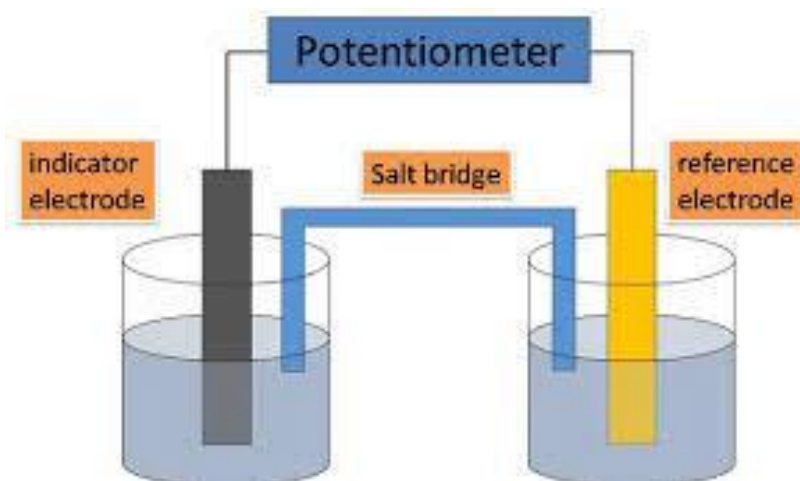


Electroanalytical method of analysis (Potentiometric analysis)

Introduction :

- ❖ Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurement of electrical quantities such as current, potential or charge and their relationship to chemical parameters such as concentration.
- ❖ The major electroanalytical methods include.
 1. Potentiometry methods .
 2. Amperometry methods .
 3. Conductometry methods.
 4. Electrogravimetry methods.
 5. Voltammetry (and polarography) methods.
 6. Coulometry methods
- ❖ The term potentiometric analysis includes the measurement of concentration (or activity) by a single measurement of cell e.m.f. or electrode potential, as well as the potentiometric titration.
- ❖ In the usual potentiometric titration, the potential of one electrode is kept constant (**reference electrode**), while the other electrode (**the indicator electrode**) varies in accordance with the change in concentration or activity of the substance being titrated.



Types of electrochemical cells

There Are Two Types of Cells

- 1- Electrochemical cells** : These Cells are those Cells that produce Electricity through Chemical reactions. These Cells are also known as **Voltaic Cells** or **Galvanic Cells**. Chemical Energy is converted into Electrical Energy by the Cells. An example of an Electrochemical Cell is the Daniell Cell.
- 2-Electrolytic Cells** :These Cells which use Electricity to carry out non-spontaneous Chemical reactions. So, it's clear that these Cells convert Electrical Energy into Chemical Energy.

Difference between electrochemical cells & electrolytic cells:

The basic difference between Electrochemical Cells and Electrolytic Cells are listed in the table below:

Electrochemical Cell	Electrolytic Cell
It converts chemical energy into electrical energy.	It converts electrical energy into chemical energy.
It is based upon the redox reactions which are spontaneous.	The redox reactions are non-spontaneous and take place only when energy is supplied.
The chemical changes occurring in the two beakers are different.	Only one chemical compound undergoes decomposition.
Anode (-ve) - Oxidation takes place.	Anode (+ve) - Oxidation takes place.
Cathode (+ve) - Reduction takes place.	Cathode (-ve) - Reduction takes place.

Other features of the electrochemical cell are:

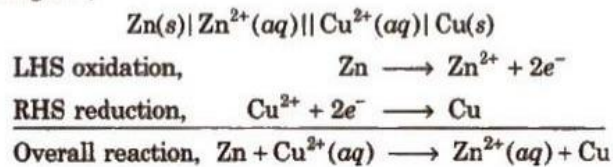
1. There is no evolution of heat.
2. The solution remains neutral on both sides.
3. The reaction and flow of electrons stops after some time.

Daniell Cell:

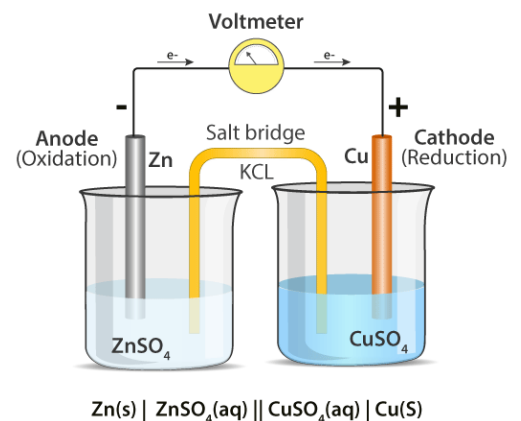
- Daniell cell a cell which converts chemical energy into electrical energy.
- Daniell cell consists of two electrodes of dissimilar metals Zn and Cu. Each electrode is in contact with a solution of its own ion i.e. Zinc sulphate and copper sulphate, respectively.

- **It is represented as:**

Cell diagram,



By convention **cathode** is represented on the RHS and **anode** on the LHS.

