



430 chem Practical

اعداد

أ.د. ليلى الجهيمان- أ.د. عبد الله المعيوف- أ.د. محمد غانم

قسم الكيمياء – كلية العلوم

Table of Experiments

Week No.	Name of experiment
1.	Nernst Equation
2.	Concentration Cell- Nernst equation
3.	Difference between a galvanic cell and an electrolytic cell
4.	Thermodynamics of a galvanic cell
5.	Determination of Activity Coefficients by electrochemical method
6.	Determination of the solubility products of sparingly soluble salt
7.	Galvanic corrosion
8.	Electroplating
9.	Verification of Tafel Equation
10	Cyclic Voltammetry

Experiment # 1
Title of experiment: Nernst Equation
<p>Aim:</p> <ol style="list-style-type: none"> 1- To verify Nernst Equation. 2- To calculate the concentration of an unknown $[Cu^{2+}]$ by constructing a Galvanic Cell
<p>Introduction:</p> <p>Chemical reactions involving the transfer of electrons from one reactant to another are called oxidation-reduction reactions or redox reactions. In a redox reaction, two half-reactions occur; one reactant gives up electrons (undergoes oxidation) and another reactant gains electrons (undergoes reduction). When immersed in water, a piece of zinc going into a solution as zinc ions, with each Zn atom giving up 2 electrons. This is an example of an oxidation half-reaction.</p> $Zn(s) \rightarrow Zn^{2+}(aq) + 2e \quad (1)$ <p>Another example of reduction is the formation of solid copper from copper ions in solution.</p> $Cu^{2+}(aq) + 2e \rightarrow Cu(s) \quad (2)$ <p>The redox reaction results when an oxidation and a reduction half-reaction are combined to complete the transfer of electrons as in the following example:</p> $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad (3)$ <p>A measure of the tendency for a reduction to occur is its reduction potential, E, measured in units of volts. Standard reduction potentials have been measured for many half-reactions and they are listed in tables.</p> <p>A galvanic cell or voltaic cell is a device in which a redox reaction, such as the one in equation (3), occurs spontaneously and produces an electric current. 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 conducting wire instead of being directly transferred between the oxidizing and reducing agents. The design of a galvanic cell (shown in Figure 1 for equation (3) reaction) 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 separated compartments called half-cells.</p> <p>For each half-cell, the metal, which is called an electrode, is placed in the solution connected to an external wire. The electrode at which oxidation occurs is called the anode [Zn in equation (3)] and the electrode at which reduction occurs is called the cathode [Cu in equation (3)].</p> <p>The two half-cells are connected by a salt-bridge which allows a “current” of</p>

Electrons 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.

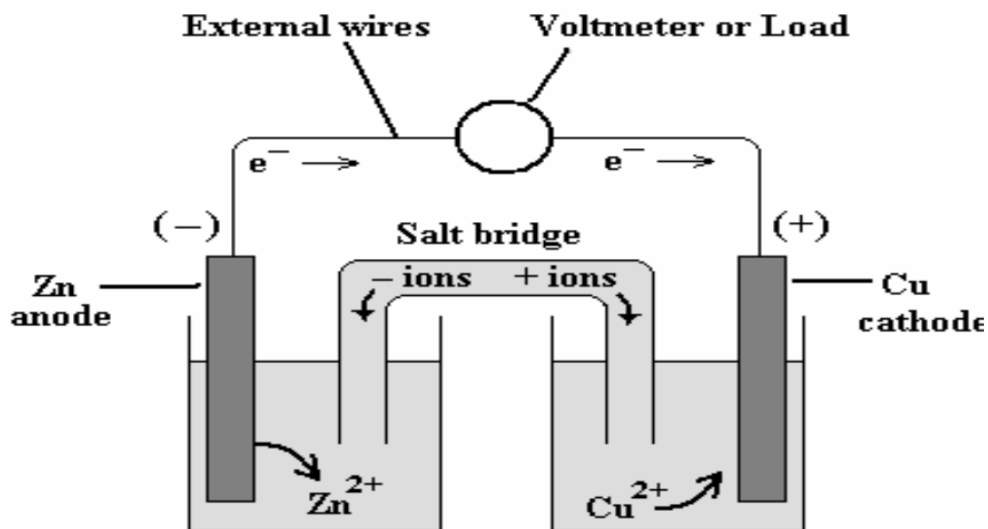


Figure 1. Galvanic cell (or battery) based on the redox reaction in equation (3).

The cell potential, E_{cell} , is a measure of the voltage that the battery can provide. E_{cell} is calculated from the half-cell reduction potentials: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

At standard conditions, the standard cell potential, E°_{cell} , is based upon the standard reduction potentials, as shown in equation (4).

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \quad (4)$$

Based on the values for the standard reduction potentials for the two half-cells in equation (4)

[+0.34 V for copper cathode and -0.76 V for zinc anode and], the standard cell potential, E°_{cell} , for the galvanic cell in Figure 1 would be:

$$E^{\circ}_{\text{cell}} = +0.34 \text{ V} - (-0.76 \text{ V}) = +1.10 \text{ V}$$

The positive value of the voltage for E°_{cell} indicates that at standard conditions the reaction is spontaneous. Recall that $\Delta G^{\circ} = -nFE^{\circ}$

cell, so that a positive E° of a cell results in a negative ΔG° . Thus the redox reaction in equation (3) would produce an electric current when it is set up as a galvanic cell.

When conditions are not standard, the Nernst equation (5), is used to calculate the potential of a cell. In the Nernst equation, R is the universal gas constant with a value of 8.314 J/(K·mol), T is the temperature in K, . F is the Faraday constant with a known value of 96,500 J/(V·mol) and n is the number of electrons transferred in the redox reaction, for example, 2 electrons in equation (3). Q is the reaction quotient for the [ion products]/[ion reactants] of the cell.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{RT}{nF} \right) (\ln Q) \quad (5)$$

For our equation (3) example, $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad \text{and} \quad \ln Q = \ln [\text{Zn}^{2+}] - \ln [\text{Cu}^{2+}] \quad \text{For}$$

Nernst equation in equation (3), n= 2, and this redox reaction becomes:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{RT}{2F} \right) \ln [\text{Zn}^{2+}] + \left(\frac{RT}{2F} \right) \ln [\text{Cu}^{2+}] \quad (6)$$

Thus we perform a series of galvanic cells, in which $[\text{Zn}^{2+}]$ is kept constant while $[\text{Cu}^{2+}]$ is varied, E_{cell} can be measured and it will be found to vary with $\ln[\text{Cu}^{2+}]$.

A plot of the data obtained in which y is E_{cell} and x is $\ln[\text{Cu}^{2+}]$ will result in a straight line: $y = mx + b$. For equation (6), the terms E_{cell}° and $-[\text{RT}/2\text{F}]\ln [\text{Zn}^{2+}]$ are constant and together they equal the intercept, b, of the line. $[\text{RT}/2\text{F}]$ will be the constant slope, m, provided the temperature is constant.

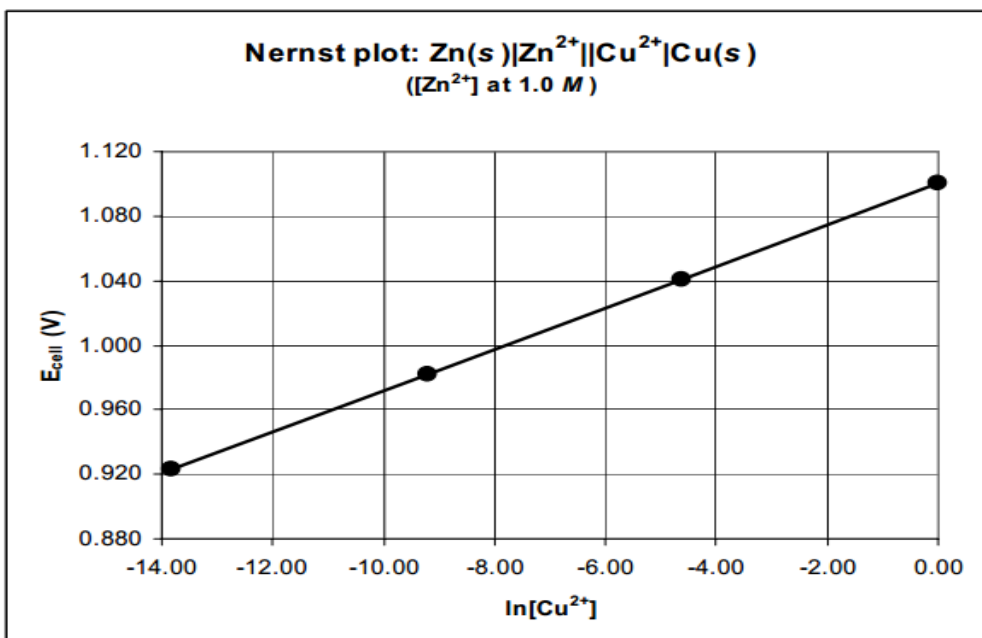


Figure 2. Nernst plot of E_{cell} vs. $\ln [\text{Cu}^{2+}]$ with $[\text{Zn}^{2+}]$ constant at 1.0 M. Note the standard cell notation in the graph title for the galvanic cell.

