



**Science College**

**Chemistry Department**

**430 Chem practical**

## **Table of contents**

Introduction

Experiment 1: Measurement of a chemical cell (Daniel cell)

Experiment 2: Verification of Nernst equation using a concentration cell

Experiment 3: Determination of Activity Coefficients by an electrochemical method

Experiment 4: Determination of the solubility products of sparingly soluble salt

Experiment 5: Thermodynamics of a galvanic cell

Experiment 6: Difference between a galvanic cell and an electrolytic cell

Experiment 7: Verification of Tafel equation for hydrogen evolution reaction at a platinum electrode

Experiment 8: Corrosion of two different metals

Experiment 9: Cyclic voltammetric study of ferrocyanide/ferricyanide redox couple

Experiment 10: Hydrogen evolution reaction overpotential on different electrodes

**Introduction:**

Electrochemistry is a branch of physical chemistry dealing with chemical reactions that involve electrical currents and potentials and usually occur in electrochemical cells.

This lab manual deals with practical electrochemistry in more detail from both thermodynamic (experiments 1-6) and kinetic (experiment 7) perspectives. Important applications of electrochemistry are represented by experiments (8-10).

Experiments were selected to cover the topics in 430 Chem. Each experiment starts with a brief theoretical foundation, aim of the experiment followed by procedure and results processing and presentation.

## Experiment # 1

**Title of experiment:** Nernst Equation

**Aim:**

- 1- To verify Nernst Equation.
- 2- To calculate the concentration of an unknown  $[\text{Cu}^{2+}]$  by constructing a Galvanic Cell

### Introduction:

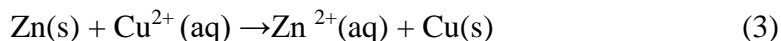
Chemical reactions involving the transfer of electrons from one reactant to another are called oxidation-reduction reactions or redox reactions. In a redox reaction, two half-reactions occur; one reactant gives up electrons (undergoes oxidation) and another reactant gains electrons (undergoes reduction). 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.



Another example of reduction is the formation of solid copper from copper ions in solution.



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:

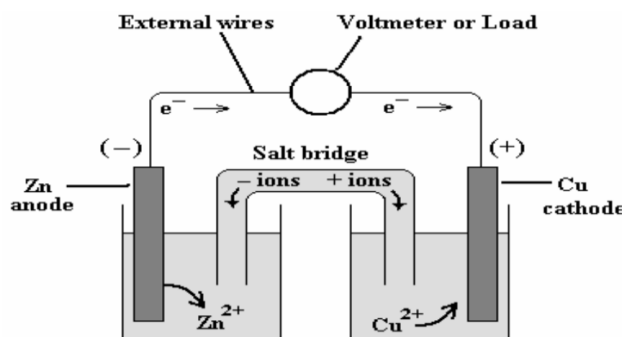


A measure of the tendency for a reduction to occur is its reduction potential,  $E$ , measured in units of volts. Standard reduction potentials have been measured for many half-reactions and they are listed in tables.

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.

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)].

The two half-cells are connected by a salt-bridge which allows a “current” of 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,  $E_{\text{cell}}$ , is a measure of the voltage that the battery can provide.  $E_{\text{cell}}$  is calculated from the half-cell reduction potentials:  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

At standard conditions, the standard cell potential,  $E^{\circ}_{\text{cell}}$ , 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,  $E^{\circ}_{\text{cell}}$ , 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  $E^{\circ}_{\text{cell}}$  indicates that at standard conditions the reaction is spontaneous. Recall that  $\Delta G^{\circ} = -nFE^{\circ}$  so that a positive  $E^{\circ}$  of a cell results in a negative  $\Delta G^{\circ}$ . 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.

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

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

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

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

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

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

A plot of the data obtained in which y is  $E_{cell}$  and x is  $\ln[Cu^{2+}]$  will result in a straight line:  $y = mx +$

b. For equation (6), the terms  $E_{cell}^{\circ}$  and  $-\frac{RT}{2F} \ln [Zn^{2+}]$  are constant and together they equal the intercept, b, of the line.  $\frac{RT}{2F}$  will be the constant slope, m, provided the temperature is constant.

