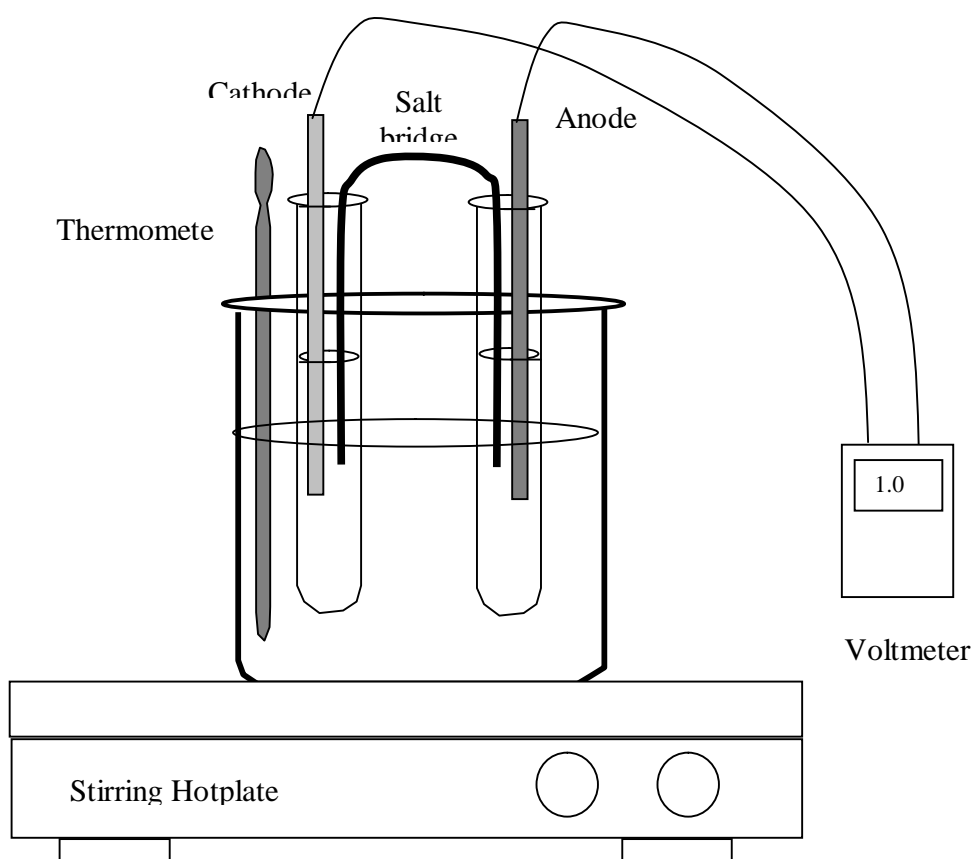


E10

***Electrochemistry and
Thermodynamics***



E10 Electrochemistry and Thermodynamics

INTRODUCTION

In this experiment you will study the electrochemistry of voltaic (galvanic) cells and in the process determine the values of the thermodynamic functions ΔG , ΔH , and ΔS . You will construct electrochemical cells by combining different metallic systems and their solutions. Measuring the potential of the prepared cells at various temperatures will render the values of the thermodynamic functions ΔG , ΔH , and ΔS corresponding to the electrochemical system studied.

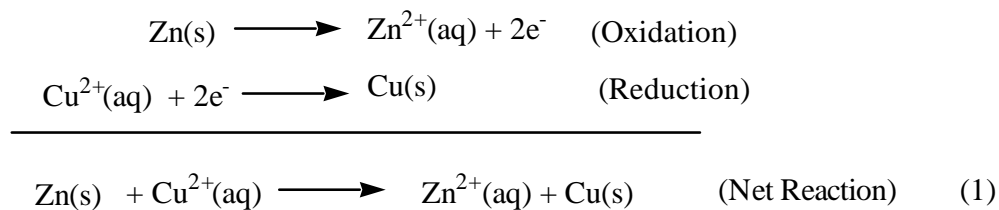
THEORETICAL BACKGROUND

Electrochemistry:

Electrochemistry is the area of chemistry that deals with the relation between chemical changes and electrical energy. Chemical reactions can be used to produce electrical energy in *voltaic (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. A *redox reaction* is the simultaneous occurrence of the two components or half reactions. *Oxidation* occurs when a chemical species loses or gives up electrons to another chemical species. *Reduction* occurs when a chemical species receives or gain electrons. The oxidation process provides the electrons necessary for reduction to occur. Therefore, the oxidized species is the *reducing agent*., and the reduced species is the *oxidizing agent*.

