Electrochemistry

B.Sc. 4th Sem (H)

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By

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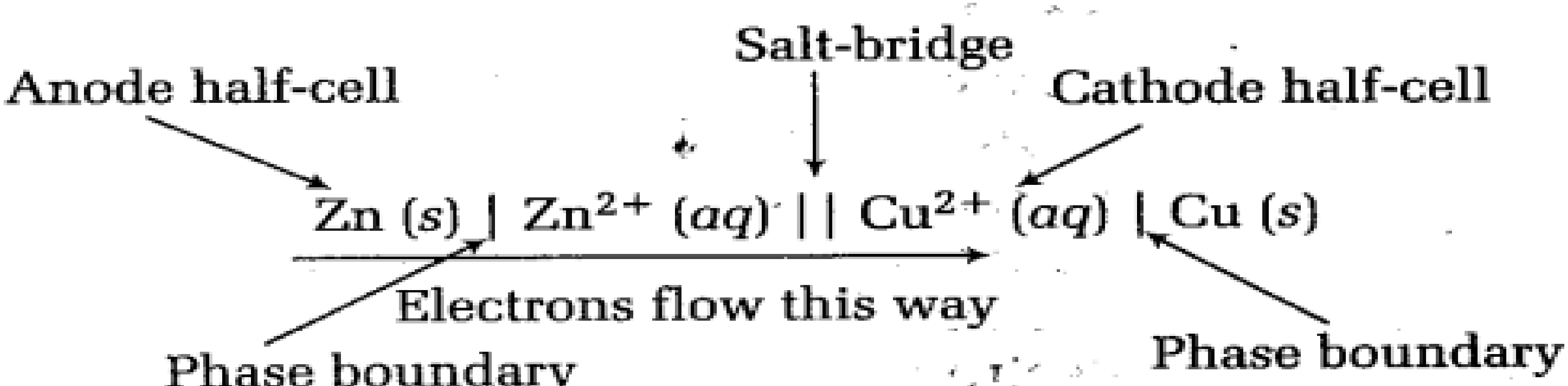
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

In writing a cell diagram, following points are considered. We divide the cell into two half-cells

	The anode	**The cathode**
Reaction	Oxidation takes place	Reduction takes place
	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
Terminal	Negative	Positive
Side	LHS	RHS
Diagram	$Zn\,(s) \mid Zn^{2+}\,(aq)$	$Cu^{2+}(aq) \mid Cu(s)$

Complete cell diagram may be represent as follows

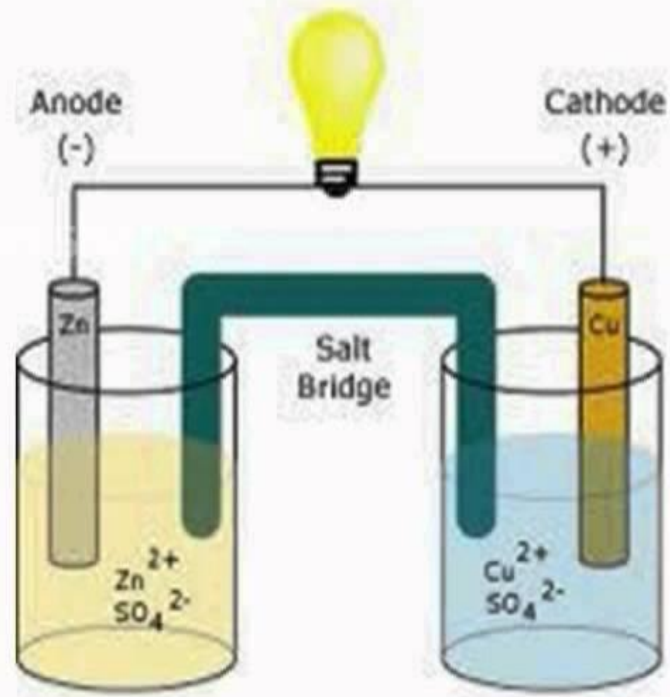


Emf of cell or cell potential

- The *cell potential or emf of cell* is the difference between the electrode potentials (reduction potentials) of the cathode and anode

