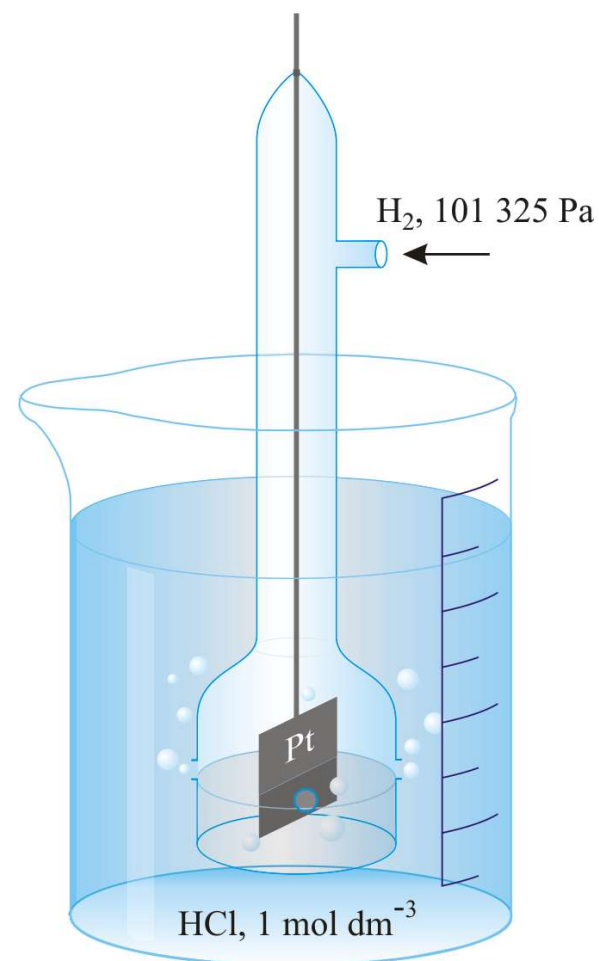
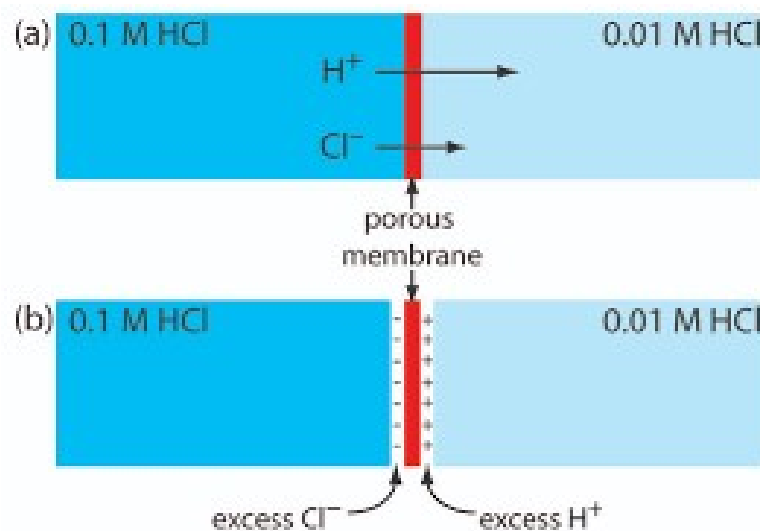
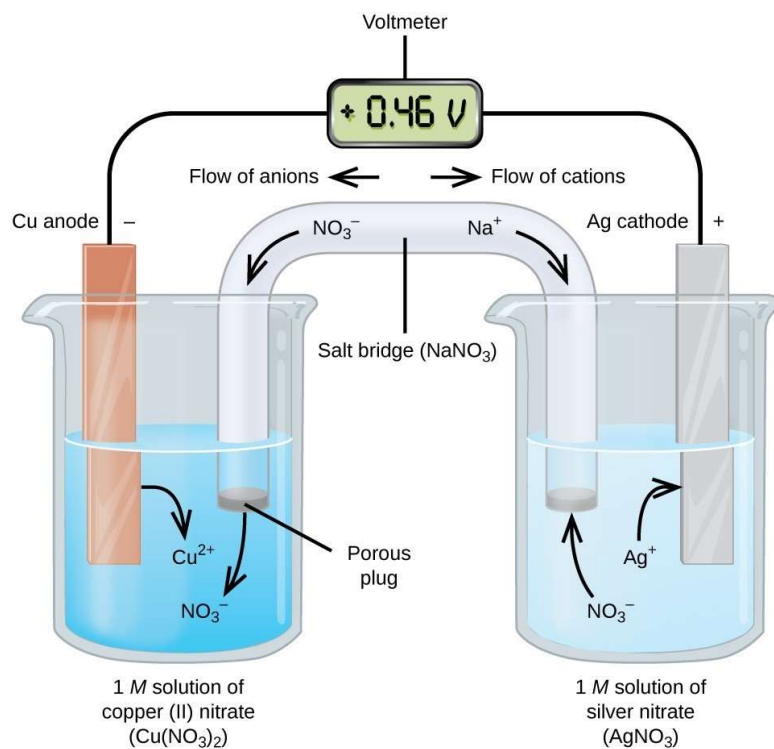


