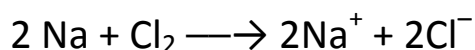


Electro chemistry

2- ELECTROCHEMICAL CELLS

Let us consider the reaction



It occurs by the transfer of electrons from Na to Cl. Na loses an electron and is said to be oxidized to Na⁺ ion. At the same time, Cl gains an electron and is reduced to Cl⁻ ion. Such a reaction which is brought about by loss of electrons (oxidation) and gain of electrons (reduction) simultaneously, is called an **Oxidation-Reduction reaction or Redox reaction** in brief.

2-1 Types of electrodes

1- Metal-Metal ion electrodes

A metal rod that dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode

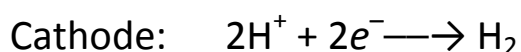
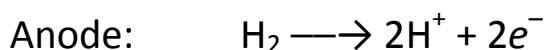


The potential of a single electrode in a half-cell is called the **Single electrode potential**. So the Nernst eq. takes the form:

$$E = E^\ominus - \frac{RT}{zF} \ln a_{\text{M}^{n+}}$$

2--Gas electrode (Standard Hydrogen Electrode (SHE))

Electrode gases like H_2 , Cl_2etc. are used with their respective ions , for example: H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.



This electrode is also used to measure other potentials (**emf**). Its own potential is est to 0v as a reference , the Con. Of HCl is 1M and the electrode is called **Standard Hydrogen Electrode (SHE)** ,(fig.6)

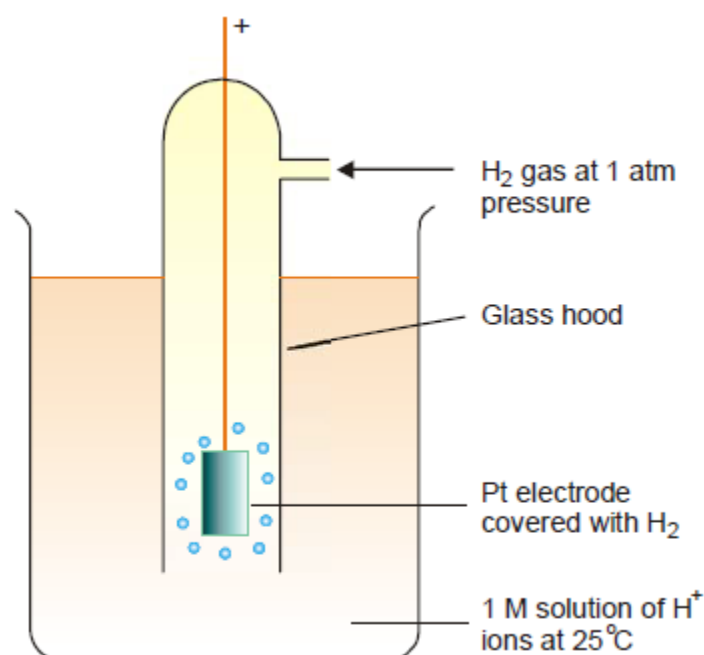


Fig.6: **Standard Hydrogen Electrode (SHE)**

The emf of the unknown half-cell, E° , can then be calculated from the expression

$$E_{\text{measured}} = E_R - E_L$$

where E_R and E_L are the **reduction potentials** of the right-hand and left-hand electrodes respectively, The standard hydrogen half-cell or **Standard Hydrogen Electrode (SHE)**, is selected for coupling with the unknown half-cell.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

Example/ it is desired to determine the emf of the zinc electrode, $Zn | Zn^{2+}$. It is connected with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

$$\begin{aligned} E_{\text{cell}} &= E_R - E_L \\ &= -0.76 - 0 = -0.76 \text{ V} \end{aligned}$$

- 0.76 V is the emf for Zn

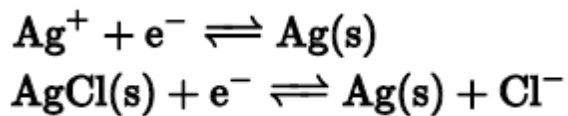
3- Metal- insoluble salt electrode

The standard hydrogen electrode (SHE) is not the most convenient standard electrode to use in the laboratory. The gas has to be carefully controlled. Metal- insoluble salt electrode system whose potential has been determined relative to the SHE can also be used as Secondary standard electrode.