For example, if a piece of zinc metal is immersed into a solution containing copper (II) ions, zinc will be oxidized by the copper (II) ions. Zinc loses electrons and it is oxidized while copper (II) ions gain electrons and are reduced. We can conveniently express these two processes by the following two half-reactions, which add to give the overall redox reaction.



The function of a voltaic cell is based upon reactions similar to the one illustrated in equation (1). The system Zn/Cu is called the Daniell cell in honor of John Frederick Daniell (1790-1845) who developed the cell for the first time. A salt bridge must be used to avoid polarization of the electrodes by facilitating the circulation of ions from both cell compartments. (see figure 1).

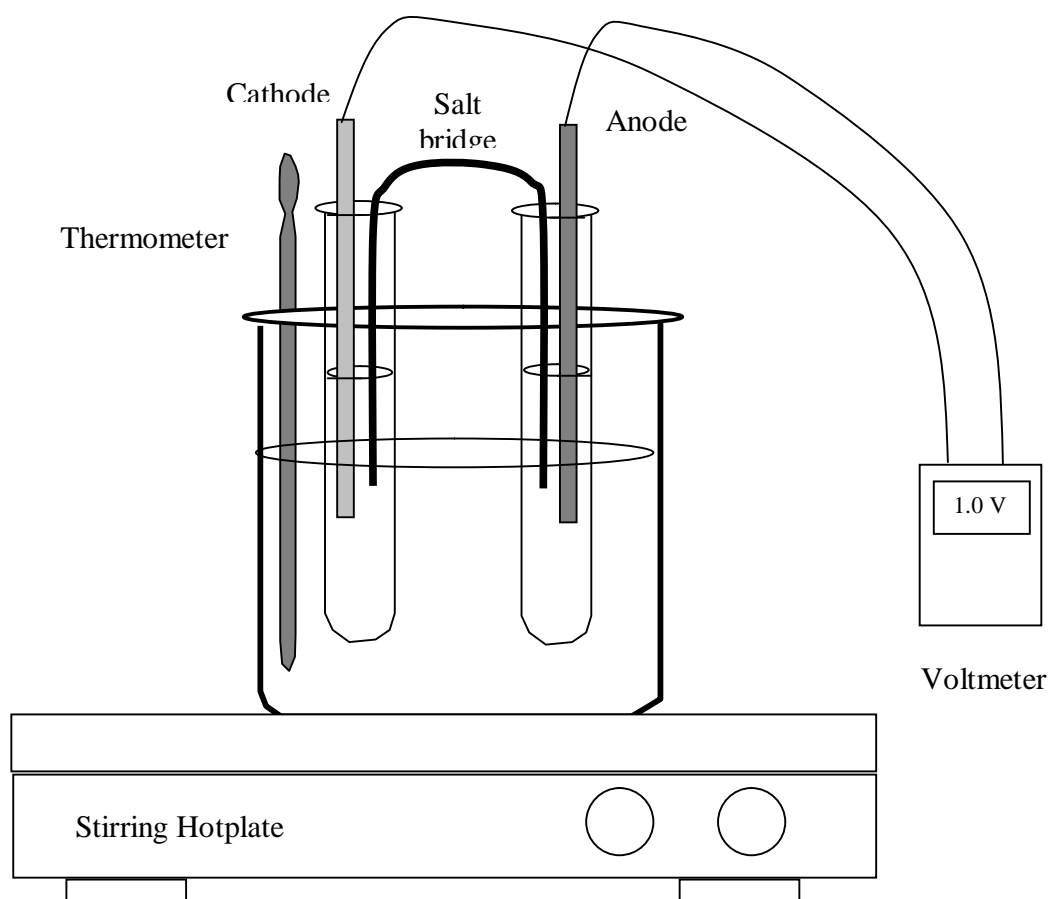


Figure 1 Electrochemical Cell

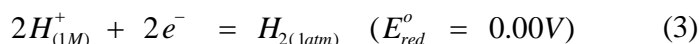
The cell voltage, or the electromotive force (abbreviated emf), is indicated on the

voltmeter in volts. The cell emf is also called the cell potential. The magnitude of the 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_{cell}^0 . These potentials correspond to cell voltages under standard state conditions—gases at 1 atm pressure, solutions at 1 M concentration, and temperature at 25°C.