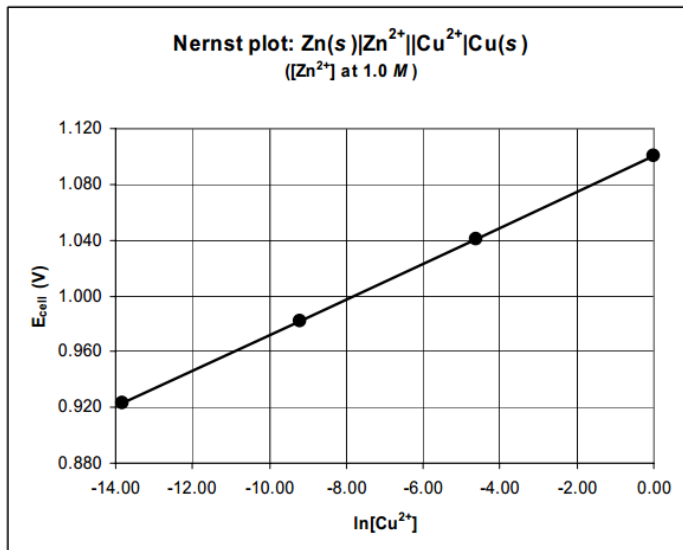


Figure 2. Nernst plot of  $E_{\text{cell}}$  vs.  $\ln [\text{Cu}^{2+}]$  with  $[\text{Zn}^{2+}]$  constant at 1.0 M. Note the standard cell notation in the graph title for the galvanic cell.

### Materials:

Voltmeter , 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  $\text{KNO}_3$

### 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  $E_{\text{cell}}$  for the unknown  $\text{Cu}^{2+}$  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.

$[\text{Cu}^{2+}]$	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,  $E_{\text{cell}}$  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



## Experiment # 2

**Title of experiment:** Verification of Nernst equation using a concentration cell

**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)

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q \quad (1)$$

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:

$$E = E^o - \frac{0.0257}{n} \ln \frac{[Cu^{2+}]_{anode}}{[Cu^{2+}]_{cathode}} \quad (2)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = \text{zero}$$

$$E = -\frac{0.059}{n} \log \frac{[Cu^{2+}]_{anode}}{[Cu^{2+}]_{cathode}} \quad (3)$$

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:



The net reaction is  $Cu^{2+}(aq)_C \rightarrow Cu^{2+}(aq)_A$

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  $\text{Cu}^{2+}$ . The voltage decreases until the  $\text{Cu}^{2+}$  concentration of both sides is equal and the voltage approaches zero.

**Materials:**

Voltmeter, 50 mL Beakers (2), two connection leads with Alligator clips, sand paper, Cu strips (or sheets), solutions of Copper sulfate 1M- 0.010  $[\text{Cu}^{2+}]$ , salt bridge filled with 3M  $\text{KNO}_3$

**Procedure:**

1. Each pair of students will get 2 sheets of Cu. The Cu sheets are washed with distilled water then dried.
2. Fill a clean 50-mL beaker with 30 mL of 1 M  $\text{CuSO}_4$  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  $[\text{Cu}^{2+}] = 0.1\text{M}$ . 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 30 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 1 M solution in the cathode half -cell and fill a clean beaker with 30 mL of 0.010 M  $\text{CuSO}_4$  solution. Add a fresh solution in the anode half -cell 0.001 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 20 mL of distilled water in the cathode half -cell. Read the voltage. What do you notice?

**Results:**

Report your data in the table below

$\text{CuSO}_4$ solution	Voltage	Anode solution	Cathode solution
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0.10M/1 M			
0.001M/0.01M			
Dilution of cathode solution			

**Report:**

1. From your observations, for every combination of difference electrolyte concentration, 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 (1.0M/0.1M) OR when highly diluted (<0.001M) solutions are used. Give your reasons.

3. What is your conclusion?

### Experiment # 3

**Title of experiment:** Determination of Activity Coefficients by an electrochemical method

**Aim:**

Determination of activity coefficients of zinc chloride solution

**Introduction:**

The activity coefficient  $\gamma$ , based upon molality ( $m$ ) is defined as:

$$a = m \gamma \quad (1)$$

where  $a$  is the activity,  $\gamma$  is activity coefficient.

An ideal solution is defined as one for which  $\gamma$  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;

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

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  $(\gamma)_{\pm}$  by the equation:

$$\log(\gamma)_{\pm} = -A |Z_+ Z_-| \sqrt{I} \quad (3)$$

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,  $I = C$ .

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.