Electrochemistry-II

- Electrochemical Cell (Galvanic and Electrolytic)
- *Types of electrodes*
- *Concentrations cells*
- *Liquid junction potential*



Electrochemical Cell (Galvanic)

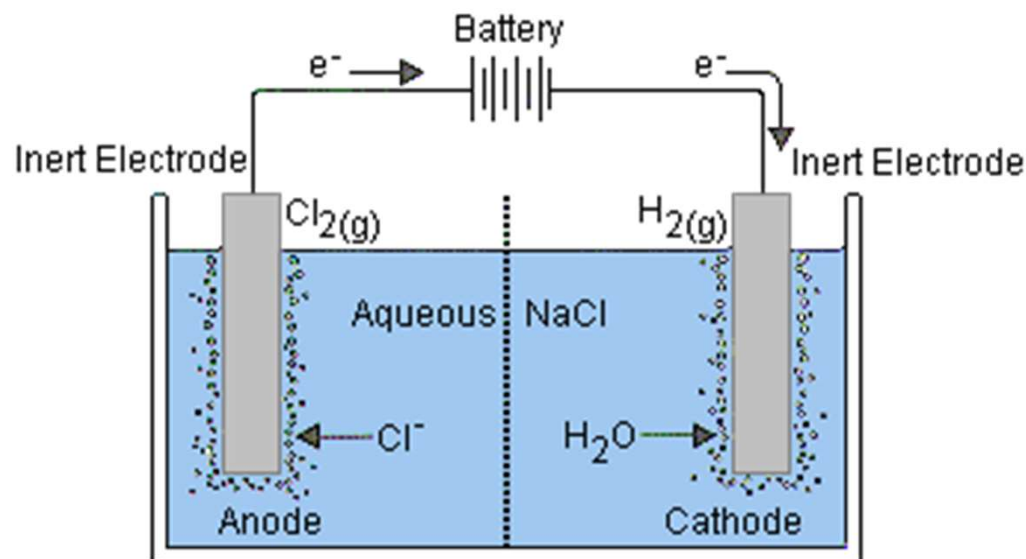


Cell Notation:



*Chemical energy is converted
into electrical energy*

Electrochemical Cell (Electrolytic)



*Electrical energy is converted
into chemical energy*

Reversible Cell and Electrodes

Reversible Cell: A galvanic cell is said to be reversible if it generates an infinitesimally small current so that the cell reaction always remains virtually in a state of equilibrium. (reversible reaction takes place)

Thermodynamically, a cell is said to be reversible, if following criteria is satisfied by cell:

- $E_{\text{ext}} = E_{\text{cell}}$, No current flows, no chemical reaction takes place
- $E_{\text{ext}} < E_{\text{cell}}$, small current flows, and small amount of chemical reaction takes place
- $E_{\text{ext}} > E_{\text{cell}}$, small current flows in opposite direction and small amount of chemical reaction takes place

Reversible Cell: It will have two **reversible electrodes**: cathode and anode
In case of reversible electrodes, the half-cell reaction is in equilibrium

Irreversible cell and Electrodes

- If any conditions (applicable for reversible cell) is not met, the cell is said to be Irreversible cell. e.g. electrolytic cell
- Similarly, irreversible electrodes are defined. Reactions are one way only i.e. irreversible which occur at the electrodes e.g. reactions occurring at electrodes in electrolytic cell

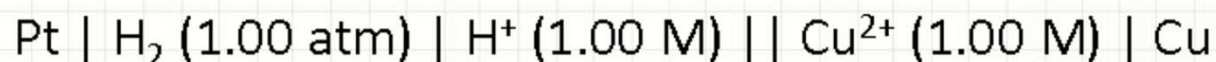
Standard Electrode Potential vs Cell Potential

Standard as a Reference

The standard electrode potential of SHE is used as Reference cell

The cells are formed by connecting the Standard Hydrogen Electrode (SHE) as the anode and the other half-cell as the cathode.