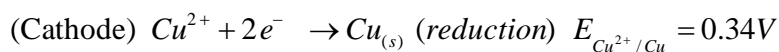
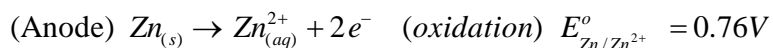
Just as the overall cell reaction may be regarded as the sum of two half-reactions the overall cell emf can be thought of as the sum of two half-cell potentials, that is, the sum of the voltage of the oxidation half-reaction ($E_{(ox)}^0$) and the voltage of the reduction half-reaction ($E_{(red)}^0$)

$$E_{cell}^0 = E_{(ox)}^0 + E_{(red)}^0 \quad (2)$$

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 standard reduction potential of exactly 0.000 V;



Let's look again at the Daniell cell described above. The standard half-cell potentials are:



Therefore,

$$\begin{aligned}
 E_{\text{cell}}^{\circ} &= E_{(\text{ox})}^{\circ} + E_{(\text{red})}^{\circ} \\
 E_{\text{cell}}^{\circ} &= 0.76 + 0.34 \text{ V} \\
 E_{\text{cell}}^{\circ} &= 1.10 \text{ V}
 \end{aligned}
 \tag{4}$$

The complete notation scheme for a galvanic cell is written with the anode on the left and a double vertical line denoting the presence of a porous plate or salt bridge. For the Daniell cell:



Each electrode is connected to the voltmeter by alligator clips and metal wiring. The voltmeter measures the voltage generated by the redox reaction. The voltage reading will be positive when the electrodes are connected properly for spontaneous reaction. A spontaneous redox reaction occurs when the species with higher reduction potential is connected as the cathode. Otherwise, the voltage reading will be negative. The meter reading will be positive when the cathode is connected to the (+) outlet and the anode is connected to the (-) outlet. Physically, a negative voltage reading means that you have connected the wrong electrode as cathode. This is equivalent to reversing equation (1). When equation (1) is reversed, the measured cell potential difference becomes

$E_{\text{cell}}^{\circ} = -1.10 \text{ V}$. The absolute value of $\Delta E_{\text{cell}}^{\circ}$ is the same in both cases, but the sign is different. The sign of $\Delta E_{\text{cell}}^{\circ}$ is positive for a spontaneous reaction and negative for non-spontaneous reaction.

The Nernst Equation:

For measurements taken under standard conditions (1 atm, 1 M solutions), $\Delta E_{\text{cell}}^{\circ}$ measures the electric potential difference between the half-cells. For measurements taken under non-standard conditions (the usual laboratory situation), the Nernst equation is used to calculate ΔE_{cell} . The Nernst equation gives us the relationship between the overall cell potential difference for a redox reaction ΔE_{cell} and the concentrations of the metal-ion solutions. The Nernst equation is;

$$\Delta E_{cell} = \Delta E_{cell}^o - \frac{RT}{nF} \ln Q \quad (5)$$

where F is Faraday constant. R the universal gas constant, n the number of electrons transferred, and Q is the reaction quotient. When natural (ln) is converted to base ten (log) and (RT/nF) are evaluated using R=8.315 JK⁻¹mol⁻¹, T=295.15 K, and F=96,485 Cmol⁻¹ the equation becomes;

$$\Delta E_{cell} = \Delta E_{cell}^o - \frac{0.0592V}{n} \log Q \quad (6)$$

In this form, galvanic cells are used to determine the concentration of the metal ions present under conditions other than standard conditions. If we apply the Nernst equation to equation (1) we will get

$$\Delta E_{cell} = \Delta E_{cell}^o - \frac{0.0592V}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad (7)$$

Thermodynamics:

More than a century ago, scientists observed the effect of temperature on natural processes and formulated the laws of thermodynamics. Thermodynamics is the study of the flow of energy, especially in the form of heat, and its conversion from one form to another (for example, from chemical energy to heat energy). The laws of thermodynamics are a set of mathematical functions, which govern all forms of energy and their inter-conversion.

The *zeroth law* of thermodynamics is concerned with *temperature equilibrium*; it states that heat always flows from a hot to a cold body.

The *first law* of thermodynamics describes the *conservation of energy*. It states that energy cannot be created or destroyed; it can only be converted from one form to another.

The *second law* of thermodynamics is concerned with the *reversibility and direction* of natural events; it states that the entropy of the universe tends to increase. Therefore, all spontaneous events are accompanied by an increase in the *entropy* of the universe. Entropy (S) is a measure of disorder. The higher the entropy of a system, the lower the order of that system. For example, the entropy of helium sealed inside a balloon is lower than its entropy when it is released to open space. When in the balloon, the individual helium atoms are confined to the space within the balloon. When the gas is released the atoms rush out into a less ordered state.

The *Third law* defines the *zero of entropy for a system*. It states that pure substances at *absolute zero* (0 Kelvin), the temperature at which all atomic motion ceases, have entropy of zero.