Materials:

Volt meter (pH meter). 50 mL Beakers (5), two connection leads with Alligator clips, Sand paper

Zinc sheet (or electrode), solution of $\text{Zn}(\text{NO}_3)_2 = 1 \text{ M}$.

Copper strips (or electrode), Solutions of $[\text{Cu}^{2+}]$ 1M, 0.1M, 0.01M, 0.001M, and unknown solution of $[\text{Cu}^{2+}]$, salt bridge filled with 3M KNO_3

Procedure:

- 1- Clean the Zinc with sand paper then with tap water followed with distilled water and dry. The Cu electrode is washed with immersing in 2M KCl for 1 minute then with distilled water several times then dried.
- 2- Prepare the Cu half-cell by immersing the Cu sheet (or Cu electrode) in a beaker filled with 30 mL solution of $[\text{Cu}^{2+}] = 0.001 \text{ M}$.
- 3- Prepare the Zn half-cell by immersing the Zinc sheet in a beaker filled with 30 mL of 1.0 M $\text{Zn}(\text{NO}_3)_2$ next to the Cu half-cell. Connect the two half-cells with a freshly prepared salt bridge. Connect the copper and zinc electrodes to the correct voltage probe leads in the pH meter adjusted to read potential.
- 4- Measure and record the cell potential in your laboratory notebook using the same technique (5-10 second immersion) with the voltage probe

Repeat the previous procedure by changing the concentration of Solutions of $[\text{Cu}^{2+}]$ in order of increasing concentration. Then, in the same way, measure the E_{cell} for the unknown Cu^{2+}

to 0.01M, 0.1M, 1 M, and the unknown solution of $[\text{Cu}^{2+}]$. Be careful to wash the Cu electrode each time with distilled water and dry.

Results:

1. Record the measured voltage values in a table as shown below in your notebook.

[Cu ²⁺]	1	2	3	4	5	Unknown
solution	0.0001M	0.001M	0.01M	0.1M	1.0 M	??
Voltage (V)						
Notes						

2. Plot the Nernst equation, E_{cell} vs $\ln[\text{Cu}^{2+}]$.
3. Record the voltage value of an unknown solution of $[\text{Cu}^{2+}]$.
4. Use the data to find from the constructed graph of $[\text{Cu}^{2+}]$ the concentration of the unknown solution

Reference:

1. Advanced Chemistry with Vernier: Experiments for AP, IB, and College General Chemistry, Jack Randall, Vernier Software and Technology, 2004, 20-1UCCS Chem 106 Laboratory Manual

Experiment # 2
Title of experiment: Concentration Cell- Nernst equation
Aim: To demonstrate the concentration-dependence of the potentials of the half cells with different electrolyte concentrations
Introduction: The magnitude of the potential difference in Nernst equation depends on the potential difference between metals, concentration and temperature. The general relationship is given by the following equation (1) $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{RT}{nF} \right) (\ln Q) \quad (1)$ If the anode and the cathode are the same metal, we will have a concentration cell. A concentration cell acts to dilute the more concentrated solution and concentrate the more dilute solution, creating a voltage as the cell reaches an equilibrium. This is achieved by transferring the electrons from the cell with the lower concentration to the cell with the higher concentration. The Nernst equation is given by: $E = E^{\circ} - \frac{0.0257}{n} \ln \left(\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}} \right) \quad (2)$ $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = \text{zero}$ $E = - \frac{-0.059}{2} \lg \left[\frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}} \right] \quad (3)$ In this experiment we will demonstrate the dependence of the potential on concentration by using two different concentrations copper metal. The reactions in anode and cathode are: Less concentrated is anode $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq})\text{A} + 2 \text{e}^{-}$ More concentrated is cathode $\text{Cu}^{2+}(\text{aq})\text{C} + 2 \text{e}^{-} \rightarrow \text{Cu(s)}$ The net reaction is $\text{Cu}^{2+}(\text{aq})\text{C} \rightarrow \text{Cu}^{2+}(\text{aq})\text{A}$ The difference in concentration leads to a concentration gradient and produces a voltage difference and a current flow where oxidation occurs in the anode to increase the concentration of Cu^{2+} in the solution and reduction occurs in the cathode to decrease the concentration of Cu^{2+} . The voltage decreases until the Cu^{2+} concentration of both sides is equal and the voltage approaches zero.

Materials:

Volt meter (pH meter)- 50 mL Beakers (2) -two connection leads with Alligator clips - Sand paper
 -Cu strips (or sheets)- Solutions of Copper sulfate 0.02 M- 0.010 [Cu²⁺] - salt bridge filled with 3M KNO₃

Procedure:

1. Each pair of student will get 2 long sheets of Cu. The Cu sheets are washed with distilled water then dried.
2. Fill a clean 50-mL beaker with 30 mL of .02 M CuSO₄ solution. Connect the alligator lead to the Cu Sheet and immerse half of the sheet into the solution. Plug the lead into the positive side of the Voltmeter, this is your cathode half-cell.
2. Prepare the anode Cu half cell by immersing the Cu sheet into a beaker filled with 30 mL solution of [Cu²⁺] = 0.1M. Connect the alligator clip to the copper sheet in the beaker and plug the lead into the negative side of the Voltmeter.
3. Be sure the dial on the voltmeter is set to DC Volts and after 20 seconds record the voltage. Does this voltage reading make sense? Record the voltage every 10 seconds until it reaches equilibrium.
4. Put the Voltmeter on hold. Dispose of the .020 M solution in the cathode half -cell and fill a clean beaker with 30 mL of 0.020 M CuSO₄ solution. Add a fresh solution in the anode half -cell 0.01 M. Turn on the Voltmeter. After about 10 seconds, read the voltage.
5. Record the results in the table below.
6. Put the Voltmeter on hold after the voltage reach equilibrium. Add 50 mL of distilled water in the cathode half -cell. Read the voltage. What do you notice??

Results:

Report your data in the table below

CuSO ₄ solution	Voltage	Anode solution	Cathode solution
0.10M / .02 M			
0.02M / 0.01M			
Dilution of cathode solution			

Report:

1. From your observations, for every combination of difference electrolytes concentrations , does the potential difference decreases with time? Why?
2. Compare the measured & theoretical values for these cell potentials.

From your experiment, result which deviate greatly from the theoretical value may arise when more concentrated (0.2.0M/0.1M) OR when highly diluted (<0.01M) solutions are used. Give your reasons. What is your conclusion ?

Experiment # 3**Title of experiment:** Difference between a galvanic cell and an electrolytic cell**Aim:**

There are two types of electrochemical cells; galvanic and electrolytic cells. The former one is known to have a spontaneous cell reaction with a **negative** value for $\Delta_r G$ whereas the latter is distinguished by a non-spontaneous reaction with a **positive** value of $\Delta_r G$.

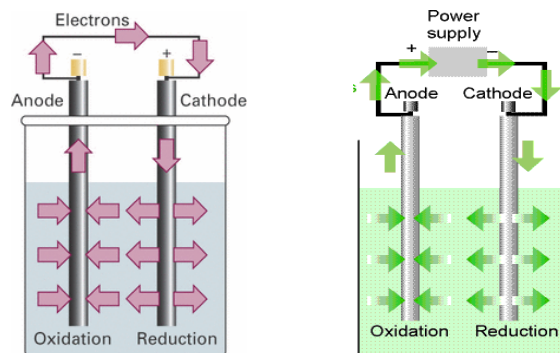
In this experiment, you will learn how to setup the two types of electrochemical cell and measure their potential.

Introduction:

A galvanic cell (left photo) is a system in which an oxidation-reduction reaction occurs spontaneously. The oxidation and reduction half-reactions are separated so that the current moves through an external wire. This spontaneous reaction produces an electrical potential. The potential for any galvanic cell can be calculated using the standard reduction potentials using the equation

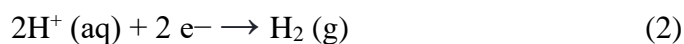
$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \quad (1)$$

In an electrolytic cell (right photo), electricity is supplied externally to drive a nonspontaneous redox chemical reaction. This process is known as *electrolysis*.



Source: Physical chemistry. Atkins & Paula

As in galvanic cells, the number of electrons required to drive electrolysis is directly related to the number of electrons needed in the reduction half reaction. One of the famous electrolysis reaction is the evolution of hydrogen gas from an acid solution where the hydrogen ions are reduced at the cathode, usually a metal, to give hydrogen gas as:



Reduction of H^+ ions to form hydrogen gas can be a spontaneous reaction if the metal has a standard reduction potential lower than that of H^+/H_2 whereas it can be non-spontaneous if the metal has a higher standard reduction potential than that of H^+/H_2 .

The objective of this experiment is:

1. To setup a galvanic cell
2. To setup an electrolytic cell
3. To distinguish between galvanic and electrolytic cells.
4. To measure the relative reduction potentials for a number of redox couples in a galvanic cell.
5. To identify the reactions occurring at the anode and cathode during the electrolysis of various aqueous salt solutions.