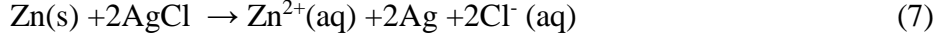
Consider the following cell:



The reactions in anode and cathode are:



The net reaction is:



The potential of this cell) is given by

$$E = E_{cell}^o - \frac{RT}{2F} \ln a_{\text{Zn}^{2+}} a_{\text{Cl}^{-}}^2 \quad (8)$$

where  $a_{\text{Zn}^{2+}}$  is the activity of  $\text{Zn}^{2+}$  and  $a_{\text{Cl}^{-}}$  is the activity of  $\text{Cl}^{-}$ . Zinc metal and silver metal activities are considered equal to unity:

Since we can only measure the mean ionic activity of  $\text{ZnCl}_2$  ( $a_{\pm}$ ) is given by the expression

$$a_{\pm} = (a_{\text{Zn}^{2+}} a_{\text{Cl}^{-}}^2)^{1/3} \quad (9)$$

Substituting ( $a_{\pm}$ ) in equation (8) gives

$$E = E_{cell}^o - \frac{RT}{2F} \ln a_{\pm}^3 \quad (10)$$

$$E = E_{cell}^o - \frac{3RT}{2F} \ln a_{\pm} \quad (11)$$

Mean ionic activity is related to mean molality ( $m_{\pm}$ ) and mean activity coefficient ( $\gamma_{\pm}$ ) as

$$a_{\pm} = m_{\pm} \gamma_{\pm} \quad (12)$$

$$E = E_{cell}^o - \frac{3RT}{2F} \times \ln(m_{\pm} \cdot \gamma_{\pm}) \quad (13)$$

$$E = E_{cell}^o - \frac{3RT}{2F} \times \ln(m_{\pm}) - \frac{3RT}{2F} \times \ln(\gamma_{\pm}) \quad (14)$$

$$E + \frac{3RT}{2F} \times \ln(\gamma_{\pm}) = E_{cell}^o - \frac{3RT}{2F} \times \ln(m_{\pm}) \quad (15)$$

At 25°C this equation becomes

$$\ln \gamma_{\pm} = \frac{E_{cell}^o - E - 0.0385 \ln m_{\pm}}{0.0385} \quad (16)$$

Equation (16) is used to calculate mean activity coefficient ( $\gamma_{\pm}$ ) mathematically at a known molality.

**Materials:**

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

Different concentration of ZnCl<sub>2</sub> solution (0.0005, 0.001, 0.003, 0.005, 0.008 M).

**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<sub>2</sub>, 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 Lugin tube with filter paper and be sure that no solution is dripping then fill the tube with saturated KCl solution. Be sure no bubbles are present. Add a few drops of AgNO<sub>3</sub> until a white ppt of AgCl is formed at the bottom. Hold the Ag with the Alligator clips then immerse the Ag electrode and be sure that it touches the white ppt of AgCl.
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 ZnCl<sub>2</sub> into 0.001M.
7. Repeat the previous steps until you record the potential of all solutions.

**Results:**

Fill up the following table

ZnCl <sub>2</sub> (M)	Potential reading from Voltmeter	Left side of eq. 16
0.0005		
0.001		
0.003		
0.005		
0.08		

**Report:**

1. Calculate  $\gamma_{\pm}$  for each concentration of ZnCl<sub>2</sub> from eq. 16 and from the simple Debye Huckel equation

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

2. Discuss the relation of  $\gamma_{\pm}$  with concentration from your data.

## Experiment # 4

**Title of experiment:** Determination of the solubility products of sparingly soluble salt

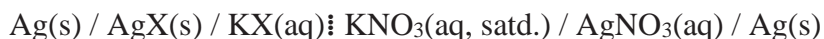
**Aim:**

To use a concentration cell made from two Ag(s) / Ag<sup>+</sup> (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<sup>o</sup> by subtracting them, together with a second expression, which takes the activities 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:

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

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

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

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

where  $a_{\text{X}^-, \text{L}}$ , 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:

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

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

The solubility product of the silver halide may therefore be calculated by measuring the potential of the cell E if  $a_{\text{Ag}^+, \text{R}}$  and  $a_{\text{X}^-, \text{L}}$  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  $\text{AgNO}_3$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$  at  $25^\circ\text{C}$

