

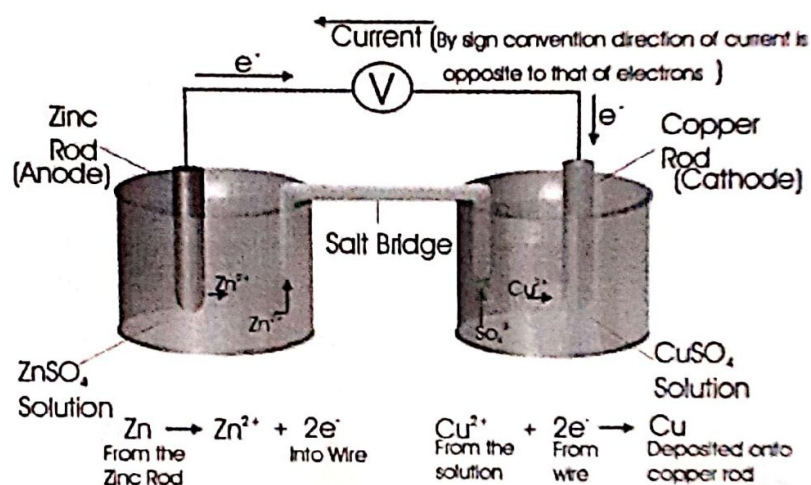
Construction and working of an electrochemical cell

An Electrochemical Cell is a device used to convert chemical energy (produced in a redox reaction) into electrical energy. Electrochemical Cells are also known as Galvanic Cells.

If we take a zinc rod and place it in a container filled with copper sulphate solution, heat will be produced. This happens due a spontaneous redox reaction given below:



As the reaction would proceed, the zinc rod would get eroded and copper particles would get deposited and solution would become warm.



An Electrochemical Cell

The oxidation reaction in the zinc rod releases 2e^- and are taken by the Copper ion in the CuSO_4 solution. If these two half reactions can be separated, then the electrons can be made to move through a wire. In this manner, we can produce electrical energy from chemical energy. The salt bridge is a concentrated solution of inert electrolytes. It is required for completing the circuit. It allows the movement of ions from one solution to the other.

Applications: Electrochemical cell would be useful to be able to convert this chemical energy to electrical energy (in Battery) instead of heat energy. This process is also used in electroplating industry to coat Fe metal with Zn/Al coatings.

Expt. No.:

Date:

| | |
|----------------------------------|---|
| Experiment | Construction and working of an Zn-Cu electrochemical cell |
| Problem definition | Measurement of electrode potential and construction of a battery system |
| Methodology | Single electrode potentials of Zn/Zn^{2+} and Cu/Cu^{2+} system and Daniel Cell |
| Solution | Electromotive force measurement (EMF) as voltage |
| Student learning outcomes | Students will learn to perform a) Electrode potential relevant to battery b) Understanding of a normal battery system |

Principle: The electromotive force (emf) of an electrochemical cell is measured by means of a potentiometer. An electrochemical cell (E_{cell}) is considered as a combination of two individual single electrodes. The potential difference between the two single electrode potentials is a measure of emf of the cell (E_{cell}). In order to measure the potential difference between electrodes in contact with electrolyte containing the same cation, it is necessary to have another electrode in contact with electrolyte of same cation, both the half-cells connected through a salt bridge. Saturated calomel electrode (SCE; E_{calomel}) whose potential is known, is used as a reference electrode and it is coupled with the metal electrode for which the potential is to be determined.

Hg / Hg₂Cl₂ (s), saturated KCl || (N/10) electrolyte of the metal / Metal

From the emf of the cell involving saturated calomel electrode and metal electrode dipped in its solution of 0.1 N electrolyte, electrode potential of the metal electrode is readily calculated using the standard potential of calomel electrode as;

$$E_{\text{cell}} = E_{\text{M/M}^+} - E_{\text{calomel}}$$

$$E_{\text{M/M}^+} = E_{\text{cell}} + E_{\text{calomel}}$$

E_{cell} is total emf of the cell. Electrode potential of the metal electrode is given by Nernst equation as;

$$E_{\text{M/M}^+} = E^{\circ} + \frac{RT}{nF} \ln a_{\text{M}^{n+}}$$

$$E_{\text{M/M}^+}^{\circ} = E_{\text{M/M}^+} - \frac{RT}{nF} \ln a_{\text{M}^{n+}}$$

$$E_{\text{M/M}^+}^{\circ} = E_{\text{M/M}^+} - \frac{0.0595}{n} \log a_{\text{M}^{n+}}$$

Requirements:

Reagents and solutions: CuSO₄ stock solution (0.1N), ZnSO₄ stock solution (0.1N), KCl salt.

Apparatus: Digital potentiometer, copper electrode, zinc electrode, calomel electrode, 100 mL beaker, burette, 50 ml standard flasks.