Materials:

12x75 test tubes (3); 10 mL graduated cylinder (2); 150 mL beaker;

Ag, Cu and Zn wires or rectangular sheets and Two sharp pencil (as graphite electrode) ; Battery 9 V digital multimeter with alligator clip leads; Sand paper

0.50 M $AgNO_3$; 0.25 M $Cu(NO_3)_2$; 0.25 M $Zn(NO_3)_2$; 200 ml of 0.50M H_2SO_4 .

2 salt bridge (h- type) filled with saturated KNO_3 solution

Procedure:

- 1) Prepare a salt bridge using saturated KNO_3 solution.
- 2) For **the galvanic cell** polish Ag and Zn electrodes with sand paper until shiny. Then rinse them by distilled water and dry it in air. For Cu rinse it in distilled water and dry.
- 3) Take a rubber band and hold three small test tubes together, Label one with A, C and Z for $AgNO_3$, $Cu(NO_3)_2$, M $Zn(NO_3)_2$ solutions respectively.
- 4) Place a salt bridge in two test tubes with Ag and Zn solutions.
- 5) Insert the Ag and Zn electrodes in the corresponding solutions and attach the positive wire of the volt meter to the Ag metal and the negative wire to Zn metal and record the potential and your visual observation.
- 6) Repeat step #5 using Ag and Cu electrodes and record the potential of the cell and your visual observation.
- 7) Repeat step #5 using Cu and Zn electrode and record the potential of the cell and your visual observation.

8) For **electrolytic cell**, use a Zn anode and graphite cathode. The solution is 0.50M H₂SO₄.

9) Connect the two electrodes to the volt meter and measure the potential. In the same time, observe if any reactions are undergoing at the electrodes or any gases are evolved.

10) Repeat step 9 using a graphite anode and measure the potential. In the same time, observe if any reactions are undergoing at the electrodes or any gases are evolved. Now connect the graphite electrode to the **negative pole** of the power supply and the graphite electrode to the **positive pole**. Observe any activity at the electrode surface. Observe the volume of the gas evolved as a function of time. Record your observation in table 2.

Results:

Using the given galvanic cells and recording the measured potentials at a known temperature in table 1 given below and determine the polarity of each cell and the reactions of its electrodes.

Table 1 Experimental data-

Redox couples	Potential, V	Cathode reaction	Anode reaction
Ag-Zn			
Ag-Cu			
Cu-Zn			

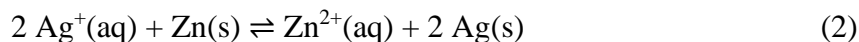
Table 2 Experimental data of an electrolytic cell

Redox couples	Potential, V	Cathode reaction	Anode reaction
Zn-graphite			
Graphite-graphite			

Experiment # 4
Title of experiment: Thermodynamics of a galvanic cell
<p>Aim:</p> <p>Thermodynamics is an important branch of physical chemistry. Using thermodynamic it is possible to discuss how energy is transformed from one form into another,</p>
<p>Introduction:</p> <p>The purpose of this experiment is to explore the thermodynamics of an electrochemical cell, and the relationships of energy, work and power associated with this spontaneous electron-transfer (oxidation reduction) redox reaction. In a galvanic cell the electrons transferred between reactants in an oxidation-reduction reaction can be used to do work. The work that is done in the environment (the surroundings) comes from the change in energy of the chemicals in the galvanic cell (the system) as the reaction proceeds. The free energy change for a reaction ($\Delta_r G$) represents the maximum work available from a reaction, if spontaneous, or the minimum energy required to drive the process, if non-spontaneous. A galvanic cell, of course, encapsulates a spontaneous reaction, so it provides energy for work. Maximum value of work corresponding to $\Delta_r G$ are only encountered in the specialized (and impossible) circumstances of thermodynamic reversibility. An electrochemical cell probably come closest to thermodynamic reversibility of any energy conversion device. Work is defined as the energy transfer that occurs as a mass is moved through a distance against an opposing force. In an electrochemical cell there is another type of work called electrical work defined as w_{elec}, equal to the energy transfer as a charge is moved through an electrical potential energy difference. This can be expressed as</p> $w_{\text{elec}} = q \cdot E \quad \text{or} \quad w_{\text{elec}} = n \cdot F \cdot E \quad (1)$ <p>where q is the charge (in coulombs, C) and E is the electrical potential difference (in volts, V).</p> <p>One joule of work is associated with moving a coulomb of charge across a potential energy difference of one volt, so $1 \text{ V} = 1 \text{ J/C}$. That will relate voltage and energy units.</p> <p>In the wires of an electrical circuit, the charge is carried by moving electrons, but each electron carries only a very small charge, $1.602 \times 10^{-19} \text{ C}$. So, the charge is typically described in terms of the number (n) of moles of electrons exchanged in a reaction, where each mole contains Avogadro's number of electron charges. The latter quantity (symbolized F) is called the Faraday constant, and has the value of 96485 coulombs/mole e^-.</p> <p>A galvanic cell provides the electrical potential energy difference (voltage) to drive the electrons through the circuit. The cell does work on a charge to move it from the low energy terminal to the</p>

high energy terminal. The energy of the cell that is transferred in the form of work comes from the chemical potential energy change that occurs as the chemical reaction of the battery proceeds.

The reaction for the galvanic cell Zn(s)/ Zn(NO₃)₂// AgNO₃/Ag(s) is:



For the reaction to be spontaneous reaction $\Delta_r G < 0$. Since $\Delta_r G$ represents the maximum non-PV work that can be obtained from the cell (and we will assume that all of it is electrical), we can relate $\Delta_r G$ to the voltage obtained from the cell.

$$\Delta_r G = -n \cdot F \cdot E \quad (3)$$

The negative sign appears because of the convention that E is positive for spontaneous cells.

$\Delta_r G$ is defined as

$$\Delta_r G = \Delta_r H - T\Delta_r S \quad (4)$$

$$\Delta_r S = -\frac{d(\Delta_r G)}{dT} \quad (4A)$$

where $\Delta_r H$ and $\Delta_r S$ are the enthalpy change and entropy change for a reaction, respectively.

We know that ΔG is strongly dependent on temperature, while $\Delta_r H$ and $\Delta_r S$ are constant over a small temperature range. In this experiment we will examine the change in voltage of a cell, $\frac{dE}{dT}$, over a small temperature range. Combining equations (3) and (4A), provides the following equations

$$-\frac{d(\Delta_r G)}{dT} = nF \left(\frac{dE}{dT} \right) = \Delta_r S \quad (5)$$

$$\Delta_r H = -nFE + nFT \left(\frac{dE}{dT} \right) \quad (6)$$

Measurement of E of a galvanic over a suitable temperature range will give a straight line when plotted as E vs. T . The slope of this straight line is called the *temperature coefficient* of the galvanic cell from which $\Delta_r S$ and $\Delta_r H$ can be calculated using equations 5 and 6.

Materials:

12x75 test tubes (3); thermometer with rubber stopper for test tube;

4" Ag and Zn wire electrodes;

salt bridges; water bath;

digital multimeter with alligator clip leads;

0.50 M AgNO_3 ; 0.25 M $\text{Zn}(\text{NO}_3)_2$

Procedure:

- 1) Prepare a salt bridge using saturated KNO_3 solution.
- 2) Cut silver electrodes (50 x 10 mm) from the silver sheet and clean them by a small piece of polishing paper until shiny. Then clean it rinse by distilled water and leave it to dry in air.
- 3) Cut zinc electrodes (50 x 10 mm) from the zinc sheet and clean them by small piece of polishing paper until shiny , rinse by distilled water and leave it to dry in air.
- 4) Take a rubber band and hold three small test tubes together, Label one with A for AgNO_3 solution and the other with Z for $\text{Zn}(\text{NO}_3)_2$ solution. Fill the two tubes with the corresponding solutions and the third test tube with distilled water.
- 5) Place a wet salt bridge in two test tubes with Ag and Zn solutions.
- 6) Place the three test tubes in the water bath and start recording the temperature.
- 7) Insert the two metals in the corresponding solutions and attach the positive wire of the multimeter to the Ag metal and the negative wire to Zn metal. A potential reading should be displayed on the multimeter. If not then check that, the metals are inserted in the solution.
- 8) Measure the temperature using the temperature probe and record a stable value of the potential in the given table below.

Results:

Using the given galvanic cell and recording its potential at a known temperature in table 1 given below, the thermodynamic quantities of the reaction can be calculated using equations 3, 5 and 6. Plot the average potential vs. absolute temperature and estimate the slope of the straight line and the correlation coefficient R^2 .

Table 1 Experimental data

Heating		
Temperature, °C	Temperature, K	Potential, V
25		
30		
35		
40		
45		

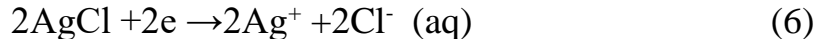
Report:

Use Table 2 to report the values obtained from the measurements and calculation.