C, mol/l	$\text{AgNO}_3$	$\text{KCl}$	$\text{KBr}$	$\text{KI}$
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  $\text{KNO}_3$  solution.
- 2) Cut silver electrodes (50 x 10 mm) from the silver sheet and clean them by placing them in the 0.5 molar nitric acid solution for a few minutes (caution nitric acid is very corrosive).
- 3) To form a thin layer of the silver halide on Ag metal surface, soak Ag sheets in the corresponding silver halide solution overnight.
- 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.
- 5) Dip the Ag electrode with formed the Ag halide into the potassium halide / silver halide solution and connect it to ground 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	Ksp
0.001	0.001	$9.64 \cdot 10^{-4}$	$9.65 \cdot 10^{-4}$		
0.01	0.01	$8.97 \cdot 10^{-3}$	$9.02 \cdot 10^{-3}$		
0.1	0.1	$7.34 \cdot 10^{-2}$	$7.70 \cdot 10^{-2}$		
$[\text{AgNO}_3]$ , mol/l	$[\text{KBr}]$ , mol/l	$a_{\text{Ag}^+, \text{R}}$	$a_{\text{Br}^-, \text{L}}$	E, mV	Ksp
0.001	0.001	$9.64 \cdot 10^{-4}$	$9.65 \cdot 10^{-4}$		
0.01	0.01	$8.97 \cdot 10^{-3}$	$9.03 \cdot 10^{-3}$		
0.1	0.1	$7.34 \cdot 10^{-2}$	$7.72 \cdot 10^{-2}$		

[AgNO <sub>3</sub> ], mol/l	[KI], mol/l	$a_{\text{Ag}^+, \text{R}}$	$a_{\text{I}^-, \text{L}}$	E, mV	K <sub>sp</sub>
0.001	0.001	$9.64 \cdot 10^{-4}$	$9.65 \cdot 10^{-4}$		
0.01	0.01	$8.97 \cdot 10^{-3}$	$9.05 \cdot 10^{-3}$		
0.1	0.1	$7.34 \cdot 10^{-2}$	$7.78 \cdot 10^{-2}$		

Report:

## Experiment # 5

**Title of experiment:** Thermodynamics of a galvanic cell

**Aim:**

To use potential measurement of a galvanic cell to calculate the thermodynamics quantities of the cell reaction.

**Introduction:**

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  $w_{\text{elec}}$ , equal to the energy transfer as a charge is moved through an electrical potential energy difference. This can be expressed as

$$w_{\text{elec}} = q \cdot E \quad \text{or} \quad w_{\text{elec}} = n \cdot F \cdot E \quad (1)$$

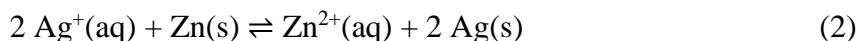
where  $q$  is the charge (in coulombs, C) and  $E$  is the electrical potential difference (in volts, V).

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.

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  $e^-$ .

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 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(NO<sub>3</sub>)<sub>2</sub>// AgNO<sub>3</sub>/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

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

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

We know that  $\Delta_r G$  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 (4), 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);

10 mL graduated cylinder (2), 150 mL beaker, 4" Ag and Zn wire electrodes, salt bridges,

water bath, digital multimeter with alligator clip leads, thermometer with rubber stopper for test tube, 0.50 M AgNO<sub>3</sub>; 0.25 M Zn(NO<sub>3</sub>)<sub>2</sub>; 1.5 M NaNO<sub>3</sub>; 3 M HCl.

**Procedure:**

- 1) Prepare a salt bridge using saturated KNO<sub>3</sub> 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. Then clean it by dipping in 3M HCl for 15 seconds (*caution nitric acid is very corrosive*), then quickly 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<sub>3</sub> solution and the other with Z for Zn(NO<sub>3</sub>)<sub>2</sub> 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<sup>2</sup>.

Table 1 Experimental data

Heating			Cooling		
Temperature, °C	Temperature, K	Potential, V	Temperature, °C	Temperature, K	Potential, V
30.0			30.0		

35.0			35.0		
40.0			40.0		
45.0			45.0		
50.0			50.0		
55.0			55.0		
60.0			60.0		

**Report:**

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

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

## Experiment # 6

**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  $\Delta_r G$ .

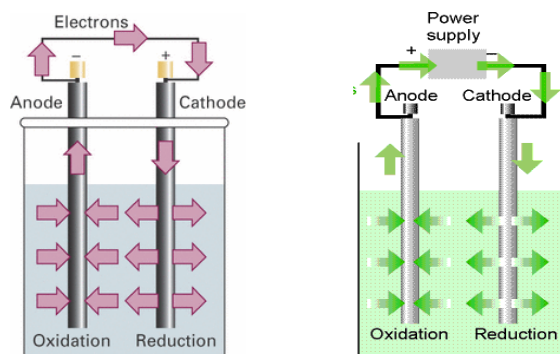
In this experiment, you will learn how to setup the two types of electrochemical cell and measure their potential.