Consider: (anode) (cathode)



Measured potential (E_{cell}) = $E_{\text{cathode}} - E_{\text{anode}} = +0.340 \text{ V}$

All components in the Cu cell are standard, hence,

STANDARD REDUCTION POTENTIAL of the Cu^{2+}/Cu couple
= +0.340 V

Electrode potential is cell potential and absolute potential can't be measured.

Electrochemical Series

	Half Reaction	Standard Potential (V)
	$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+2.87
	$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.67
	$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
	$\text{Ag}^+ + 1\text{e}^- \rightleftharpoons \text{Ag}$	+0.80
	$\text{Fe}^{3+} + 1\text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00
	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
	$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
	$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66
	$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.36
	$\text{Li}^+ + 1\text{e}^- \rightleftharpoons \text{Li}$	-3.05

Nernst Equation

- ❖ In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions, we write:



For Cathode:

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E_{(\text{Cu}^{2+}/\text{Cu})}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} \quad (3.9)$$

For Anode:

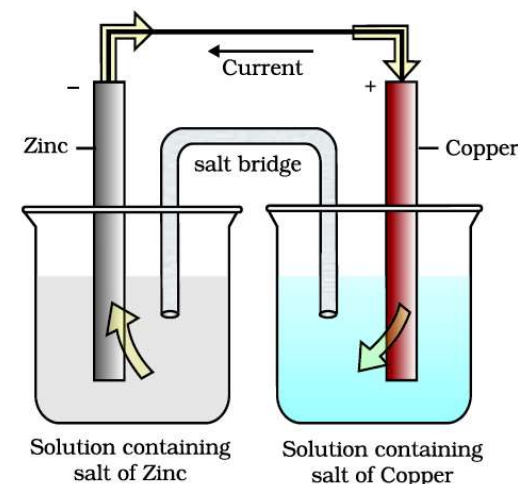
$$E_{(\text{Zn}^{2+}/\text{Zn})} = E_{(\text{Zn}^{2+}/\text{Zn})}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]} \quad (3.10)$$

The cell potential, $E_{(\text{cell})} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})}$

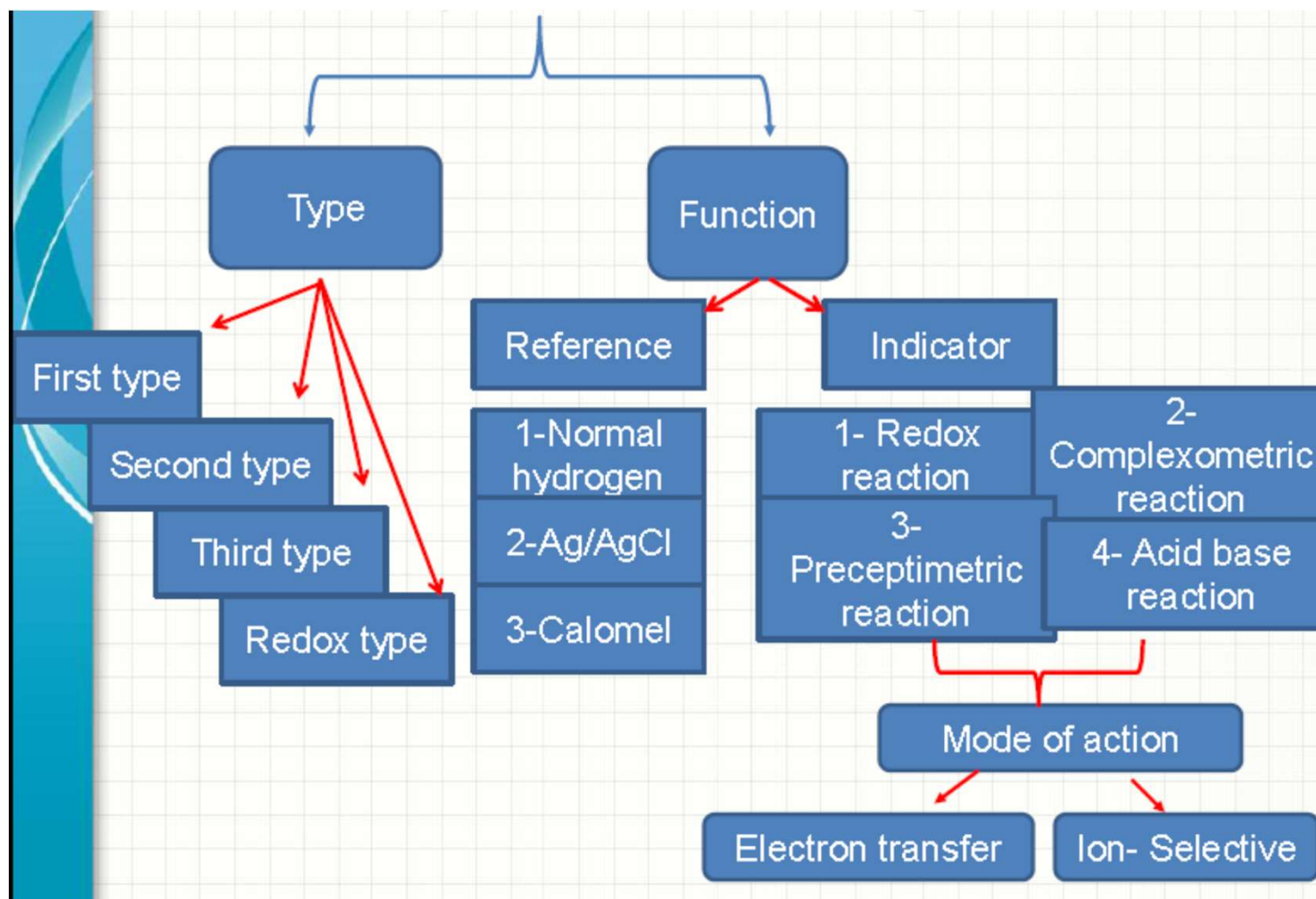
$$= E_{(\text{Cu}^{2+}/\text{Cu})}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} - E_{(\text{Zn}^{2+}/\text{Zn})}^{\ominus} + \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]}$$