Table 2

Slope	Intercept	R^2
Number of moles of e^- in cell reaction		
E_{298K} , V		
Thermodynamic quantity	Value	Unit
$\Delta_r G$		
$\Delta_r S$		
$\Delta_r H$		
W_{elec}		

Experiment # 5
Title of experiment: Determination of Activity Coefficients by electrochemical method
Aim: Determination of Activity Coefficients of Hydrochloric Acid Solutions
<p>Introduction:</p> <p>The activity coefficient γ, based upon molality (m) is defined as:</p> $a = m \gamma \quad (1)$ <p>where a is the activity, γ is activity coefficients</p> <p>An ideal solution is defined as one for which γ is unity, but for a non-ideal solution it differs from unity. However, even for non-ideal solutions, in the limit of zero ionic strength, the activities of ions are equal to their concentrations. The activity coefficients, thus, become unity in the limit of zero ionic strength. The ionic strength I is defined by the expression;</p> $I = \frac{1}{2} \sum C_i Z_i^2 \quad (2)$ <p>where C is the concentration and Z is the charge of the ions of type i. The Debye-Hückel "limiting law" predicts the mean ion activity coefficient (γ_{\pm}) by the equation:</p> $\log(\gamma)_{\pm} = -A Z_+ Z_- * \sqrt{I} \quad (3)$ <p>where Z_+, Z_- are the charges of anion and cation respectively. The constant A has the value 0.509 at 25 °C for aqueous solutions. For 1:1 (uni-univalent) electrolytes the ionic strength equals the concentration, $I = C$. For high concentrated solutions, the following equation may be used.</p> $\log(\gamma)_{\pm} = -A Z_+ Z_- \sqrt{I} + CI \quad (4)$ <p>Where C is a constant.</p> <p>There are several methods for the determination of activity coefficients. The measurement of electromotive force of a cell is one of the most convenient methods.</p> <p>Consider the following cell:</p> $\text{Zn} \text{ZnCl}_2(x\text{M}) \text{AgCl} \text{Ag}$ <p>The reactions in anode and cathode are :</p>



The net reaction is:



The electromotive force of this cell (E.M.F) is

$$E = E_{\text{Ag/AgCl}} - E_{\text{Zn/Zn}^{2+}} \quad (8)$$

For the two electrodes, the potential is:

$$E_{\text{cathod}} = E_{\text{Ag/AgCl}} = E^{\circ}_{\text{Ag/AgCl}} - \frac{RT}{2F} \ln a^2_{\text{Ag}^+} a^2_{\text{Cl}^-} \quad (9)$$

$$E_{\text{anode}} = E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - \frac{RT}{2F} \ln \frac{a_+}{a_m} \quad (10)$$

where $(a_-)^2$ is the activity of Cl^- , a_+ is the activity of Zn^{2+} and a_m is the activity of zinc metal and the activity of silver metal is constant

$$E = E_C - E_a = E_{\text{Ag/AgCl}} - E_{\text{Zn/Zn}^{2+}} \quad (11)$$

$$E = (E^{\circ}_{\text{AgCl}} - E^{\circ}_{\text{Zn}}) - \left[\frac{RT}{2F} \ln a^2_m a^2_- \right] - \left[\frac{RT}{2F} \ln \frac{a_+}{a_m} \right] \quad (12)$$

Rearranging the equation and adding a_m to E° we get a new constant \bar{E} instead

$$E = \bar{E} - \frac{RT}{2F} \ln a^2_- - \frac{RT}{2F} \ln a_+ \quad (13)$$

$$E = \bar{E} - \frac{RT}{2F} \ln a^2_- a_+ \quad (14)$$

Since we can only measure the mean Ionic Activity (a_{\pm})

$$(a_{\pm})^v = (a_+)^{v^+} \times (a_-)^{v^-} \quad (15)$$

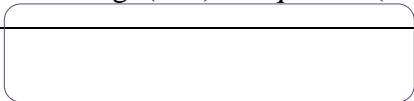
For an electrolyte of v_+ cation and v_- anion we can find:

$$v = v^+ + v^-$$

For ZnCl_2 :

$$(a_{\pm})^3 = (a_+)^1 \times (a_-)^2 \quad (16)$$

Substituting (a_{\pm}) in equation (14)



$$E = \bar{E} - \frac{RT}{2F} \ln (a_{\pm})^3 \quad (17)$$



$$E = \bar{E} - \frac{3RT}{2F} \ln(a_{\pm}) \quad (18)$$

Mean Ionic Activity is related to mean molality (m_{\pm}) and mean activity coefficient (γ_{\pm}) as

$$a_{\pm} = m_{\pm} \gamma_{\pm} \quad (19)$$

Equation (20) is used to calculate mean activity coefficient (γ_{\pm}) mathematically

$$E = \bar{E} - \frac{3RT}{2F} \times \ln(m_{\pm} \times \gamma_{\pm}) \quad (20)$$

However we need to calculate the value of \bar{E} graphically after rearranging eq.(20)

$$E + \frac{3RT}{2F} \times \ln(\gamma_{\pm}) = \bar{E} - \frac{3RT}{2F} \times \ln(m_{\pm})$$

Changing ln into log gives:

$$E + \frac{6.909RT}{2F} \times \log(\gamma_{\pm}) = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3 \quad (21)$$

The mean activity coefficient (γ_{\pm}) for $ZnCl_2$ is related to ionic strength as:

$$\log(\gamma)_{\pm} = -0.5 |Z_+ Z_-| \sqrt{I} + CI$$

$$\log(\gamma)_{\pm} = -\sqrt{I} + CI \quad (22)$$

Substituting in equation (21)

$$E - \frac{6.909RT}{2F} \sqrt{I} + \frac{6.909RT}{2F} \times CI = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3$$

For $ZnCl_2$ $m_+ = m$, $m_- = 2m$

$$(m_{\pm})^3 = (m)^1 \times (2m)^2 = 4m^3$$

$$I = \frac{1}{2} \sum C_i Z_i^2$$

$$I = 3M$$

Since we use dilute solutions, **m=molarity**

$$E - \frac{6.909RT}{2F} \times \sqrt{3m} + \frac{6.909RT}{2F} \times 3Cm = \bar{E} - \frac{2.303RT}{2F} \times \log(m_{\pm})^3$$

Note that $(m_{\pm})^3 = 4m^3$

and $\frac{2.303RT}{2F} \times \log(m_{\pm})^3$ is moved to the left side of this equation.

$$E - \frac{6.909RT}{2F} \sqrt{3m} + \frac{2.303RT}{2F} \times \log 4(m^3) = \bar{E} - \frac{6.909RT}{2F} \times 3Cm \quad (23)$$

From eq. (23) E is the potential value from the Voltmeter of each concentration. The left side of equation 23 is drawn as (Y) with the independent variable **molarity (x)**. We draw the equation to get the value of \bar{E} which is the intercept

Materials:

Ag rod, Zn electrode or sheet, Sand paper, pH meter, two connection leads with Alligator clips.

Different concentration of $ZnCl_2$ 0.0005, 0.001, 0.003, 0.005, 0.008 M

$AgNO_3$ (0.01 M), Saturated KCl solution. Lugen tube with side arm. 50 mL beaker.

Procedure:

1. Clean the Ag rod and Zn electrode by the sand paper then wash with tap water followed with distilled water and dry.
2. Start with the lowest concentration of $ZnCl_2$, add 50 mL of 0.0005M into the beaker, hold Zn electrode with Alligator clips then immerse the Zn electrode from the top.
3. Close the tip of the Lugen tube with filter paper and be sure that no solution is dripping. In

a nother test tube fill the tube with saturated KCl solution. Add a few drops of AgNO₃ until a white ppt of AgCl is formed. Transfer the white solution to the lugin tube. Be sure no bubbles are present. Hold the Ag with the Alligator clips then immerse the Ag electrode and be sure that it touches the white ppt of AgCl. You can add 2 drops of AgNO₃ .Immerse the tip of the lugin tube in the Zn solution.

4. Turn on the Voltmeter, choose the potential mode and put on stand -by. Connect the Zn electrode to the anode and Ag electrode to the cathode.
5. Turn on the Voltmeter on potential mode, wait for 5 seconds then record reading.
6. Turn the Voltmeter to stand-by mode and change the ZnCl₂ into 0.001M.
7. Repeat the previous steps until you record the potential of all solutions.

Results:

Fill up the following table

ZnCl ₂ (M)	Potential reading from Voltmeter	Left side of eq. 23
0.0005		
0.001		
0.003		
0.005		
0.008		

Report:

1. Plot Left side of eq. 23 versus m of ZnCl₂
2. Find \bar{E} from the intercept of the straight line.
3. Calculate γ_{\pm} for each concentration of ZnCl₂ from eq. 21 and from the simple Debye Huckel equaion

$$\log(\gamma)_{\pm} = -0.5 |Z_+Z_-| \sqrt{I}$$

4. Discuss the relation of γ_{\pm} with concentration from your data.

Experiment #6**Title of experiment:** Determination of the solubility products of sparingly soluble salt**Aim:**

Use a concentration cell made from two Ag(s) / Ag^+ (aq) electrodes to determine the solubility product of the three silver halides AgCl , AgBr and AgI .

Introduction:

A concentration cell is constructed from two half-cells which are identical, except that the concentration of the ionic species to which the electrode is sensitive is different on the two sides of the cell. Such a cell can be used to measure the solubility product of a sparingly soluble salt. In one half-cell the concentration

of these ions is known, in the other it is determined by the solubility product of the salt under investigation. The ratio of the two concentrations (more accurately, activities) determines the potential of the cell.

A concentration cell used here can be expressed as:



where X refers to the halide ion.

The cell potential is the difference between the cathode potential (right half-cell R) and the anode potential (left half-cell L) and is always positive, otherwise the process runs in the other direction. The cathode is the electrode with the higher potential. It is the positive pole in a galvanic cell. The processes which take place at the cathode are always reductions. Cations are deposited, non-metals go into solution as anions, oxidizing agents are reduced.