### Introduction:

A galvanic cell 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

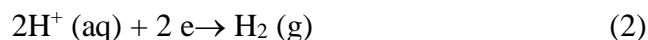
$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \quad (1)$$

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





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 reactions 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  $\text{H}^+$  ions to form hydrogen gas can be a spontaneous reaction if the metal has a standard reduction potential lower than that of  $\text{H}^+/\text{H}_2$  whereas it can be non-spontaneous if the metal has a higher standard reduction potential than that of  $\text{H}^+/\text{H}_2$ .

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.
6. 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 and graphite rod electrodes, salt bridges, digital multimeter with alligator clip leads, 0.50 M  $\text{AgNO}_3$ , 0.25 M  $\text{Cu}(\text{NO}_3)_2$ , 0.25 M  $\text{Zn}(\text{NO}_3)_2$ , 1.5 M  $\text{NaNO}_3$ , 3 M  $\text{HCl}$ .

### Procedure:

1) Prepare a salt bridge using a saturated  $\text{KNO}_3$  solution.

2) Cut Ag, Cu and Zn electrodes (50 x 10 mm) from the metal sheets 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) Take a rubber band and hold three small test tubes together, Label one with A , C and Z for  $\text{AgNO}_3$ ,  $\text{Cu(NO}_3)_2$ , M  $\text{Zn(NO}_3)_2$  solutions respectively.

5) Place a wet salt bridge in two test tubes with Ag and Zn solutions.

6) Insert the Ag and Zn electrodes in the corresponding solutions and attach the positive wire of the multimeter to the Ag metal and the negative wire to Zn metal and record the potential and your visual observation.

8) Repeat step #6 using Ag and Cu electrode and record the potential of the cell and your visual observation.

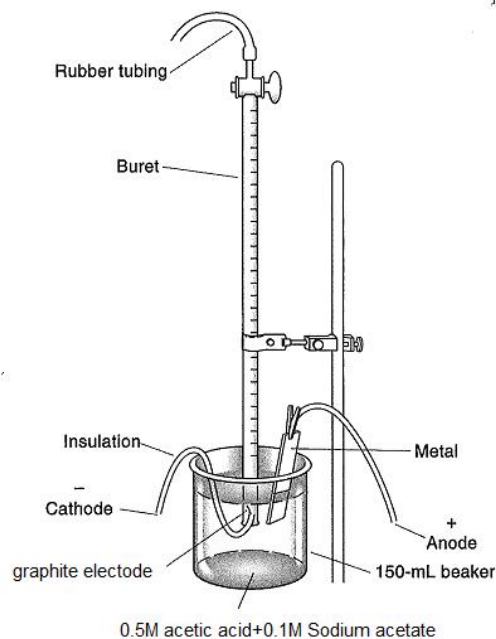
9) Repeat step #6 using Cu and Zn electrode and record the potential of the cell and your visual observation.

10) Prepare the shown setup as an example for electrolytic cell. Use a Zn anode and graphite cathode.

The solution is a mixture of 0.5M acetic acid and 0.1M sodium acetate. The burette should be full with distilled water.

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

12) Repeat step 11 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 Zn 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			

Allow the reaction in step 12 to proceed until the hydrogen gas collected in the burette is equal to 20 mL. By using the ideal gas law calculate the number of moles of hydrogen gas evolved calculate the quantity of charge involved in the cell reaction.

Table 2 Experimental data

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

## **Experiment # 7**

**Title of experiment:** Verification of Tafel Equation for hydrogen evolution reaction at platinum electrode

### **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.

### **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 oxidized 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,

$$E_e = E_e^o + \frac{RT}{nF} \ln \frac{C_O}{C_R} \quad (2)$$

Where  $E_e^o$  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 take 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:

$$I_o = I_A + I_C \quad (3)$$

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.  $I_o$  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 ( $\eta$ )**. 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:

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

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

- (i) over potential ( $\eta$ )
- (ii) exchange current density ( $I_o$ ) and
- (iii) anodic and cathodic transfer coefficients ( $\alpha_A$ , and  $\alpha_C$ ).

Transfer coefficients are not independent variables.

In general,

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

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:

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

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  $I_o$ . Equation 6 may also be written as:

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

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:

$$I = I_A = I_o \left\{ \exp \left[ \frac{\alpha_A n F \eta}{RT} \right] \right\} \quad (8)$$

$$\log I_A = \log I_o + \frac{\alpha_A n F \eta}{2.303 RT} \quad (9)$$

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  $I_o$  and transfer coefficients ( $\alpha_A$ , and  $\alpha_C$ ).