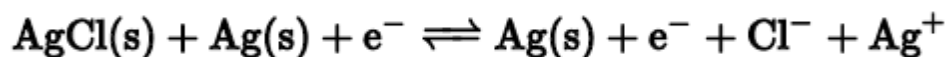
a-The Standard Silver-Silver chloride Electrode:

In this electrode system, silver wire is covered with silver chloride (a highly insoluble substance). It is dipped in potassium chloride solution in which the concentration of Cl^- ion is 1 M This electrode can be represented as

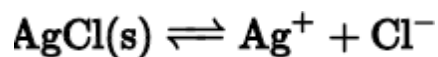
The corresponding half-reactions can be presented as follows:



or can be written together:



which can be simplified:



The Nernst equation below shows the dependence of the potential of the silver-silver(I) chloride electrode on the activity or effective concentration of chloride-ions:

$$E = E^0 - \frac{RT}{F} \ln a_{\text{Cl}^-}$$

The standard electrode potential E^0 against standard hydrogen electrode (SHE) is 0.230 V

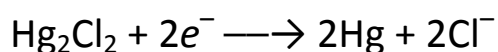
b- The Calomel Electrode

It is the most commonly used secondary standard reference electrode. The standard calomel electrode, **SCE**,

The calomel electrode is represented as



and the half-cell reaction is:



4- Glass Electrode

A commonly used secondary standard electrode is the so-called glass electrode. Its emf is determined by coupling with a standard calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A simple type of glass electrode (Fig. 7) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains a 1M HCl solution. Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode.

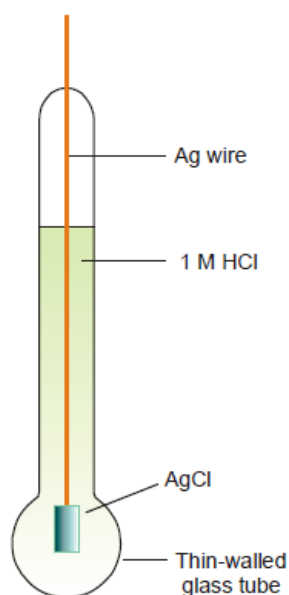
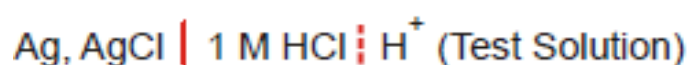


Fig. 7:glass electrode

The glass electrode represented as



When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential

develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

The potential Equation of a glass electrode can be determined :

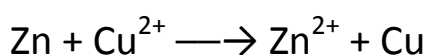
$$E = E^\circ + \frac{2.303RT}{nF} \text{ PH}$$

2-ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

1- Galvanic Cells

A **galvanic cell**, also known as a **Voltaic cell** one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown in Fig. 5. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.



A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

The oxidation half-reaction occurs in the **anode** compartment.



The reduction half-reaction takes place in the **cathode** compartment.