$$= E_{(\text{Cu}^{2+}/\text{Cu})}^{\ominus} - E_{(\text{Zn}^{2+}/\text{Zn})}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} - \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]}$$

$$E_{(\text{cell})} = E_{(\text{cell})}^{\ominus} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (3.11)$$



Types of electrodes



Electrode of First Kind

Electrode of this type are reversible with respect to the ions of the metal phase (cations). It consists of a metal in contact with a solution of its own ion.

Examples:

I. Zinc rod in ZnSO_4 solution II. Cu rod in CuSO_4 solution



$$E = E^\circ - 0.0295 \log(1/a_{\text{Zn}^{2+}})$$

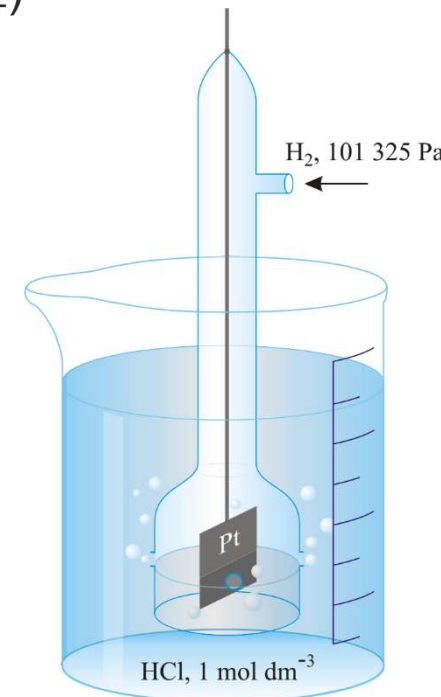
Standard Hydrogen Electrode (SHE):



$$E = E^\circ - (0.0591/2) \log[p\text{H}_2/(a_{\text{H}^+})^2]$$

Since $E^\circ = 0$ for SHE,

$$E = - (0.0295) \log[p\text{H}_2/(a_{\text{H}^+})^2]$$



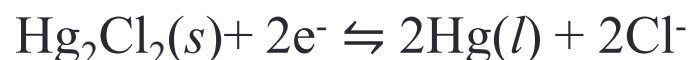
Electrode of Second Kind

Metal Indicator Electrodes of IInd type for anions: These electrodes consists of a metal coated with a layer of its sparingly soluble salt dipped in a solution of a soluble salt having same anion.

Example: silver-silver chloride electrode, calomel electrode

Calomel Electrode: It consists of mercury, solid mercurous chloride and a solution of KCl.