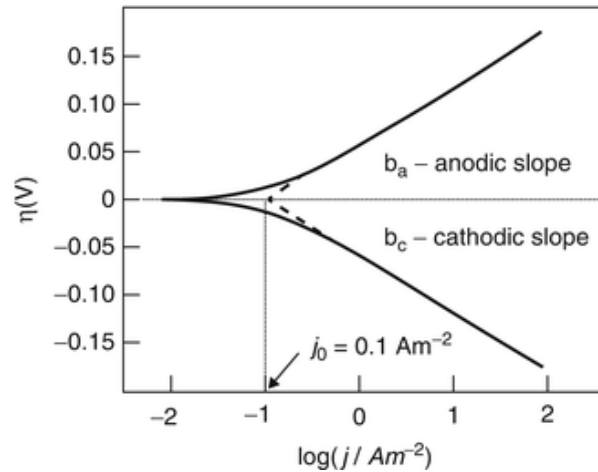
**Materials:** standard electrochemical three electrodes glass cell, platinum electrode (1 mm diameter), Ag/AgCl reference electrode, platinum or carbon counter electrode, 0.1 M solution of sulfuric acid, potentiostat

**Procedure:**

Experimental Determination of  $I_o$  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  $10 \text{ mV S}^{-1}$ , from starting potential of 200 mV to -250 mV vs. Ag/AgCl.

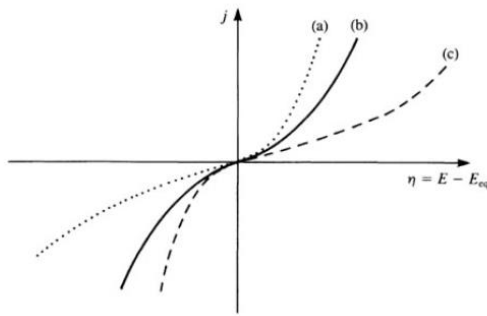
The corresponding potential-current diagram is recorded and the log values of these current values are plotted against the over potential as shown in figure below.



### 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  $\alpha_A$ , and  $\alpha_C$  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  $\alpha_C$  on current density is shown in the following plot.





The effect of the value of  $\alpha_c$  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  $\alpha_c$ .

### Results:

Run the linear scan voltammetry at scan rate of 10 mV s<sup>-1</sup> 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,  $\alpha_A$  and  $\alpha_C$  using equation (7).

## Experiment # 8

**Title of experiment:** Corrosion of two different metals

### **Aim:**

The objective of this experiment is to measure the corrosion rate of two different metals and to show the effectiveness of the use of inhibitors to protect metals from corrosion.

### **Introduction:**

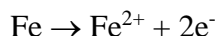
Corrosion is harmful to both humans and the economy. A little knowledge of the electrochemistry of corrosion and material science could save nations some 25% of this loss.

Corrosion is an electrochemical process that takes place at the metal (electrode) surface in contact with the corrosion medium (solution).

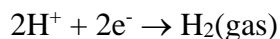
The first thing that must be understood in the corrosion process is whether a metal reacts with its environment. If so, the nature of the reaction must be understood. It is generally accepted that corrosion processes are caused by the formation of electrochemical cells. The electrochemical reactions in these cells can be divided into two reactions; anodic reactions and cathodic reactions usually called a half-cell reaction. In the anodic reaction, metal goes into solution as an ion:



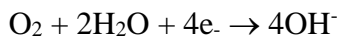
where M is a metallic element,  $e^-$  is an electron and n is the valence of the metal as an ion. An example of this is iron (Fe) where:



In the cathodic reaction, electrons provided by the anode, flow through the metal until they reach the cathode where they can be combined with positively charged ions. In acidic solutions, this reaction is:



Whereas in neutral solutions the reaction is:



Both the anodic and cathodic reactions must occur simultaneously for a corrosion process to proceed.

When a metal is placed in an electrolyte, an electrode potential develops that is related to the tendency (**but not the rate**) of the material to give up electrons (i.e. oxidize or corrodes). To

measure this tendency, the potential difference between the metal and a standard electrode using a half-cell is measured.