The potential E is generally calculated from the two standard potentials E° by subtracting them, together with a second expression, which takes the activities a of the participating substances into account. As in the law of mass action, the substance on the right appears in the numerator, the substance on the left in the denominator. In this case, we have:

$$E = E_{\text{Ag}}^\circ + \frac{RT}{F} \ln a_{\text{Ag}^+, \text{R}} - E_{\text{Ag}}^\circ - \frac{RT}{F} \ln a_{\text{Ag}^+, \text{L}} = \frac{RT}{F} \ln \frac{a_{\text{Ag}^+, \text{R}}}{a_{\text{Ag}^+, \text{L}}} \quad (1)$$

Where $a_{\text{Ag}^+, \text{R}}$ is the activity of the silver ions in the silver nitrate solution of known concentration and $a_{\text{Ag}^+, \text{L}}$ is the activity of the silver ions in the potassium halide / silver halide solution.

Measurement of potential of a concentration cell such as the above, can be used to determine solubility products. For this purpose, one half-cell containing a saturated solution of the substance is connected to a second half-cell containing a solution of known activity. The connection is made via a switch which is filled with an electrolyte that is inert with regard to the saturated solution.

$a_{Ag+,L}$ is controlled by the solubility product K_{sp} of the silver halide AgX

$$K_{sp} = a_{Ag+,L} \cdot a_{X-,L} \quad (2)$$

where $a_{X-,L}$, the activity of the halide ions in the left half-cell, is assumed to arise from the fully dissociated potassium halide, whereas the contribution from the sparingly soluble silver halide being negligible in comparison.

Substituting equation (2) into equation (1) allows the cell potential to be expressed as:

$$E = \frac{RT}{F} \ln \frac{a_{Ag+,R} \cdot a_{X-,L}}{K_{sp}} \quad (3)$$

$$\ln K_{sp} = \ln (a_{Ag+,R} \cdot a_{X-,L}) - \frac{EF}{RT} \quad (4)$$

The solubility product of the silver halide may therefore be calculated by measuring the potential of the cell E if $a_{Ag+,R}$ and $a_{X-,L}$ are known.

The activity of an ion in solution is given by

$$a_i = f_{\pm} \cdot C_i \quad (5)$$

where c_i is the concentration of the species i and a_i is the mean activity of the electrolyte. The electrolyte concentrations required for this experiment are listed in Table 1.

Table 1: Mean activity coefficients f_{\pm} for $AgNO_3$, KCl , KBr , KI at $25^\circ C$

C, mol/l	$AgNO_3$	KCl	KBr	KI
0.001	0.945	0.965	0.965	0.965
0.01	0.897	0.902	0.903	0.905
0.1	0.734	0.770	0.772	0.778

Using these values the ion concentrations can be converted to activities and the solubility products calculated from equation (5). By measuring the potential of the above cell, the solubility product of the corresponding sparingly soluble salt can be calculated from equation (4).

Materials:

Beakers, salt bridge, digital voltmeter, silver metal sheet, temperature probe, stand and clamps.

Ag salts solution shown in table 1.

Procedure:

- 1) Prepare a salt bridge using saturated KNO_3 solution.
- 2) Cut silver electrodes (50 x 10 mm) from the silver sheet and clean them by polishing
- 3) To form a thin layer of the silver halide on Ag metal surface, soak Ag sheets in the corresponding silver halide solution overnight. Note that $\text{Ag(s)} / \text{AgX(s)}$ represents one electrode only.
- 4) Place one of a clean silver electrode in the silver nitrate solution and connect it to the input socket of the voltmeter with a connecting cord to cathode.
- 5) Dip the Ag electrode with formed Ag halide into the potassium halide / silver halide solution and connect it to the anode potential.
- 6) Connect the two electrode solutions by means of the salt bridge.
- 7) Measure the temperature using the temperature probe.
- 8) Record the cell potential for the given concentration cells.

Results:

By using the mean activity coefficient value for the various silver halides for the corresponding concentration, measure the potential of the cells, record it in the following tables, and calculate the solubility product of Ag halides.

Table 2: Experimental data

$[\text{AgNO}_3]$, mol/l	$[\text{KCl}]$, mol/l	$a_{\text{Ag}^+, \text{R}}$	$a_{\text{Cl}^-, \text{L}}$	E, mV	K _{sp}
0.001	0.001	9.45×10^{-4}	$9.65 \cdot 10^{-4}$		
0.01	0.01	8.97×10^{-3}	$9.02 \cdot 10^{-3}$		
0.1	0.1	7.34×10^{-2}	$7.70 \cdot 10^{-2}$		
$[\text{AgNO}_3]$, mol/l	$[\text{KBr}]$, mol/l	$a_{\text{Ag}^+, \text{R}}$	$a_{\text{Br}^-, \text{L}}$	E, mV	K _{sp}
0.001	0.001	9.45×10^{-4}	$9.65 \cdot 10^{-4}$		
0.01	0.01	8.97×10^{-3}	$9.03 \cdot 10^{-3}$		
0.1	0.1	7.34×10^{-2}	$7.72 \cdot 10^{-2}$		

[AgNO ₃], mol/l	[KI], mol/l	$a_{\text{Ag}^+, \text{R}}$	$a_{\text{I}^-, \text{L}}$	E, mV	K _{sp}
0.001	0.001	9.45×10^{-4}	$9.65 \cdot 10^{-4}$		
0.01	0.01	8.97×10^{-3}	$9.05 \cdot 10^{-3}$		
0.1	0.1	7.34×10^{-2}	$7.78 \cdot 10^{-2}$		

Report:

Experiment # 7**Title of experiment:**

Galvanic corrosion

Aim:

To observe and explain the galvanic corrosion of metals.

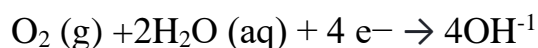
Introduction:

In reality, the material from which a product is made can deteriorate as a result of interaction with the service environment; in the limit, the product may fail. Examples of this interaction in metals include the corrosion of steel by sea water, the stress corrosion cracking of brass, and the high temperature oxidation of nickel. In this experiment, two experiments will be performed. The first experiment will examine the galvanic corrosion of steel. In the second experiment, the high

temperature oxidation of steel and aluminium will be studied and compared. Galvanic corrosion is the process which causes the surface of metals and alloys to deteriorate. It occurs when the metal or alloy loses electrons and becomes a positive ion in solution.



For the reaction to proceed, a complete electrical circuit must exist so that the electrons and the metal ions are removed. The location of the electron-loss reaction is called the anode. Here, the electrons are supplied to the external circuit. Electron gain occurs at the cathode; this electrode receives electrons from the external circuit. In the air think of the following cathodic equation:



Anode and cathode locations and the external circuit for the electron schematically in Figure 1.

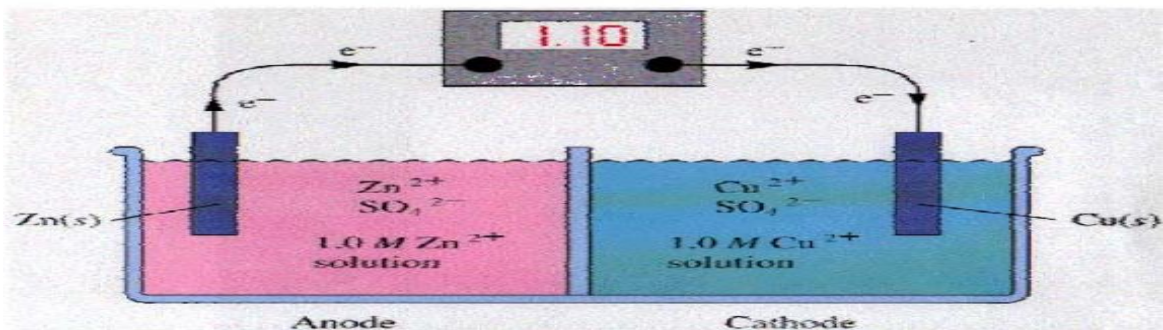


Figure 1 : Galvanic cell consisting of Zn and Cu electrodes

Materials:

Iron nails ,Aluminum foil ,Copper electrical wire , zinc sheet,

Sand paper ,Ceramic or glass dish

10% w/w NaCl solution .

Procedure:

1. Clean each nails with sandpaper.
2. Clean the metals .
3. Wrap a piece of aluminium foil tightly around the head of the first nail.
4. Wrap a piece of copper wire around the second nail. Make sure that the end of the copper wire do not touch the nail.
5. Wrap a piece of zinc sheet tightly around the head of the third nail.
6. The fourth nail must have no contact with another metal.
7. Pour the NaCl (10% w/w) solution into the dish)..
8. Place the dish where it can remain for 24 hours without being disturbed, but be easily observed without moving it.
9. Gently place each nail into the dish so that they are not touching each other.
10. Make sure all the nails are covered with the solution (see Figure 2). Label the samples properly. Cover your dish.



Figure 2 Test materials

Results:

1. Observe the nails every 24 hours for 1 week and take notes on what you see.
2. Rate the level of corrosion for each metal from 1 to 10 with no corrosion
3. being 0 and fully corroded being 10. Arrange the level of corrosion from high
4. to low.
5. Compare and contrast the differences after 24 hours. What changes do you observe in the metals?
6. Compare your results in No. (1) with galvanic series. What can you conclude

7. about the level of corrosion in this experiment from the galvanic series?
8. Compare the four metals with the iron nail that was not protected with any
9. metals in the NaCl solution; are there any differences? Which nails with what metals have corroded, and by how much?
10. Have some nails corroded faster than others?