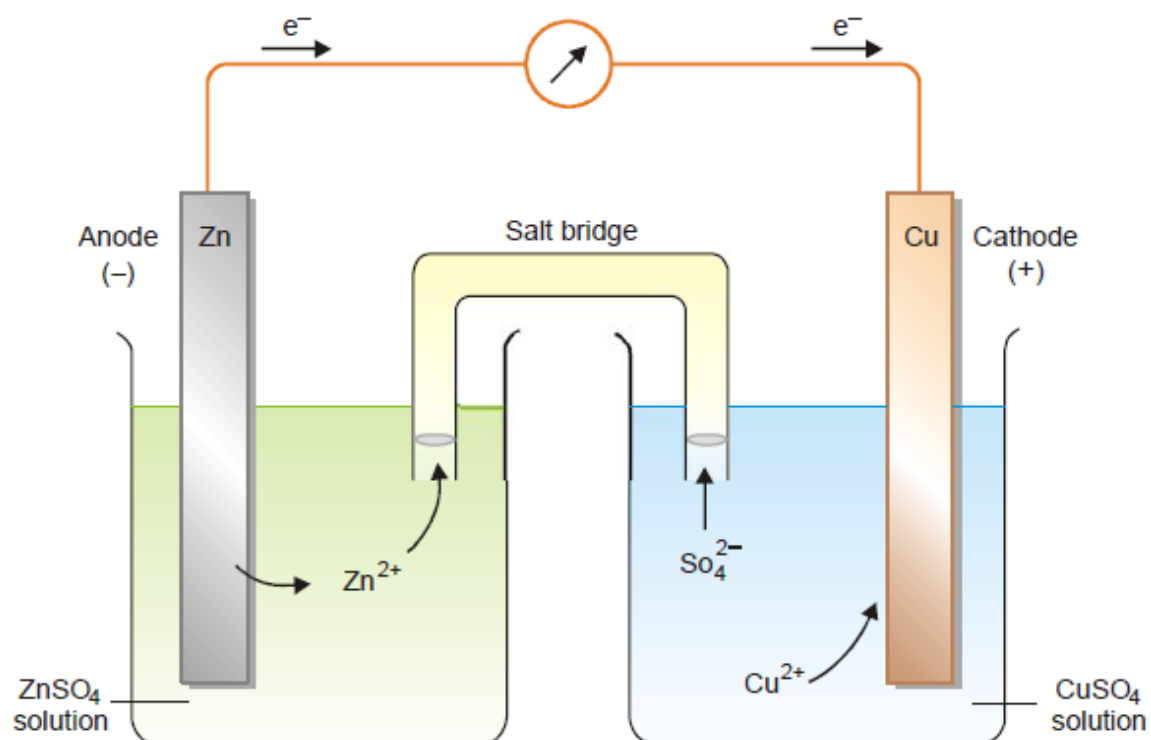
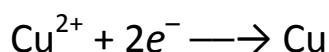


Fig. 5: A simple galvanic cell

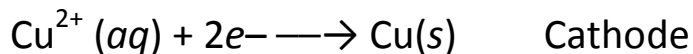
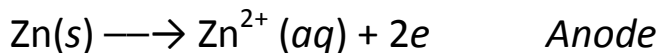
When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time, SO_4^{2-} ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensure continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up

Cell reaction:

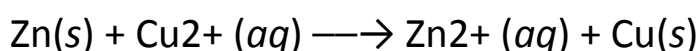
The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change

obtained by adding the two half-reactions is called the **cell reaction**. Thus, for a simple voltaic cell described above, we have

(a) Half-reactions :



(b) Cell reaction(cell over all reaction) by adding up the half-reactions



Cell diagram or Representation of a Cell

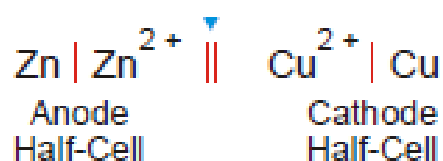
In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a **single vertical line (|)** represents a phase boundary between metal electrode and ion solution (electrolyte).

(2) A **double vertical line (||)** represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left and cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as



Calculating the emf (electromotive force) of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

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

$$= E_R - E_L$$

Let us predict the emf of the cell



by using the E° values from the Table

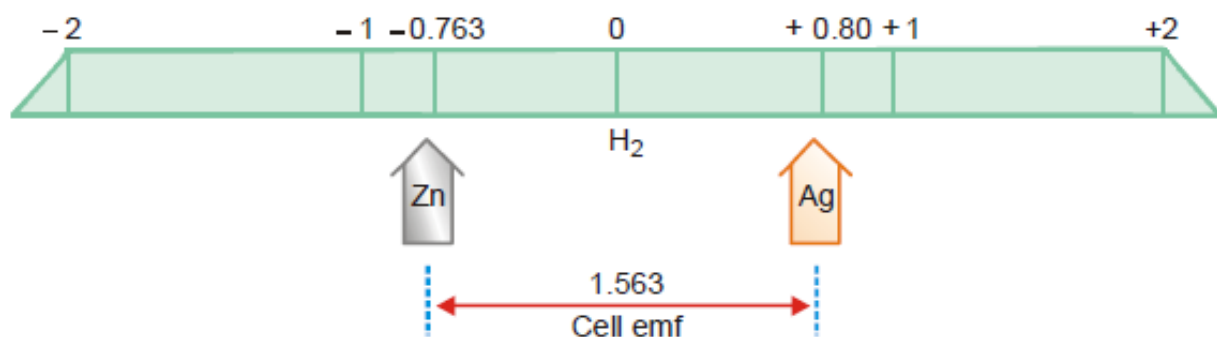
$$E^\circ_{\text{cell}} = E^\circ_R - E^\circ_L$$