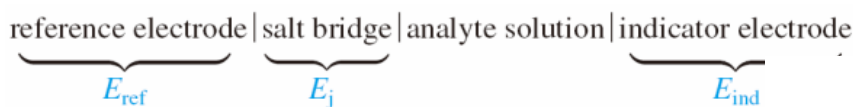


Potentiometric Methods :

Potentiometric Methods: based on measurements of the potential of electrochemical cells in the absence of appreciable currents ($i \approx 0$)

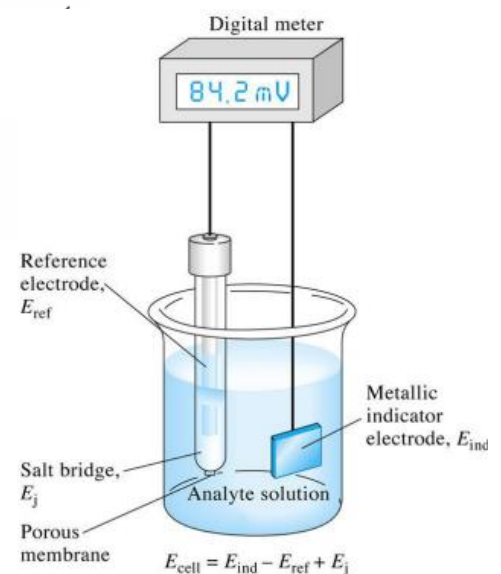
Basic Components:

- reference electrode** : gives reference for potential measurement
- indicator electrode**: where species of interest is measured
- salt bridge**
- potential measuring device**



$$E_{\text{cell}} = (E_{\text{ind}} - E_{\text{ref}}) + E_j$$

For most electroanalytical methods, the junction potential is small enough to be neglected.



A) Reference Electrodes:

Need one electrode of system to act as a reference against which potential measurements can be made relative comparison.

Purpose: provide stable potential against which other potentials can be reliably measured

Desired Characteristics:

- stable (time, temperature)
- constant response (shouldn't be altered by passage of small current in the cell)
- insensitive to composition of solution under study
- obeys Nernst Equation
- reversible
- rugged and easy to assemble
- Always treated as the left-hand electrode

Common Reference Electrodes used in Potentiometry:

1- **Saturated Calomel Electrodes (SCE)** : (Hg in contact with Hg_2Cl_2 & KCl)

1/2 cell repr.: $\text{Hg} | \text{Hg}_2\text{Cl}_2 (\text{satd}), \text{KCl} (x\text{M}) ||$

1/2 cell react: $\text{Hg}_2\text{Cl}_2 (\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^- (\text{aq})$

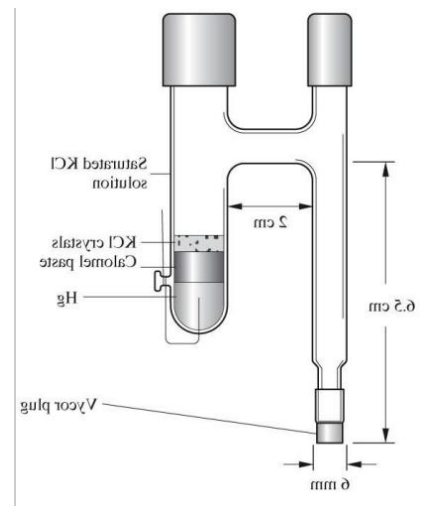
- widely used, due to ease of preparation
- equilibration due to temperature change is slow
- leakage of KCl into sample, mercury contamination
- less common than once they were
- still preferred for some certain applications

Advantages:

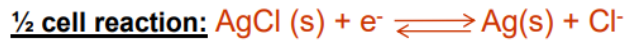
- Most polarographic data ref'd to SCE

Disadvantages :

- Hg toxic
- solubility of KCl temperature dependent $dE/dT = -0.67 \text{ mV/K}$ (must quote temperature)



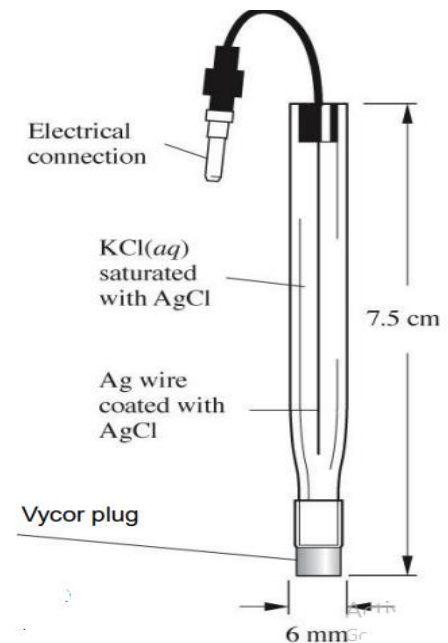
2- Silver/Silver Chloride Electrode - most widely used reference electrode system - Ag electrode immersed in KCl solution saturated with AgCl



Advantage –one advantage over SCE

is that Ag/AgCl electrode can be used at temperatures $> 60^\circ\text{C}$

Disadvantage – Ag reacts with more ions, - plugging of the junction between electrode (Ag) and analyte soln.



B) Indicator Electrodes:

Two General Types of Indicator Electrodes

1- Metallic Indicator Electrodes:

- the electrode normally consists of a metal, and the electrode potential is directly correlated to the concentration (activity) of the analyte.
- Metal in contact with its cations or nonmetal (via a noble metal) in contact with its anions
- **EXAMPLES:**
 - Cu/Cu^{2+}
 - Zn/Zn^{2+}
 - SHE (Pt, $\text{H}_2|\text{H}^+$)
 - $\text{Pt}, \text{Cl}_2(\text{g})/\text{Cl}^-$
 - Ag/Ag^+ (nonaqueous reference electrode)
 -

2- Membrane Indicator Electrodes [Ion Selective Electrodes (ISE)] :

- a key component of the electrode is a membrane (cristalline or non-cristalline membrane)
- Metal in contact with sparingly soluble salt of the metal
- Common name: anion electrodes
 - EXAMPLES: $\text{Ag}/\text{AgCl}(\text{s})$
 - Hg/Hg_2
 - $\text{Cl}_2(\text{s})/\text{Cl}^-$