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

  $= E_{right} - E_{left}$



- $E_{cell} = E_{right} - E_{left}$

  $= E_{Cu^{2+}{}_{(aq)}/Cu_{(s)}} - E_{Zn^{2+}{}_{(aq)}/Zn_{(s)}}$

  $= .34 - (-.76)$

  $= 1.10\ V$

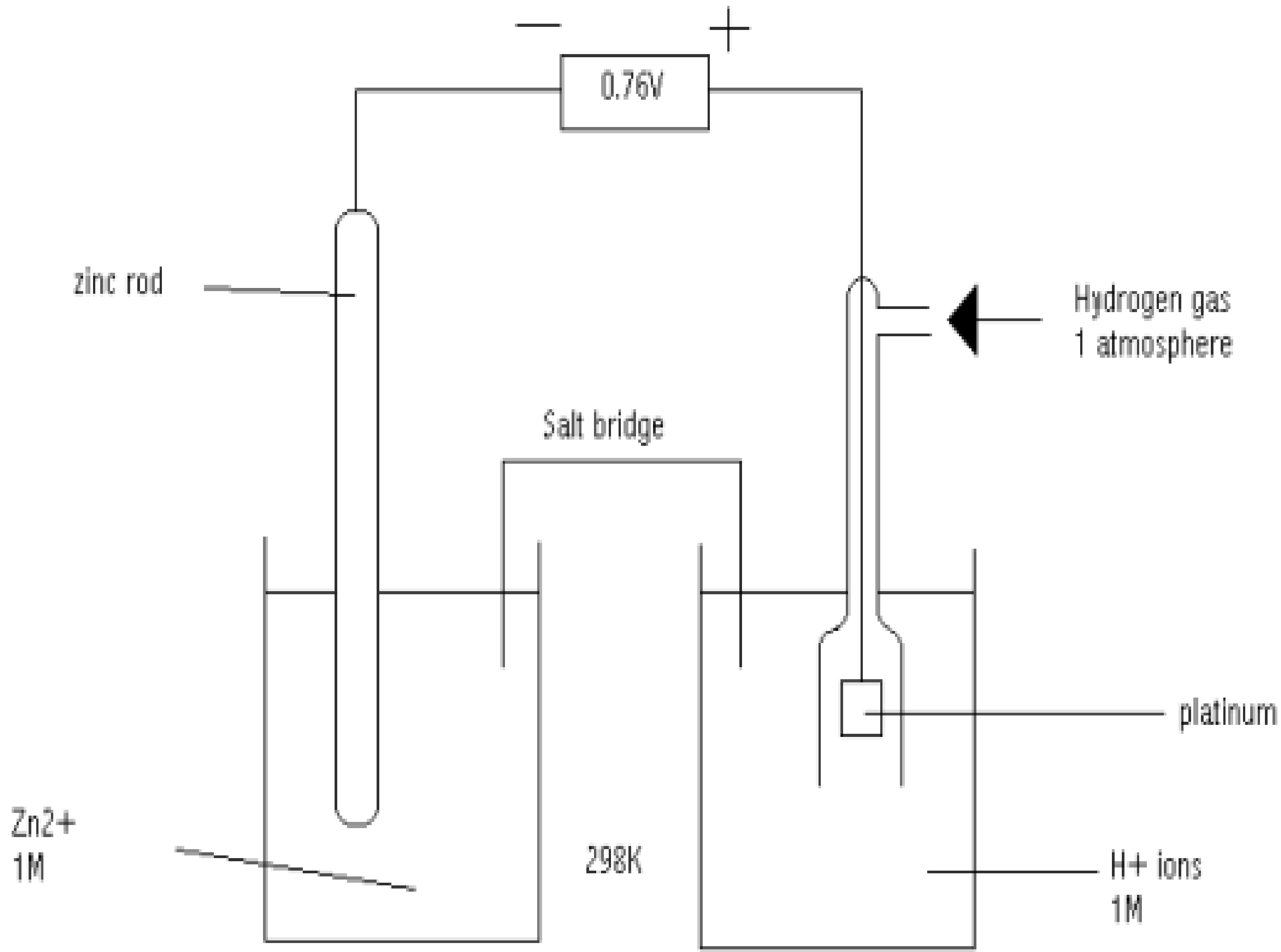
Electrode potential

- The tendency of a metal to get oxidised or reduced when it is placed in a solution of its own salt is called electrode potential.
- When a metal [M] is placed in a solution containing its own ions [M^{n+}], then the metal may undergo either oxidation or reduction. If the metal undergoes oxidation, then the positive metal ions may pass into the solution