There various ways to express the rate of corrosion of a metal, such as weight loss, which is expressed as Mils penetration per year (mpy). This is mostly used by engineers. A more rapid method is to determine the corrosion rate electrochemically by measuring the current density ( $j$ ) expressed as

$$j = \frac{I}{A}$$

Where I is the current (in mA) and A is the area in (cm<sup>2</sup>)

**Materials:** Standard electrochemical three electrodes glass cell, iron, and brass metals, Ag/AgCl reference electrode, carbon counter electrode, 0.1M HCl, corrosion inhibitor, a potentiostat

**Procedure:**

- 1-Set up the electrochemical cell with a known volume of the HCl solution.
- 2-Polish the iron and brass metal with emery paper and wash with distilled water and dry.
- 3-Immerse the reference electrode and the counter electrodes and connect to the corresponding cables of the potentiostat.
- 4-Immerse the iron electrode in the cell and connect to the WE cable.
- 5-Wait for 15 minutes to stabilize the WE potential.
- 6-scan the potential with respect to the reference electrode in a potential of  $\pm 250\text{mV}$  at a scan rate of  $1\text{mV/s}$ .
- 7-Plot the current density on a log scale vs. potential as a Tafel plot and determine the corrosion potential, Tafel slopes for the anodic and cathodic branch of Tafel plot, and current density.
- 8-Add a certain amount of the corrosion inhibitor and determine the same electrochemical parameters in the presence of corrosion inhibitor.
- 8-Repeat the same procedure in steps and 8 using the brass electrode and determine the same parameters.

**Results:**

- 1- Graph the current density versus potential. Overlay the four graphs for comparison
- 2- Tabulate the results obtained above in the table below and compare the rate of corrosion of both metals and the effect of corrosion inhibitor on the observed electrochemical parameters

solution		Corrosion potential (mV)	Anodic slope	Cathodic Slope	Corrosion current density
0.1M HCl	Fe metal				
0.1M HCl+ inhibitor	Fe metal				
0.1M HCl	Brass metals				
0.1M HCl+ inhibitor	Brass metals				

- 3- Calculate the percentage of corrosion rate in the presence of inhibitor to that in the absence of corrosion inhibitor.
- 4- Write the possible anodic and cathodic reactions for both metals.

## Experiment # 9

**Title of experiment:** Cyclic voltammetric study of ferrocyanide/ferricyanide redox couple

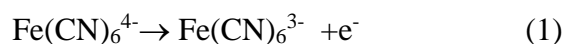
**Aim:**

To perform a cyclic voltammetric study of ferrocyanide/ferricyanide redox couple and show the reversibility of this system

**Introduction:** Cyclic voltammetry (CV) is a versatile electroanalytical technique for the study of electroactive species. CV monitors the 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,



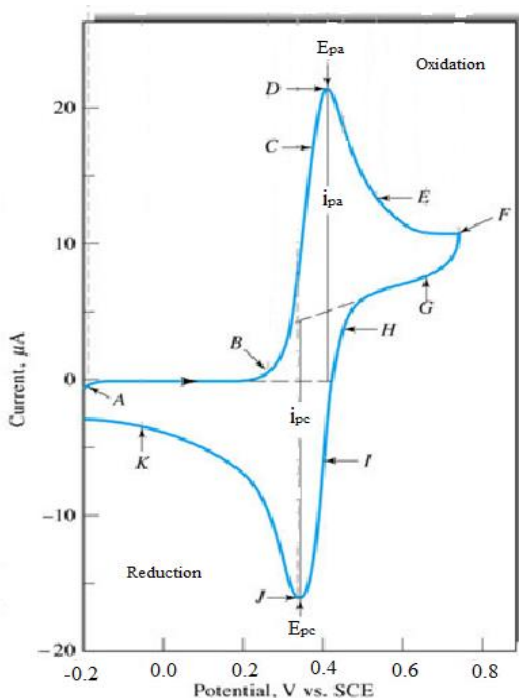
The electrode acts as an oxidant and the oxidation current increases to a peak. The concentration of  $\text{Fe}(\text{CN})_6^{4-}$  at the electrode surface depletes and the current then decays. As the scan direction is switched to negative, for the reverse scan the potential is still sufficiently positive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



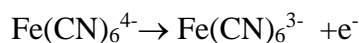
resulting in a cathodic current which peaks and then decays of  $\text{Fe}(\text{CN})_6^{3-}$  in the solution adjacent to the electrode is consumed.

In the forward scan  $\text{Fe}(\text{CN})_6^{3-}$  is electrochemically generated from  $\text{Fe}(\text{CN})_6^{4-}$  (anodic process) and in the reverse scan this  $\text{Fe}(\text{CN})_6^{3-}$  is reduced back to  $\text{Fe}(\text{CN})_6^{4-}$  (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 baseline 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:



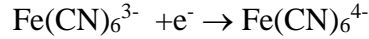
B.-D. Rapid increase in current as the surface concentration of  $\text{Fe}(\text{CN})_6^{4-}$  decreases

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

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

F. Scan direction switched (0.75 V), potential still positive enough to cause oxidation of  $\text{Fe}(\text{CN})_6^{4-}$

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



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  $E^{\circ}$ , 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.

$$E^{\circ'} = \frac{E_{pa} + E_{pc}}{2} \quad (3)$$

The number of electrons involved in the redox reaction for a reversible couple is related to the difference in peak potentials by:

$$E_{pa} - E_{pc} = \frac{57\text{mV}}{n} \quad (4)$$

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

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

$$i_p = 2.686 \times 10^5 n^{3/2} A C D^{1/2} \nu^{1/2} \quad (5)$$

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

Thus,  $i_p$  increases with the square root of  $\nu$  and is directly proportional to the 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. The ratio of peak currents may differ from unity if the reactions coupled to another electrode process.