$$= 0.80 - (-0.763)$$

$$= 0.80 + 0.763$$

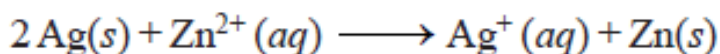
$$= 1.563 \text{ V}$$

The answer is so clear from Fig. 29.12.



■ **Figure 29.12**
Diagrammatic representation of Cell emf.

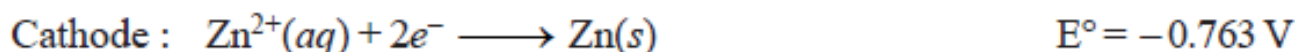
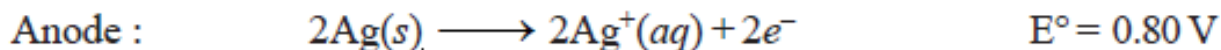
SOLVED PROBLEM 1. Predict whether the reaction



is feasible or not. Consult the table for the E° values.

SOLUTION

The cell half reactions are



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

$$\therefore E^\circ_{\text{cell}} = -0.763 \text{ V} - 0.80$$

$$= -1.563$$

Since E°_{cell} is negative, the given reaction is **not feasible**.

2-1 Electrolytic Cell

Electrolysis: The decomposition of some substance by means of an electric current.

Electrolytic Cell: A cell that requires electrical energy to cause nonspontaneous oxidation-reduction reactions to occur.

- 1- It utilizes an external source of electrical energy.
- 2- It forces electrons to flow in the opposite direction by applying a voltage greater than the cell potential.
- 3- It converts electrical energy into chemical energy
- 4- A salt bridge can be used in the Electrolytic Cell or not used