When these laws are applied to chemical reactions, they relate the equilibrium condition (whether the reaction is proceeding in the forward or reverse direction) and the temperature of the reaction to the thermodynamic functions, namely change in *enthalpy* (ΔH), change in entropy (ΔS), and change in free energy (ΔG). By studying the effect of temperature on the equilibrium condition for a chemical reaction, we can calculate these thermodynamic functions.

By examining ΔH , ΔS and ΔG in a chemical system, a wealth of information may be extracted. In thermodynamics a *system* is the particular part of the universe being studied.

Enthalpy describes changes of heat in a system. If the system absorbs heat during a given process, this process is said to be *endothermic*, and the change in enthalpy (ΔH) is greater than zero ($\Delta H > 0$). On the contrary, if the system releases heat, the process is called *exothermic*, and ($\Delta H < 0$).

As mentioned above, entropy is the measure of disorder or randomness in a system. The greater the order in a system, the lower the entropy. The lower the order in a system, the higher the entropy.

The *Gibbs Free Energy* (G) is the function derived from H and S. The change in free energy (ΔG) is a composite function that gives a measure of the spontaneity of a reaction. If $\Delta G < 0$, a reaction will occur spontaneously. If $\Delta G > 0$, the reaction is not spontaneous. If $\Delta G = 0$ the system is at equilibrium. The mathematical form of ΔG is the

following:

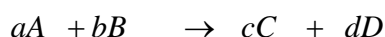
$$\Delta G = \Delta H - T\Delta S \quad (8)$$

Where T is the absolute temperature (in Kelvin). The effect of the sign of ΔH and ΔS and the effect of temperature on spontaneity of a reaction can be summarized as follows:

ΔH_{system}	ΔS_{system}	Process
-	+	Spontaneous at all temperatures
+	-	Non-spontaneous at all temperatures
+	+	Spontaneous at high temperatures
-	-	Spontaneous at low temperatures

Thermodynamics and Equilibrium:

For a general reaction or process of A and B giving products C and D :



the reaction quotient, Q, is:

$$Q = \frac{[c]^c [D]^d}{[A]^a [B]^b} \quad (9)$$

The ΔG of a process at any concentration of A, B, C, and D, is given by:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (10)$$

Where ΔG° is the free energy of the reaction under the defined standard conditions of 1 atm and 1 M concentrations of reactants. ΔG is the observed change in free energy at conditions other than standard. At equilibrium $Q = K_{\text{eq}}$. The reaction favors neither products nor reactants at equilibrium, and $\Delta G = 0$. Under these conditions equation (9) becomes:

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad (11)$$

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

$$\Delta G^{\circ} = -nFE^{\circ} \quad (12)$$

In this equation, F is Faraday's constant, the electrical charge on 1 mol of electron $1F = 96,500 \text{ C/mol e}^{-} = 96,500 \text{ J/V-mol e}^{-}$ 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 (11) takes the following form:

$$\Delta G^{\circ} = -nFE^{\circ} \quad (13)$$

DESCRIPTION OF THE EXPERIMENT

Part one

Constructing various types of cells

In this part you will construct six cells using metallic electrodes, 1.0 M solutions, voltmeter and wires as shown in Fig 1.

1.0 M solutions of the required species can be prepared from either the sulfate nitrate or chloride salts and used to fill the test tubes at a time.

You have to clamp two clean test tubes very close to each other and immerse them inside a beaker equipped with a thermometer filled with water. This assembly will be used as a constant-temperature bath. The half-cells will be connected with a salt bridge, which in this case it will be a filter paper soaked with 1.0 M KNO_3 solution. The following cells will be studied. If silver and silver nitrate are unavailable, use nickel and nickel nitrate instead.

1. $\text{Cu} | \text{Cu}_{(\text{aq})}^{2+} (1.0\text{M}) || \text{Ag}_{(\text{aq})}^{1+} (1.0\text{M}) | \text{Ag}$
2. $\text{Fe} | \text{Fe}_{(\text{aq})}^{2+} (1.0\text{M}) || \text{Cu}_{(\text{aq})}^{2+} (1.0\text{M}) | \text{Cu}$
3. $\text{Zn} | \text{Zn}_{(\text{aq})}^{2+} (1.0\text{M}) || \text{Cu}_{(\text{aq})}^{2+} (1.0\text{M}) | \text{Cu}$
4. $\text{Zn} | \text{Zn}_{(\text{aq})}^{2+} (1.0\text{M}) || \text{Fe}_{(\text{aq})}^{2+} (1.0\text{M}) | \text{Fe}$
5. $\text{Fe} | \text{Fe}_{(\text{aq})}^{2+} (1.0\text{M}) || \text{Ag}_{(\text{aq})}^{1+} (1.0\text{M}) | \text{Ag}$
6. $\text{Sn} | \text{Sn}_{(\text{aq})}^{2+} (1.0\text{M}) || \text{Cu}_{(\text{aq})}^{2+} (1.0\text{M}) | \text{Cu}$

Part Two

Measurement of emf at various temperatures

Select any one cell with constant emf to measure the potential at various temperatures. The beaker should be filled with an ice/water mixture and stirred to measure the emf at lower temperatures.