$$M \longrightarrow M^{n+} + ne^-$$

- If the metal undergoes reduction, then the negative ions may get deposited over the metal.

$$M^{n+} + ne^- \longrightarrow M$$



−
+
0.76V
zinc rod
Hydrogen gas
1 atmosphere
Salt bridge
platinum
Zn2+
1M
298K
H+ ions
1M

Electrode potential, *E*, in chemistry or electrochemistry, according to a IUPAC definition,[1] is the electromotive force of a cell built of two electrodes:

- on the left-hand side of the cell diagram is the standard hydrogen electrode (SHE), and
- on the right-hand side is the electrode in question.

The SHE is defined to have a potential of 0 V, so the signed cell potential from the above setup is

$$E_{\text{cell}} = E_{\text{left (SHE)}} - E_{\text{right}} = 0\text{ V} - E_{\text{electrode}} = E_{\text{electrode}}.$$

Reversible Cells

A reversible cell is a cell in which the driving and opposing force differ infinitesimally small amount from each other and the chemical change taking place in it can be reversed by applying an external force infinitesimally greater than the emf of the cell. A reversible cell should satisfy the following conditions:

i)When the external emf of the cell is infinitesimally greater than the emf of the cell, then current should flow through the cell and the cell reaction of the cell should get reversed.

Ii) When the external emf of the cell is infinitesimally less than the emf of the cell, then current should flow from the cell.

iii) When the external emf of the cell is exactly equal to the emf of the cell, then no current should flow through the cell

REVERSIBLE AND IRREVERSIBLE CELLS

Reversible Cells

Daniel cell, secondary batteries (rechargeable batteries). Daniel cell is a very good example for a reversible cell. Its emf is 1.1 volt. It is represented as

$$Zn/ZnSO_4(1\ M)//CuSO_4\ (1\ M)/Cu.$$

A cell which obey the following three conditions of thermodynamic reversiblity is called reversible cell.

(i) If the daniel cell is connected to an external source of emf equal to 1.1 volt, no current flows and also no chemical reaction takes place in the cell.

(ii) If the external emf is made slightly less than 1.1 volt, small amount of current flows from the cell and small chemical reaction occurs.

(iii) If the external emf is made slightly greater than 1.1 volt, the current will flow in the opposite direction. Copper will pass into the solution as copper ions and zinc will get deposited on the zinc electrode.

Irreversible Cells

Zinc – silver cell, Dry cell (Primary Cells)

Cells which do not obey the conditions of thermodynamic reversibility are called irreversible cells. Zinc-Silver cell is an example for a irreversible cell. It is represented as

$$Zn/H_2SO_4(aq)/Ag$$

The cell reactions occur at anode and cathode are,

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow \text{ (at anode)}$$

$$2Ag^+ + 2e^- \longrightarrow 2Ag \text{ (at cathode)}$$

Reversible electrochemical cells are the cells whose cell reactions can be get reversed when an external emf greater than its capacity is applied. (A cell which obeys thermodynamic conditions of reversibility is known as reversible cells).

For example

Daniel cell is a galvanic cell with capacity of 1.1 V, when an external emf of 1.1 V is applied, the cell reaction stops.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

But when an increased amount of emf greater than 1.1 V is applied, the cell reaction is get reversed.

$$Zn^{2+} + Cu \longrightarrow Zn + Cu^{2+}$$

Irreversible cell

A cell is irreversible if the cell reaction cannot be reversed e.g., the cell

$$\mathbf{Zn} \mid \mathbf{H_2SO_4} \mid \mathbf{Cu}$$