### Materials:

Potentiostat, glassy carbon working electrode (radius 3.0 mm), platinum auxiliary electrode,

Ag/AgCl reference electrode, nitrogen cylinder, polishing material. 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 1.0 M

potassium nitrate solution, 1.0 M KNO<sub>3</sub> (matrix), Unknown: K<sub>3</sub>Fe(CN)<sub>6</sub> in 1.0 M KNO<sub>3</sub>, 1000ppm K<sub>3</sub>Fe(CN)<sub>6</sub> 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<sub>3</sub>Fe(CN)<sub>6</sub> in 1.0 M KNO<sub>3</sub>. 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 the 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 the 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 to determine the concentration of the unknown solution



## Experiment # 10

**Title of experiment:** hydrogen evolution reaction overpotential on different electrodes

### Aim:

1-To show that hydrogen evolution takes place at different potentials depending on the electrode material (Pb, Ag).

2- To determine the overvoltage, the exchange current density, and Tafel slope for the hydrogen evolution reaction on two metals.

### Introduction:

The potential  $E$  at which a reaction takes place depends on the nature and physical condition of the electrode surface.  $E$  is different from the reversible potential  $E_e$ , given by the Nernst equation. The difference between these potentials is a direct measure of the irreversibility of the electrochemical process and is known as the overvoltage or overpotential,

$$\eta = E - E_e \quad (1)$$

Basic electrode kinetics shows that the overpotential ( $\eta$ ) is correlated to the rate of the electrode reaction given by the current density ( $j$ ) using the known Tafel equation expressed as

$$\eta = a - b \log j \quad (2)$$

Whereas  $b$  is the Tafel slope.

$J$  is calculated by the dividing current ( $I$ ) by the electrode area ( $A$ ) i.e.

$$j = \frac{I}{A} \quad (3)$$

At equilibrium, the net current density is zero which means that the rate of the anodic and cathodic reaction is equal. At this case the current density is known as the exchange current density ( $j_o$ ):

$$\eta = 0 \quad \log j_o = a/b \quad (4)$$

Exchange current density is considered as a measure of the rate of reaction on the electrode surface.

The higher the value of  $j_o$  the higher the rate and the lower the value of  $\eta$ .

From equation (4) the value of  $j_o$  depends on both the reaction and electrode nature.

### Materials:

Standard electrochemical three electrodes glass cell, Ag/AgCl reference electrode, carbon counter electrode, 0.1M H<sub>2</sub>SO<sub>4</sub> solution, a potentiostat, Pb, and Ag electrodes.

### Procedure:

1-Set up the electrochemical cell with a known volume of the H<sub>2</sub>SO<sub>4</sub> solution.

2-Polish the Pb and Ag metals with emery paper and wash with distilled water and dry.

- 3- Immerse the reference electrode and the counter electrodes and connect to the corresponding cables of the potentiostat.
- 4- Immerse the Pb electrode in the cell and connect to the WE cable.
- 5- Wait for 15 minutes to stabilize the WE potential.
- 6- Scan the potential with respect to the reference electrode in a potential of - 250mV at a scan rate of 0.5mV/s.
- 7- Plot the current density on a log scale vs. potential as a Tafel plot and determine the overpotential at 10 mA/cm<sup>2</sup>, cathodic Tafel slope of Tafel plot, and exchange current density.
- 8- Repeat the same procedure in steps and 7 using the Ag electrode and determine the same parameters

**Results:**

- 1- Graph the log current density versus the potential for both metals. Overlay the two graphs for comparison.
- 2- Tabulate the results obtained above in the table below and compare the rate of hydrogen evolution reaction on both metals on the observed electrochemical parameters

Electrode	Overpotential (mV) @ 10 mA/cm <sup>2</sup>	Cathodic Slope (mV/dec)	Exchange current density (mA/cm <sup>2</sup> )
Pb			
Ag			

- 3- Based on the mechanism of HER, suggest the possible mechanism on both electrodes.