^{2+} + 2H^+$ $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ E° = 0.154 V

$Ni^{2+} + H_2 \rightarrow Ni + 2H^+$ $Ni^{2+} + 2e^- \rightarrow Ni$ E° =-0.250 V

$Cd^{2+} + H_2 \rightarrow Cd + 2H^+$ $Cd^{2+} + 2e^- \rightarrow Cd$ E° = -0.403 V

From your answers decide which of the above metals could be reduced by hydrogen.

8. Identify the oxidizing agents and reducing agents in the reactions in question 7.

PROCEDURE:

Construct the apparatus shown in the Figure 6.1 with great care when installing the U-tube salt bridge.

A. Cell Voltage

1. Pour about 150 mL of 0.5 M $CuSO_4$ into a beaker. Bend a sand papered Cu strip and hang over the side of the beaker so that it is partly immersed in the solution.
2. Clean a Zn strip by briefly immersing it in about 75 mL diluted HC1 in a beaker. Do not let the strip remain for very long in the, HCl solution. Otherwise, it will react liberating H_2. (HCl cleans Zn by dissolving the surface layer exposing the fresh metal.) **Immediately rinse the Zn strip thoroughly** in distilled water.
3. Bend the Zn strip and hang it over the side of the beaker containing 150 mL of 0.5 M $ZnSO_4$.
4. Use the crocodile clips to connect the terminals of the multimeter to the metal electrodes.
5. Construct the salt bridge as described above and immediately read the initial cell voltage. Be certain that the clips make good contact with the metal strips. Record this voltage and the temperature of the cells on your data sheet. If your measured potential is negative, reverse the wire connection.

Record the voltage and temperature of each cell on your data sheet.

DO NOT MOVE any part of the cell, because the voltage will fluctuate if you do.

B. Concentration Effects on Cell Voltage

In order to observe the concentration effects on cell voltage, vary the concentration of the salt solution in one of the compartments by adding successive amounts of salt or by dilution of solutions. For example, double the concentration of $CuSO_4$ solution in the corresponding compartment or dilute $ZnSO_4$ solution by some factor. So the experiments that will reveal the effects varying solution concentrations will be designed.

The following points should be considered for the design of the experiment:

1. The effect may be investigated for only the cathode compartment solution instead of both solutions.
2. Vary the concentration of reactants from 0.5 M to 0.25 M and 0.05 M to determine the effects of concentration changes. Before coming to the laboratory, make the necessary calculations for the design of the experiment in order to observe significant changes in the cell potential.
3. Try to determine if the cell voltage varies in some regular way with concentration. Is variation linear or exponential or whatever?

CALCULATIONS:

1. For each cell write the anode half reaction and the cathode half reaction.
2. For each cell measure the initial cell potential. Calculate the cell potential using the Nernst equation and compare it with the measured value. What is the percent error in your measurement?
3. Calculate the maximum work in Joule for the galvanic cell you constructed.

QUESTIONS:

1. Write the chemical equations that occur in the following cells;

$Pb \mid Pb(NO_3)_2 \parallel AgNO_3 \mid Ag$

$Zn \mid ZnCI_2 \parallel Pb(NO_3)_2 \mid Pb$

$Pb \mid Pb(NO_3)_2 \parallel NiCl_2 \mid Ni$

2. Which of the following reactions should have the larger ernf under standard conditions? Why?

$CuSO_4(aq) + Pb(s) \rightarrow PbSO_4(s) + Cu(s)$

$Cu(NO_3)_2(aq) + Pb(s) \rightarrow Pb(NO_3)_2(aq) + Cu(s)$.

3. Calculate ΔG for the reaction in Example 2.
4. Voltages listed in textbooks and handbooks are given as *standard-cell potentials*

(voltages). What does a standard cell mean? Were the cells constructed in this experiment standard cell? Why or why not?

5. As a standard voltaic cell runs, it "discharges" and the cell potential decreases with time. Explain.
6. Using standard potentials given in the appendices, calculate the equilibrium constants for the following reactions:

$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$

DATASHEET

Electrochemical cells and Thermodynamics

Student's Name : Date:

Laboratory Section/Group No :

Assistant's Name and Signature :

Calculations:

Cathode half reaction:

Anode half reaction:

T (°C):

Cu^{2+} (mol/L)	Zn^{2+} (mol/L)	E_{cell} (Nernst Eqn)	E_{cell} (exp)	% error	W_{max} (J)
0.50	0.50				