Report:

Make a table and conclude which coating provides the best protection of the iron against galvanic corrosion.

Experiment # 8
Title of experiment: Electroplating of metals
Aim: To use electroplating to plate copper metal onto a key.
Introduction: <p>Electroplating is an economically important process, often used to reduce corrosion or improve the appearance of objects. During electroplating a thin layer of a desirable metal is deposited onto another object.</p> <p>If you have ever purchased inexpensive jewelry with a fine coating of precious metal, then you have witnessed the end result of electroplating. It's an electrochemical reaction used to put a fine metallic coating on an object. Aside from making cheap jewelry, electroplating has important uses in the automotive industry for chrome plating, and in the electronics industry for optics and sensors.</p> <p>The process of electroplating began at the beginning of the 20th century and continues to evolve today. Many common objects such as tin cans are actually electroplated steel with a protective layer of tin. Metallurgists have experimented with electroplating to create synthetic joints with electroplated coatings, and new advances in electronics have been made with electroplated materials.</p> <p>A familiar example of this process is the experiment you will perform in which a key is plated with copper. The key (called the cathode) is connected to the negative terminal of a battery and is placed in an electrolyte bath containing copper ions. The positive terminal of the battery is connected to a piece of copper (called the anode--and often just a copper plate), which is placed in the electrolyte solution. The copper sheet slowly oxidizes, making copper ions that are then attracted to the key, regaining their lost electrons and becoming copper metal again, but now in the form of a thin coating on the key. The battery forces all of this to happen.</p> <p>A copper-plated key will be prepared using the electroplating technique. In the preparation of the copper-plated key, positive Cu^{2+} ions from the electrolyte bath will become attracted to a key carrying a negative charge. When the Cu^{2+} ions reach the key they will gain electrons and become reduced to form copper on its surface:</p> $\text{Cu}^{2+} (\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$ <p>The copper (II) ions removed from the bath must be replenished; this is accomplished at the anode where a solid copper strip undergoes oxidation:</p> $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{e}^{-}$

Materials:

- cathode - a key or a steel spoon
- a copper strip --anode
- electronic balance
- electrolytic solution – approx. 50 mL of 2.0 mol/L CuSO₄
- battery or power source (9-12 V) DC
- insulated wire leads with alligator clips at both end
- Glass rod that will cross the top of the beaker or jar – and copper wire to suspend the key

Procedure:

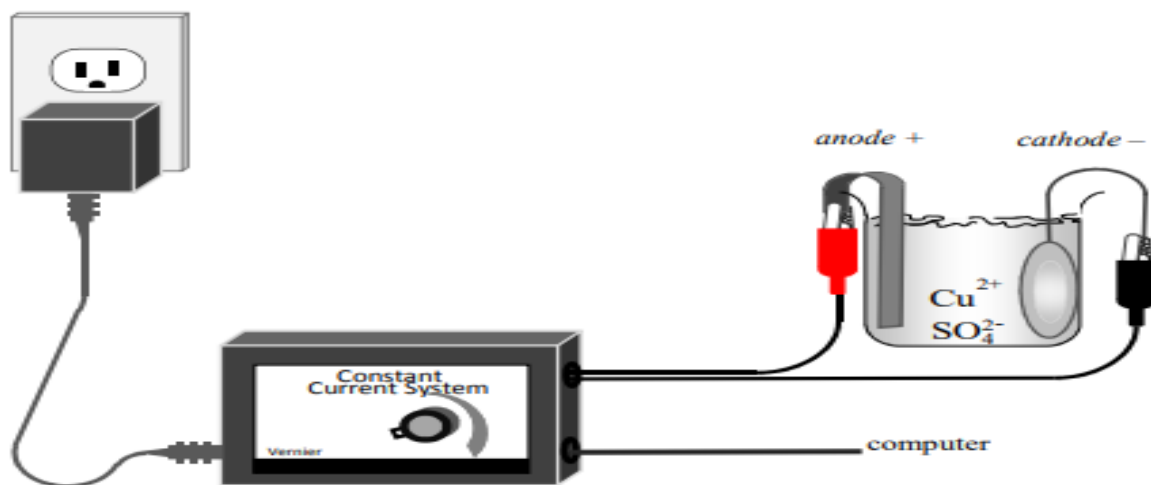
1. The **key/spoon** must be cleaned prior to electroplating. Prepare by polishing with some sand paper. Wash in distilled water, rinse and dry. Record its mass as in Table 1.
2. Use the copper wire (wrapped around a glass rod) to suspend the **key/spoon** into the empty beaker. Attach one end of a wire lead to the copper wire supporting the **key/spoon** and the other end to the **NEGATIVE** post of the battery or power source.
3. The Cu electrode/ sheet is washed with distilled water several times then dried. Record the mass.
4. Place the copper strip, the anode, into the empty beaker. Attach one end of a wire lead to the copper plate and attach the other end to the **POSITIVE** post of the battery or power source.
5. Carefully pour the 2 mol/L CuSO₄ solution into the beaker until it is about two-thirds full.
6. Hook up to the battery /power supply. The **key/spoon** should be wired to the **negative (black) electrode**. The copper strip should be wired to the **positive (red) electrode** of the battery as shown in **Fig. 1**
Have your teacher check your set-up before turning on the power supply!
7. Turn on the power supply and begin timing. (What is the purpose of the power supply?)
8. Use a timer and allow the reaction to continue for **35 minutes**.. Record your observations while electroplating is occurring. After 40 minutes, turn off the power supply.
9. Remove the **key/spoon**, rinse with distilled water and dry well. Record the mass of the anode and cathode after electroplating.

Results:

- a) Draw a diagram of the electroplating set-up (beakers, metal strip, solutions and wires) and show the electrons flowing from the anode (+) , into the cathode (-). Also show ion movement in the electrolyte bath.
- b) Carefully measure and record the new mass of the key in Table 1.

Table 1:

Item	mass before electroplating	mass after electroplating	difference in mass
Key	mg	mg	mg
Copper sheet	mg	mg	mg

**Report:**

- How did the key/spoon change after electroplating?
- How did the copper sheet change after electroplating?
- Explain, at the molecular level, what caused these changes.
- How would the concentration of the Cu^{2+} , in the solution at the end of the electrolysis compare to its original concentration? Explain.
- Compare the change in mass of the copper strip with the change in mass of the key. Explain why they should be equal. Account for any differences.
- Describe, in words, the entire electroplating process for plating copper onto a key as was done in this experiment. Include both the flow of copper ions and electrons through the system.
- List at least two applications of the electroplating process in everyday life.

Experiment # 9**Title of experiment:**

Verification of Tafel Equation for hydrogen evolution reaction at platinum electrode

Introduction:

Tafel's name is an adjective in the language of all trained electrochemists, yet not too many of them would even know his first name. The fame of the "Tafel law" and "Tafel line" overshadow Tafel's claim to fame as one of the founders of modern electrochemistry.

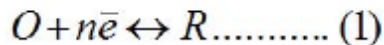
Until 1893, Tafel had lectured organic chemistry, but after 1893 he lectured physical and general chemistry. By German tradition, this would include lots of electrochemistry, and lots of experimentation. A careful observer, Tafel soon was able to summarize his major and rather far-reaching general deductions from his experimental work.



Professor Julius Tafel, around 1905. (Courtesy Chemical Institute, Wurzburg University)

Tafel equation governs the irreversible behavior of an electrode. To understand this we can consider the general mechanism of electron transfer to an electrode.

Consider an electrolyte in which an inert or noble electrode is kept immersed. It is called working electrode, (WE). Also assume that an oxidized and a reduced species are present near the electrode and exhibit the following electron transfer reaction.



O is the oxidised and R is the reduced species present at equilibrium and is stable in the solution. Let us assume that no other electron transfer reaction other than the above occurs. Let the concentration of O and R be C_O and C_R respectively and they are very low. An inert electrolyte is also present to minimize IR drop. Along with WE, a reference electrode RE is also kept immersed, to form the cell. Since the potential of RE is constant, variation in cell emf is the variation in WE, and vice versa.

At the thermodynamic equilibrium of the system no net current flows across RE and WE, no chemical reaction takes place and hence the composition of the solution remains unchanged.

The potential of the working electrode will be its equilibrium potential E_e , which according to Nernst equation is,

$$E_e = E_e^0 + \frac{RT}{nF} \ln \left[\frac{C_O}{C_R} \right] \dots\dots\dots (2)$$

Where E_e^0 is the standard or formal reversible potential and is constant. E_e depends on the ratio of C_O/C_R . The square bracketed term should be in terms of activity rather than molar concentration; but at low concentration the replacement is error free.

The equilibrium mentioned above is dynamic. Though no net current flows across the electrodes, both reduction and oxidation takes place at equal rate, so that the composition of the electrolyte does not change. The dynamic flow of electrons or charge in both directions can be written in terms of current densities as follows.

$$I_0 = I_A = -I_C \dots\dots\dots (3)$$

Where I_A is anodic and $-I_C$ is cathodic current densities. By convention, anodic current density is given +ve sign and cathodic -ve sign. I_0 is known as exchange current density. It may be defined, as "the flow of charge or electrons across an electrochemical system in equilibrium". Its value normally is very low, of the order 10^{-8} A. It refers to the extent of both oxidation and reduction that occurs.