Voltaic Cell

Electrolytic Cell

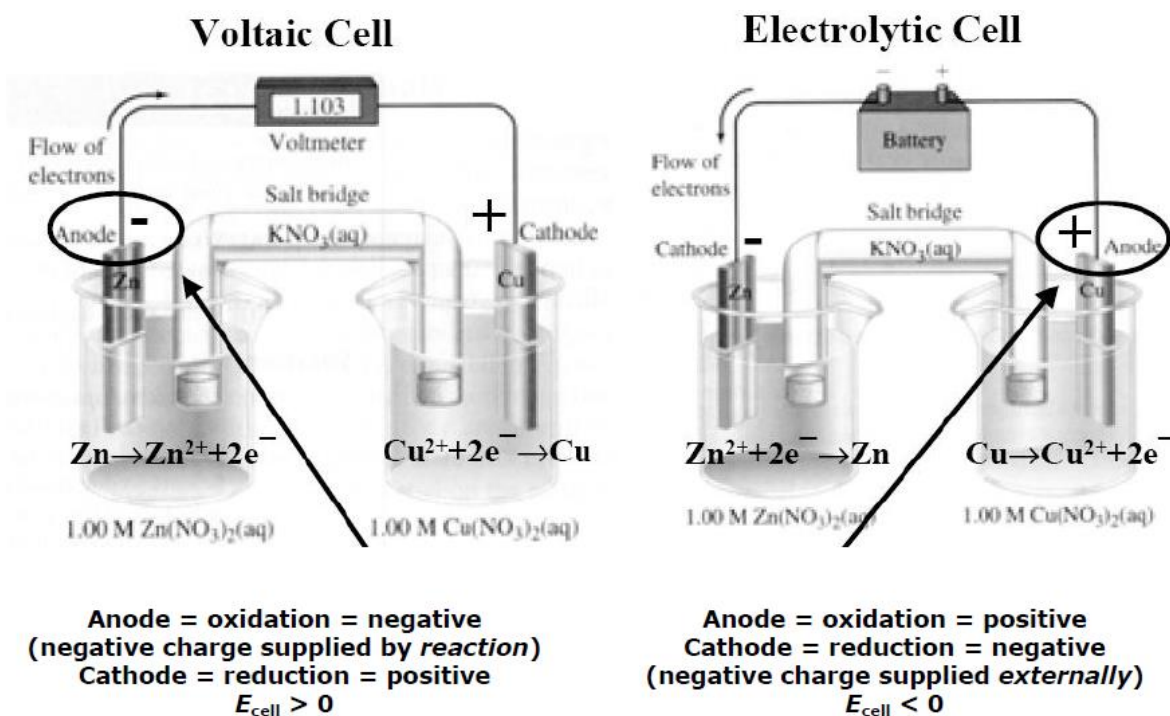
Spontaneous redox

Nonspontaneous redox

reaction releases energy

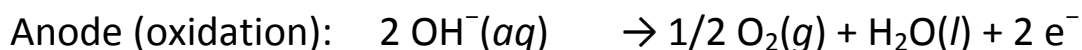
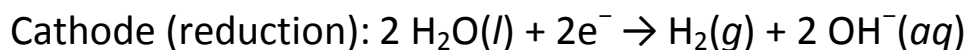
reaction absorbs energy to

drive it

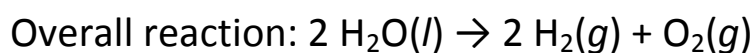


Another Example of electrolytic cells :

Electrolysis of water: is the decomposition of water into oxygen and hydrogen gas due to the passage of an electric current(fig. 6).. This technique can be used to make hydrogen gas, a main component of hydrogen fuel, and breathable oxygen gas, the base-balanced reactions predominate in basic (high pH) solutions.



Combining either half reaction pair yields the overall decomposition of water into oxygen and hydrogen:



The number of hydrogen molecules produced is thus twice the number of oxygen molecules.

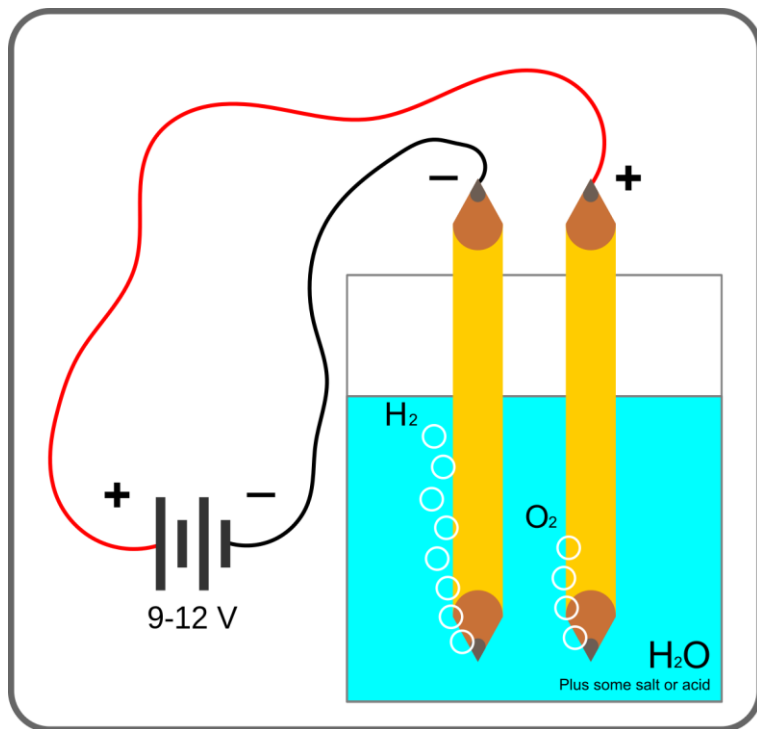


fig. 6: Electrolysis of water

