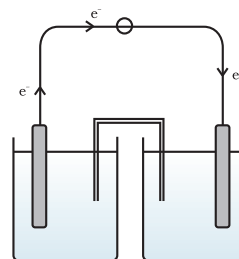


UNIT-4

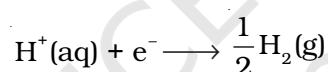
ELECTROCHEMISTRY



THE potential difference between two electrodes of a galvanic cell is called **Cell Potential** and is measured in volts. It is the difference between the reduction potentials (or oxidation potentials) of the cathode and anode. When no current is drawn from the cell it is called electromotive force (emf) of the cell.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The potential of individual half-cells cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. According to convention, standard hydrogen electrode represented by Pt, H_2 (g, 1 bar)/ H^+ (aq, 1M) is assigned zero potential at all temperatures corresponding to the reaction.

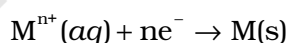


Half cell potentials are measured with respect to standard hydrogen electrode.

A cell is constructed by taking standard hydrogen electrode as anode (reference half cell) and under standard conditions of which cell potential is to be measured, is made cathode the other half cell. Then the cell potential is equal to the standard electrode potential of the other half cell.

$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} \text{ because } E_{\text{anode}}^{\ominus} = 0$$

Nernst showed that electrode potential of a cell with respect to standard hydrogen electrode can be measured at any concentration. For the electrode reaction of the type:



The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{M}]}{[\text{M}^{n+}]}$$

the concentration of solid M is taken as unity and we have

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\ominus} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

Here R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), F is Faraday constant (96487 C mol^{-1}), T is the temperature in Kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+} .

In the following experiment the variation in the cell potential of $\text{Zn}/\text{Zn}^{2+} \parallel \text{Cu}^{2+}/\text{Cu}$ cell with concentration of electrolytes will be studied.

EXPERIMENT 4.1

Aim

To study the variation in cell potential of the cell $\text{Zn}/\text{Zn}^{2+} \parallel \text{Cu}^{2+}/\text{Cu}$ with change in concentration of electrolytes ($\text{CuSO}_4/\text{ZnSO}_4$) at room temperature.

Theory

The cell under investigation in this experiment is represented as follows:



Here $x\text{M}$ denotes varying concentrations of $\text{Cu}^{2+}(\text{aq})$ ions. In other words, to study the variation in cell potential with concentration, the concentration of $\text{Cu}^{2+}(\text{aq.})$ is varied while that of $\text{Zn}^{2+}(\text{aq.})$ is kept constant. The measured cell potential enables us to calculate the electrode potential of Cu^{2+}/Cu electrode for each concentration of copper (II) ions. This variation is theoretically depicted according to the equation:

$$E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} + \frac{0.059}{2} \log[\text{Cu}^{2+}] \quad (1)$$

The variation in the electrode potential of Cu^{2+}/Cu electrode consequently brings variation in the cell potential according to the relation:

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} \quad (2)$$

Equation (2) clearly suggests that even if $E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus}$ is kept constant, the variation in $E_{\text{Cu}^{2+}/\text{Cu}}$ would bring corresponding variation in E_{cell} (cell potential). Similarly, keeping the concentration of Cu^{2+} ions constant, one can study the variations in the cell potential with the variation in concentration of Zn^{2+} ions.

Material Required



- Zinc plate : One
- Copper plate : One
- Beaker (50 mL) : Six
- Voltmeter (Potentiometer) : One
- Salt bridge : One



- 1.0M Zinc sulphate solution : 40mL
- 0.25 M, 0.1M, 0.05M, 0.025 M and 0.0125M Copper sulphate solutions : 40 mL each

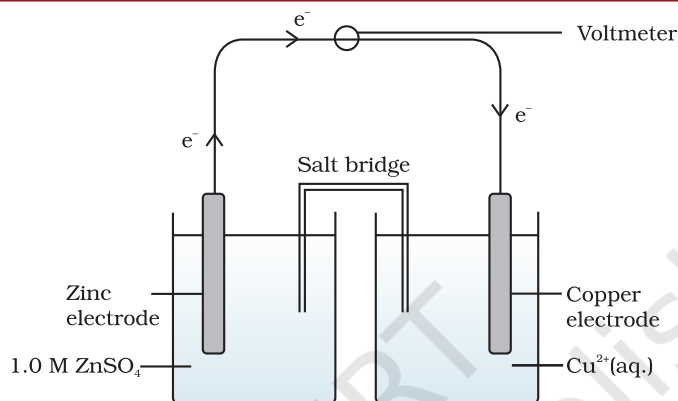


Fig. 4.1 : Set up of $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq.}), (1.0\text{M}) \parallel \text{Cu}^{2+}(\text{aq.}, x\text{M})/\text{Cu(s)}$ cell

Procedure

- (i) Set up the cell as given in Fig. 4.1, using 1.0 M ZnSO_4 and 0.2 M CuSO_4 solution.
- (ii) Measure the potential difference of the cell and also keep record of the polarity of the electrodes (this will enable us to give a sign to the cell potential E_{cell}).
- (iii) Remove the salt bridge as soon as the cell potential measurement is over.
- (iv) Replace the beaker of 0.2 M CuSO_4 with 0.1 M CuSO_4 solution in the beaker. Place the salt bridge in position and note the cell potential.
- (v) Repeat this procedure for other solutions of copper sulphate in decreasing order of concentrations of copper sulphate solution.
- (vi) Calculate $\log [\text{Cu}^{2+}(\text{aq})]$ and then $E_{\text{Cu}^{2+}/\text{Cu}}$ for each variation in the concentration of copper (II) in the solution.
- (vii) Record electrode potential values of $\text{Cu}^{2+}(\text{aq})/\text{Cu(s)}$ electrode for different concentrations of Cu^{2+} ions as given in Table 4.1.
- (viii) Plot a graph for the variation of cell potential with concentration taking ($E_{\text{Cu}^{2+}/\text{Cu}}$) on y -axis and $\log [\text{Cu}^{2+}(\text{aq})]$ on x -axis.

Table 4.1 : Record of the Cell Potential Data

Sl. No.	[Cu ²⁺ (aq)]/mol L ⁻¹	log [Cu ²⁺ (aq)]/mol L ⁻¹	E _{cell} /V	E _(Cu²⁺/Cu) Experimental value
1.	0.2			
2.	0.1			
3.	0.05			
4.	0.025			
5.	0.0125			

Result

Write conclusion on the basis of data obtained.

Precautions

- Clean copper and zinc strips and connecting wires with sand paper before use.
- Place the salt bridge immediately in distilled water after its use.
- Carry out dilution of the solution to another concentration very carefully.
- Choose appropriate scales for plotting the graph.



Discussion Questions

- For the reaction given below, apply Le-Chatelier principle to justify the results recorded by you and also bring out mathematical rationalisation of your results.

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)},$$
- Determine the slope of the graph. Match experimental value with the theoretical value. On what factors does the value of slope depend?
- Devise another experiment to study the variation in cell potential with concentration of one of the ions involved in a cell reaction.
- What factor is kept in mind while selecting an electrolytic solution for the construction of a salt bridge?
- Is it possible to measure the single electrode potential?