The equilibrium situation at an electrode is characterized by equilibrium potential and exchange current density.

For the reaction to have practical significance, a net current should flow and a net reaction either oxidation or reduction should occur. For this the kinetic aspect of the system must be considered. It is to be recalled that thermodynamics fixes the direction and kinetics determines the rate.

For this, let us apply an external potential to WE, more negative than E_e . This cause an increase in cathodic current and a net quantity of O will be reduced to R. The value of the ratio (C_O/C_R) at the electrode surface will diminish. The magnitude of net cathodic current and the time for the new value of takes to achieve depend on the rate or the kinetics of the electron transfer reaction. The net cathodic current will be due to the increase in partial cathodic current ($-I_c$) and a decrease in partial anodic current (I_A) at this new potential. Hence reversible condition changes to irreversible condition. This is achieved by applying a more -ve potential or excess potential than E_e , which is known as **over potential** (η). Conversely, it can be argued that if WE is made more positive than E_e by applying external potential more positive than (E_e), a net anodic current will flow through the cell.

To summarize the situation, at the equilibrium potential, no net current

$$E_e \xleftrightarrow{-I_c} I = -I + I_A = 0$$

Negative to , a net cathodic current

$$E_e \xleftrightarrow{-I_c} I = -I + I_A < 0$$

Positive to , a net anodic current

$$E_e \xleftrightarrow{-I_c} I = -I + I_A > 0$$

The famous Butler-Volmer equation is expressed as:

$$I = I_0 \cdot \left\{ \exp \left[\frac{\alpha_A n F \eta}{RT} \right] - \exp \left[-\frac{\alpha_C n F \eta}{RT} \right] \right\} \dots \dots \dots (4)$$

From this equation, it can be understood that the measured current density is a function of

- (i) over potential (η)
- (ii) exchange current density (I_0) and
- (iii) anodic and cathodic transfer coefficients (α_A , and α_C).

Transfer coefficients are not independent variables.

In general,

$$\alpha_A + \alpha_C = 1 \dots \dots \dots (5)$$

For many reactions $\alpha_A = \alpha_C = 0.5$

Equation (4) indicates that the current density at any over potential is the sum of cathodic and anodic current densities. At the extreme condition of over potential being highly negative, cathodic current density increases while anodic current density becomes negligible. At this stage, the first term in Butler-Volmer equation (4) becomes negligible. The equation can be written as:

$$I = -I_C = I_0 \cdot \left\{ \exp \left[-\frac{\alpha_C n F \eta}{RT} \right] \right\} \dots \dots \dots (6)$$

When the over potential is higher than above 52 mV, this equation shows that the increase in current is exponential with over potential. The current also depends on I_0 . Equation 6 may also be written as:

$$\log -I_C = \log I_0 - \frac{\alpha_C n F \eta}{2.303 RT} \dots \dots \dots (7)$$

Equation 7 is called Cathodic Tafel equation.

Similarly at positive over potentials higher than 52 mV, anodic current density is much higher than cathodic and the cathodic current density becomes negligible.

Hence

$$\log I_A = \log I_0 + \frac{\alpha_c n F \eta}{2.303 RT} \dots\dots\dots(9)$$

$$I = I_A = I_0 \cdot \left\{ \exp \left[\frac{\alpha_c n F \eta}{RT} \right] \right\} \dots\dots\dots(8)$$

Equation (9) is called Anodic Tafel equation.

When Log I values are plotted against over potential we get Tafel plots. These offer simple method for experimentally determining of I_0 and transfer coefficients (α_A , and α_C .

Aim:

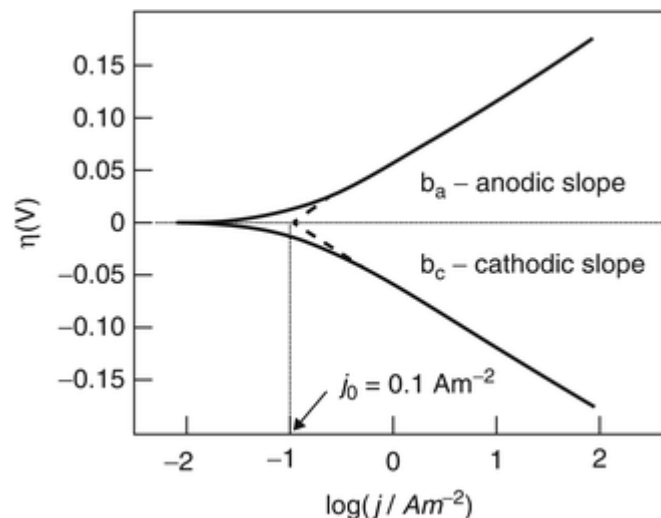
1. Study about the irreversible behavior of hydrogen evolution at Pt electrode.
2. Understand the mechanism of electron transfer to an electrode.
3. Determine the current density.
4. Verifying Tafel plot.

Procedure:

Experimental Determination of I_0 and Tafel Plot for hydrogen evolution at platinum electrode.

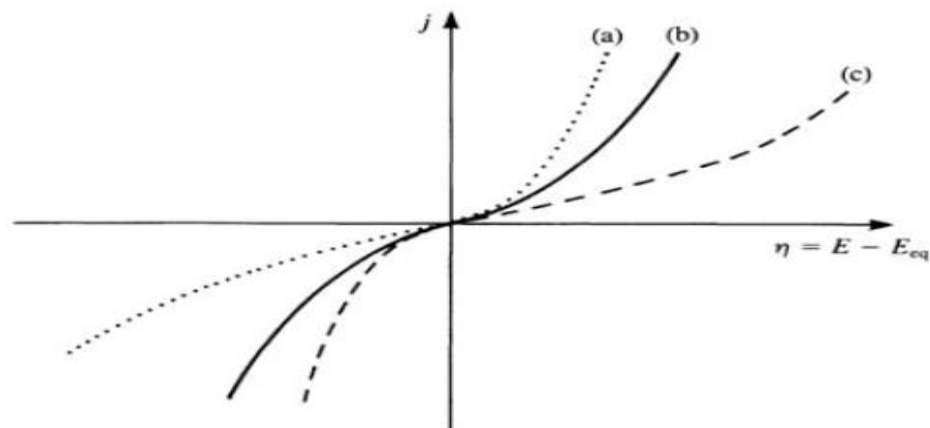
The platinum electrode is immersed in the cell with 0.1 M HCl solution. The Ag/AgCl electrode is kept very close to the working electrode. A platinum foil electrode is also taken which serves as the counter electrode. The potential scan is applied across the working and the counter electrodes at scan rate of 10 mV S^{-1} , from starting potential of 200 mV to -250 mV vs. Ag/AgCl.

The corresponding potential-current diagram is recorded and the log values of these current values are plotted against the over potential as shown in figure below.



Significance of Tafel Plots

1. The point of intersection on the Y axis of the extrapolated graph gives the value of I_0 , the exchange current density, which is otherwise very difficult to determine. It is the current passing at equilibrium conditions and a very low value.
2. The transfer coefficients α_A , and α_C can be determined; from the anodic slope, and from cathodic slope can be determined. This value is very important in industrial practice. This determines the potential that is to be applied to affect the desired rate of reduction or oxidation.
3. Knowing the value of transfer coefficient for a reaction the number of electrons 'n' for an unknown reaction can be determined. This reflects on the mechanism of the reaction; that is how many electrons are involved in that step. Whether the reaction is single step or multistep.
4. The effect of α_C on current density is shown in the following plot.



The effect of the value of α_c on the current density, j . (a) $\alpha_c = 0.25$: oxidation favoured; (b) $\alpha_c = 0.50$: symmetric; (c) $\alpha_c = 0.75$: reduction favoured.

1. $\alpha_c = 0.25$ oxidation is favored.
2. $\alpha_c = 0.50$ symmetrical.
3. $\alpha_c = 0.75$ reduction is favored.

As cathodic transfer coefficient value increases reduction is favored and oxidation is not favored and vice versa for anodic transfer coefficient.

The transfer coefficients depend on the pH of the medium; in acidic conditions (low pH) reduction is favored which is revealed by an increase in α_c .

Results:

Run the linear scan voltammetry at scan rate of 10 mV s^{-1} in 0.1 M HCl solution from potential 200 to -250 mV vs. Ag/AgCl .

Report:

Plot the $\log I$ against potential to obtain the Tafel diagram for hydrogen evolution reaction as shown above and estimate the (I_0) and Tafel slope, α_A and α_C using equation (7).

Experiment # 10**Title of experiment:**

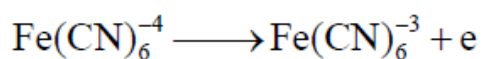
Cyclic Voltammetric Study of ferrocyanide/ferricyanide Redox Couple

Introduction:

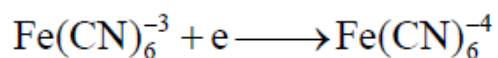
Cyclic voltammetry (CV) is a versatile electroanalytical technique for the study of electroactive species. CV monitors redox behavior of chemical species within a wide potential range. The current at the working electrode is monitored as a triangular excitation potential is applied to the electrode. The resulting voltammogram can be analyzed for fundamental information regarding the redox reaction. Cyclic voltammograms are the electrochemical equivalent to the spectra in optical spectroscopy.