EQUIPMENT AND REAGENTS

DC voltmeter

1. Silver, copper, iron, tin and zinc strips
2. Steel wool/sand paper
3. Filter paper cut into strips dipped in KNO_3 to work as a salt bridge.
4. DC Voltmeter to measure the cell potential (electromotive force in mV)
5. 1.0 M solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, AgNO_3 , SnCl_2 , KNO_3 and 0.77 M FeSO_4 . This solution is prepared from ferrous ammonium sulfate hexahydrate, 300g/L, and finally acidifying with 3M Sulfuric Acid.
6. 50mL test tubes, clamps, wire and alligator clips

WASTE

Used solutions (liquid waste) of heavy metals should be discarded into designated liquid waste container. Dispose the used pipettes in the glass trash. The salt bridges (filter paper dipped into KNO_3 solution) can be discarded in the solid waste.

PROCEDURE

Part One

Constructing an electrochemical cell

Follow this procedure to construct each one of the electrochemical cells under study.

1. Prepare a constant temperature bath by filling a 400mL beaker with distilled water. Set it up on the stirring hot plate, and using a thermometer clamp, attach a thermometer to the assembly.
2. Fill two clean test tubes to about 3/4 volume with the 1M solutions of the pair studied. Clamp these test tubes very close to each other inside the constant

temperature bath (thermostat bath if available).

- Using sand paper, clean each metallic electrode, wash it with distilled water, and wipe it dry with Kimwipe ☐ Insert the electrodes in their respective solutions with the help of alligator clips. Assemble each half cell according to figure 1.
- Insert the salt bridge (filter paper dipped in KNO₃ solution) bridging both cell compartments. Finally connect the electrodes with alligator clips and wire to the DC voltmeter.

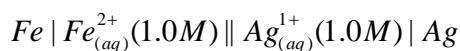
Experimental Tips:

- Dirty electrodes will not give accurate readings.
- A negative reading indicated a polarity change in the cell.
- Use a new salt bridge for each cell.

Part two

Temperature Dependence Study:

- Select one cell that shows a constant potential from the following cells, and construct the assembly as shown in Fig 1.



Start with a lower temperatures by filling the beaker with ice/water mixture and stirring it. The voltage can be recorded every five degrees starting from 10 °C (283 K) to 35 °C (308 K). For higher temperatures adjust the temperature of the thermostat bath. You need to record the exact temperature at which the measurement is taken. Allow at least five minutes to the assembly to reach thermal equilibrium. Take three readings at each temperature.

WRITE-UP: Include the answers to the following questions in your lab report.

Part one: Calculations

1. Calculate the standard electrode potentials E°_{cell} of each six cell using the values from the table for the standard reduction potential given in reference 1.
2. Calculate the standard electrode potentials E°_{cell} of each one of the cells from the observed potential E_{cell} . If the temperature and concentration of the solutions used are different from the standard conditions, you need to use the Nernst equation.
3. Compare the two values for E°_{cell} and calculate the % error.
4. Calculate ΔG° by using the experimental values of E°_{cell} with the help of the following equation:

$$\Delta G^\circ = -nFE^\circ \quad (13)$$

5. Calculate the K_{eq} for the reaction by using the equation:

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad (11)$$

Part two: Effect of temperature on the cell potential:

1. Calculate the value of ΔG° for each temperature using the equation
$$\Delta G^\circ = -nFE^\circ \quad \text{in kJ.}$$
2. Graph the values of ΔG° versus the absolute temperature.
3. From the slope of the graph $\Delta G^\circ = f(T)$, calculate the value of ΔS° for the cell in J/mol-K.
4. Calculate the enthalpy of the reaction ΔH° by using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

REFERENCES

1. Fine, L.W. Beal, H. and Stuehr, J. Chemistry for Scientists and Engineers (Preliminary paperback version of the new edition). Philadelphia: Saunders College Publishing, 1999. Chapter 14.