Schematic representation:- Hg, Hg₂Cl₂(s); KCl (solution)



$$E = E^\circ - 0.0295 \log(a_{\text{Cl}^-})^2 \quad \text{cell is reversible w.r.t. Cl}^- \text{ ions.}$$

KCl conc.	0.1N	1N(none)	Saturated
E in volt.	0.3335	0.2810	0.2422

Silver – silver chloride electrode:- It is consists of a silver wire coated with a layer of silver chloride inserted in a solution of KCl or HCl of known concentration.

If electrode acts as cathode: Hg^{++} ions given by sparingly soluble Hg_2Cl_2 get discharged at electrode. So more Hg_2Cl_2 would pass into solution and the conc. of Cl^- ion increases.



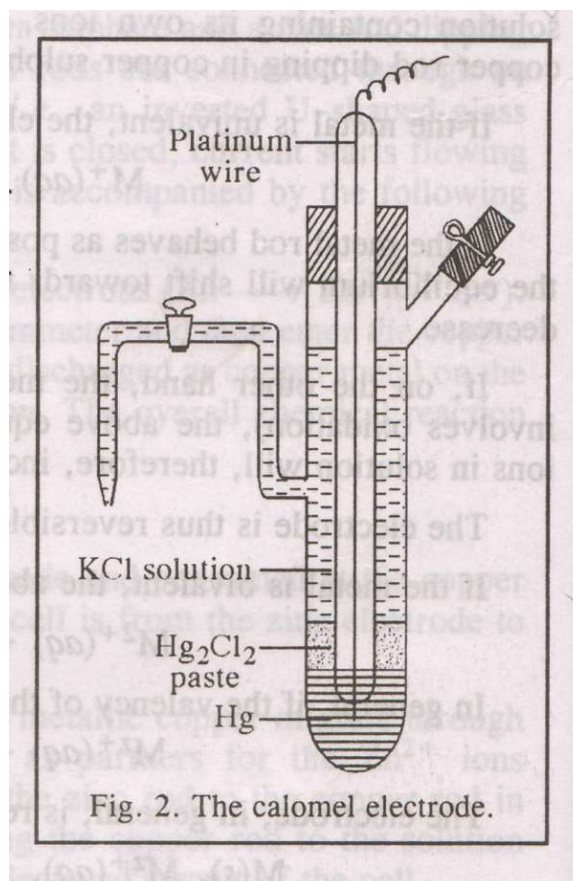
If electrode acts as anode: then it liberate electrons and send Hg^{++} ions in solution. The Hg^{++} ions combine with Cl^- ions (furnished by KCl) forming sparingly soluble Hg_2Cl_2 . So conc. of Cl^- ions decreases in solution.



Metal-Insoluble Metal Salt Electrode (Calomel Electrode, Reference Electrode)

It consists of mercury, solid mercurous chloride and a solution of KCl.

Schematic representation: $\text{Hg}, \text{Hg}_2\text{Cl}_2(\text{s}); \text{KCl}(\text{solution})$



Electrode reaction is---



So electrode is reversible with respect to Cl^- ion

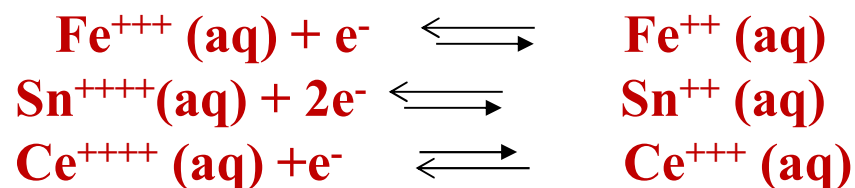
Electrode of this kind can be used for direct determination of the activity of either the metal ions the anion in the coating, also used as indicator electrode to follow titration involving either.

Electrode of the 4th kind or oxidation Reduction electrode (Inert electrode)

- The term oxidation-reduction electrode is used for those electrodes in which the potential is developed due to the presence of ions of same substance in two different oxidation states.
- It is set up by inserting an unattackable metal (Platinum or gold) in an appropriate solution.

When platinum wire is inserted in a solution containing Fe^{2+} and Fe^{3+} ions or Sn^{2+} and Sn^{4+} ions or Ce^{3+} and Ce^{4+} ions, the wire acquires potential. The potential at electrode arises due to tendency of ions in one oxidation state to change in to more stable oxidation state.