The potential at the working electrode (WE) is controlled versus a reference electrode (RE), Ag/AgCl(s)/(satd. KCl) electrode. The controlling potential that is applied across the WE and the auxiliary electrodes is the excitation signal. The excitation signal is varied linearly with time; first scan positively (-200 mV vs. RE to 800 mV vs. RE). Then the potential is scanned in reverse, causing a negative scan back to the original potential to complete the cycle. Single or multiple cycles can be used on the same surface. A cyclic voltammogram is the plot of the response current at the working electrode to the applied excitation potential.

As shown in Figure 1 the potential is scanned positively (forward scan,) and is sufficiently positive to oxidize $\text{Fe}(\text{CN})_6^{4-}$ species, the anodic current is due to the oxidation process,



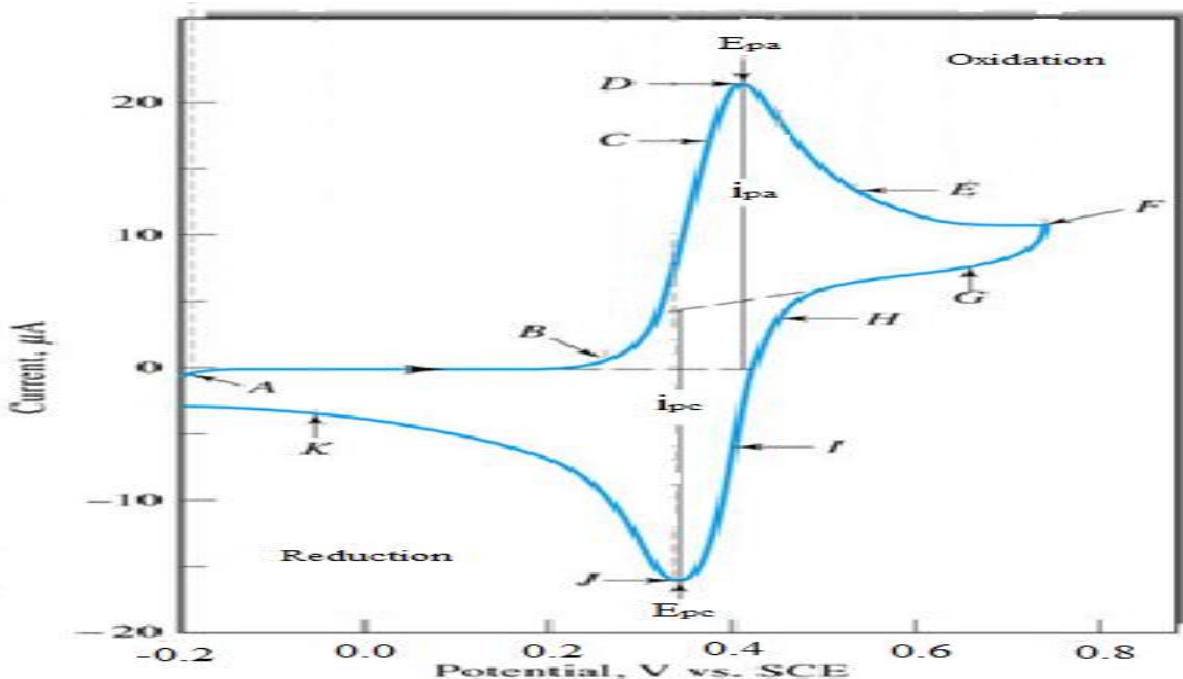
The electrode acts as an oxidant and the oxidation current increases to a peak. The concentration of Fe(CN)_6^{4-} at the electrode surface depletes and the current then decays. As the scan direction is switched to negative, for the reverse scan the potential is still sufficiently positive to oxidize Fe(CN)_6^{4-} , so anodic current continues even though the potential is now scanning in the negative direction. When the electrode becomes a sufficiently strong reductant, Fe(CN)_6^{3-} , which has been forming adjacent to the electrode surface, will be reduced by the electrode process,



resulting in a cathodic current which peaks and then decays of Fe(CN)_6^{3-} in the solution adjacent to the electrode is consumed.

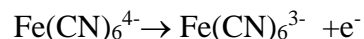
In the forward scan Fe(CN)_6^{3-} is electrochemically generated from Fe(CN)_6^{4-} (anodic process) and in the reverse scan this Fe(CN)_6^{3-} is reduced back to Fe(CN)_6^{4-} (cathodic process). Note that the technique of CV rapidly generates various oxidation states.

The quantities of note a CV plot are the anodic peak current i_{pa} , cathodic peak current i_{pc} , anodic peak potential E_{pa} , and cathodic peak potential E_{pc} . Measuring i_p does involve the extrapolation of the base-line current as shown in Figure 1 below.



A. Start of the potential scan, no reducible or oxidizable species present in this potential range.

B. Around 0.4V, current begins because of the following oxidation at the anode:



B.-D. Rapid increase in current as the surface concentration of Fe(CN)_6^{4-} decreases

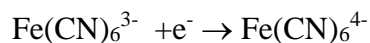
D. Anodic peak potential (E_{pa}) and peak current (i_{pa})

D.-F. Current decays rapidly as the diffusion layer is extended further from electrode surface.

F. Scan direction switched (0.75 V), potential still positive enough to cause oxidation of



F.-J. Eventually oxidation of Fe(CN)_6^{4-} no longer occurs and cathodic current results from the reduction of Fe(CN)_6^{3-}



J. Cathodic peak potential (E_{pc}) and peak current (i_{pc}).

K. Cathodic current decreases as the accumulated $\text{Fe}(\text{CN})_6^{3-}$ is used up at the cathodic reaction.

A redox couple in which half reactions rapidly exchange electrons at the working electrode are said to be electrochemically reversible couples. The formal oxidation potential $E^{\circ'}$ (different from E° , strictly speaking) for such a reversible couple is the mean of E_{pa} and E_{pc} and the i_{pa} and i_{pc} are very close in magnitude.

$$E^{\circ'} = \frac{E_{pa} + E_{pc}}{2}$$

The number of electrons involved in the redox reaction for a reversible couple is related to the

$$E_{pa} - E_{pc} = \frac{57\text{mV}}{n}$$

difference of peak potentials by:

For slow electron transfers at the electrode surface, i.e. irreversible processes, the difference of peak potentials widen.

The peak current in reversible systems for the forward scan is given by Randles-Sevcik equation,

$$i_p = 2.686 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2}$$

where, i_{pa} = peak current in Ampere; n = number of electrons involved,; A = electrode area in cm^2 ; D = diffusion coefficient, cm^2/s ; C = concentration in mol/L and v = scan rate in V/s .

Thus i_p increases with square root of v and is directly proportional to concentration of the species. The values of i_{pa} and i_{pc} are very similar for a one step reversible couple leading to their ratio to be unity. Ratio of peak currents may differ from unity if the reactions coupled to other electrode process.

Aim:

Cyclic Voltammetric Study of ferrocyanide/ferricyanide Redox Couple

Materials:

Potentiostat, glassy carbon working electrode (radius 3.0 mm), platinum auxiliary electrode, Ag/AgCl reference electrode, nitrogen cylinder, polishing material. **Chemicals:** 10 mM $K_3Fe(CN)_6$ in 1.0 M potassium nitrate solution, 1.0 M KNO_3 (matrix), Unknown: $K_3Fe(CN)_6$ in 1.0 M KNO_3 , 1000ppm $K_3Fe(CN)_6$ in 1.0 M potassium nitrate solution.

Procedure:

Polish the electrode surface to a mirror finish with alumina slurry and rinse well with DI water and dry it. Fill the cell with 15 mL 10 mM $K_3Fe(CN)_6$ in 1.0 M KNO_3 . Deoxygenate the solution by purging with nitrogen for approximately 10 min. Turn off the purging but maintain an envelope of nitrogen over the solution. Set the scan parameters suggested below, they may be changed appropriately.

Initial E (mV)	-200	Hold Initial (sec)	0
Forward E Limit (mV)	700	Current range (uA)	auto
Final E (mV)	-200	Number of scans	1
Scan rate (mV/s)	50		

Excite the working electrode with the potential scan and obtain the background CV of the supporting electrolyte solution. (Save all data in named files.) .

Using the same solution and obtain CV's at the following scan rates (v): 20, 50, 75, 125, 150, 175, and 200 mV/s. Between each scan, pass nitrogen through the cell to restore initial conditions and allow the system to acquire quiescence before applying the excitation potential scan. Determine the concentration of the unknown by standard addition method. (Use 100uL aliquots of stock standard solution at each addition)

Results:

Draw the obtained cyclic voltammograms using excel.

Report:

1. Plot i_{pc} , vs $v^{1/2}$, i_{pa} vs $v^{1/2}$.
2. Plot E_p values vs v . for the above runs - comment on the reversibility.
3. Verify the formal standard electrode potential of Fe(II)/Fe(III) system and number of electrons involved in the half reaction, n , from appropriate plots.
4. Determine the diffusion coefficients of the two species.
5. Present voltammograms of appropriate 'sets' overlapped on the same paper.
6. Using the standard addition method determine the concentration of the unknown solution.

End of Practical book