Procedure:

Calibrate the digital potentiometer with the help of the wires to display 1.018 V. The metal electrode is sensitized by dipping in a small quantity of 1:1 nitric acid containing a small quantity of sodium nitrite until effervescence occurs. Then the electrode is washed well with distilled water. 50 mL of the given concentration of the electrolyte solution (0.01 N, 0.05 N and 0.1 N) is taken in a beaker and its corresponding metal electrode is introduced. This is connected with the saturated calomel electrode (half-cell) by means of a salt bridge. The metal electrode is connected to the positive terminal and the calomel electrode is connected to the negative terminal of the potentiometer. EMF of the cell (E_{cell}) is measured and noted in Table 1. Standard electrode potential [$E^{\circ}_{M/M^{2+}}$] is computed using Nernst equation (Eq. 1).

Table 1: EMF measured for various concentrations of M/M^{n+} system

| Electrode/ Electrolyte | Electrolyte conc. (N) | E_{cell} (V) | $E_{M/M^{n+}} =$ $E_{\text{cell}} + E_{\text{calomel}}$ | $E^{\circ}_{M/M^{n+}}$ [From Eq. (1)] | Average $E^{\circ}_{M/M^{n+}}$ |
|---------------------------|--------------------------|-----------------------|--|--|-----------------------------------|
| Zn/Zn ²⁺ | 0.01 N | -1.035 | -0.791 | -0.728 | -0.757 |
| | 0.05 N | -1.043 | -0.799 | -0.753 | |
| | 0.1 N | -1.072 | -0.828 | -0.789 | |
| Cu/Cu ²⁺ | 0.01 N | 0.037 | 0.281 | 0.344 | 0.344 |
| | 0.05 N | 0.046 | 0.290 | 0.335 | |
| | 0.1 N | 0.051 | 0.295 | 0.334 | |

Solution Temperature (T) = °C; Potential of SCE = 0.244 + 0.0007 (25 °C)

$$E^{\circ}_{M/M^{n+}} = E_{M/M^{n+}} - \frac{0.0595}{n} \log [\gamma_c \times C] \text{ ----- (1)}$$

where, E° is standard electrode potential of metal electrode; $a_{M^{n+}}$ is activity of metal ions in solution ($a_{M^{n+}} = \gamma_c[C]$); γ_c is activity coefficient (Table 2) and C is concentration of electrolyte solution.

Table 2: Individual activity coefficients of Cu²⁺ and Zn²⁺ in water at 25 °C

| Metal ion system (Cu ²⁺ /Zn ²⁺) | 0.001 | 0.002 | 0.005 | 0.01 | 0.02 | 0.05 | 0.1 | 0.2 |
|---|-------|-------|-------|-------|-------|-------|-------|-------|
| Activity coefficient (γ_c) | 0.905 | 0.870 | 0.809 | 0.749 | 0.675 | 0.570 | 0.485 | 0.405 |

Use this space for detailed calculation

Construction of Daniel cell and measurement of its voltage with three different concentrations of Cu/Zn solutions:

In the Daniel cell, copper and zinc electrodes are immersed in the equimolar solution of CuSO_4 and ZnSO_4 respectively.

At the anode, zinc is oxidized as per the following half-reaction: $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^-$

At the cathode, copper is reduced as per the following reaction: $\text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)}$

The overall reaction is: $\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$

Construct Daniel cell using the following concentrations of Copper and Zinc solutions and record the voltage of the cells in Table 3.

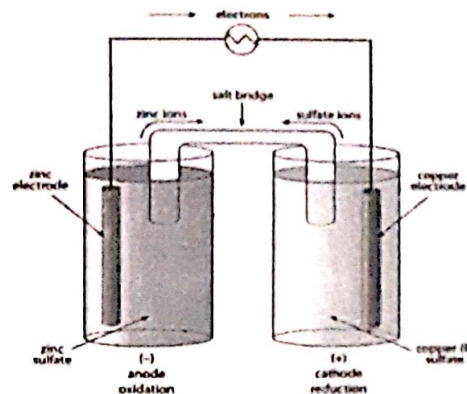


Table 3: EMF of Daniel Cell observed from three different conc. of Zn and Cu solutions

| Metal | Concentration (N) | Metal | Concentration (N) | EMF observed ($E_{\text{cell}} / \text{V}$) |
|----------------------------|-------------------|----------------------------|-------------------|---|
| Zn/Zn^{2+} | 0.01 N | Cu/Cu^{2+} | 0.01 N | 1.063 |
| | 0.02 N | | 0.02 N | 1.081 |
| | 0.05 N | | 0.05 N | 1.096 |
| Average | | | | 1.080 |

Results:

(a). Standard electrode potential of Copper (E°) = 0.344 vs. SCE

(b). Standard electrode potential of Zinc (E°) = -0.757 vs. SCE

(c). EMF of the constructed Daniel cell = 1.080

Evaluation of result:

| Sample No. | Experimental Value | Actual Value | Percentage of error | Marks awarded |
|---|--------------------|--------------|---------------------|---------------|
| a) $E^\circ_{\text{Cu}/\text{Cu}^{2+}}$ | | | 1% error | |
| b) $E^\circ_{\text{Zn}/\text{Zn}^{2+}}$ | | | | |
| c) EMF of Daniel cell | | | | |