Electrode reactions:

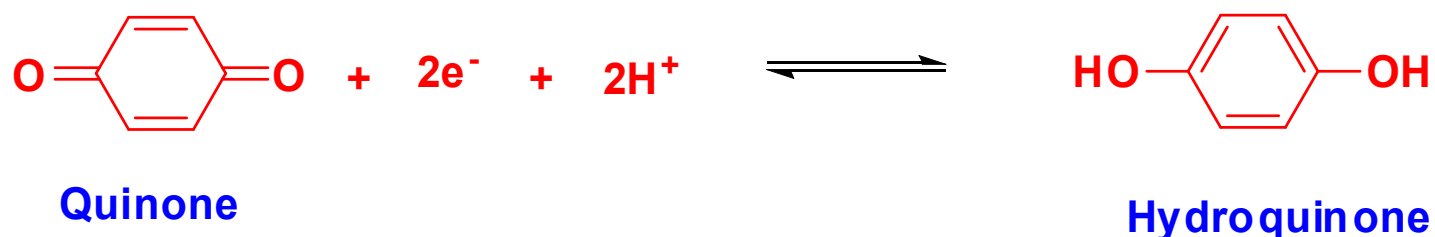


- The function of Pt wire is to ‘pick up’ the electrons and to provide electrical Contact to the electrode.

Quinhydrone electrode – Oxidation reduction electrode

- It consists of a platinum wire placed in a solution containing hydroquinone (QH₂) and quinone(Q) in equimolar amounts.

Electrode reaction:



Electrode representation:

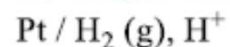


It is reversible with respect to H⁺ ions.

Gas Electrodes

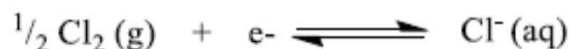
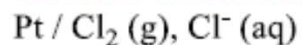
Gas Electrodes

1. H₂ Electrode **Hydrogen Electrode:** Reversible w.r.t. H⁺



H₂ at 1 bar; T = 298 K; [H⁺] = 1 mol dm⁻³

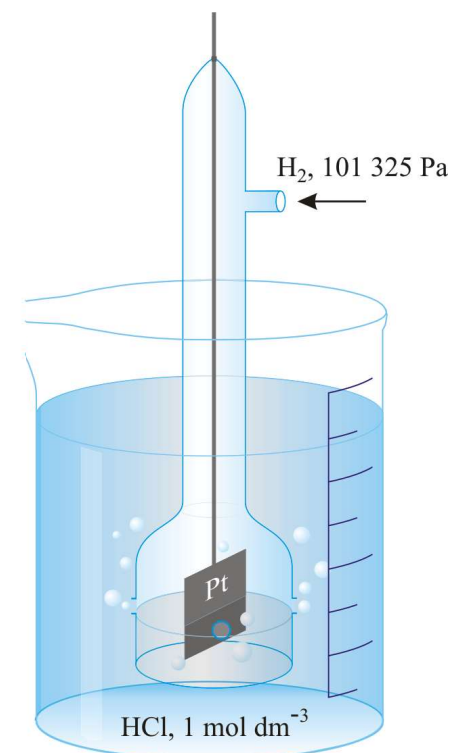
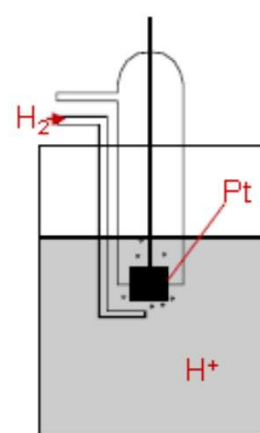
2. Cl₂ Electrode **Chlorine Electrode:** Reversible w.r.t. Cl⁻



3. O₂ Electrode **Oxygen Electrode:** Not truly reversible electrode



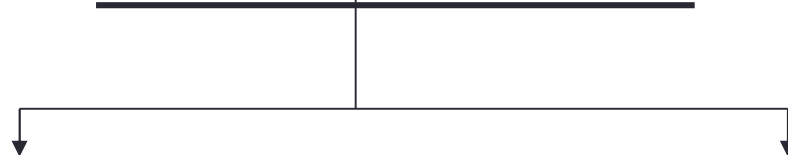
Equilibrium between O₂(g) and OH⁻ in solution cannot be established quickly



$E^\circ(\text{H}^+, \text{H}_2) = 0$ assigned conventionally

Measuring electrode potential and finding concentration of unknown solute

Potentiometric method



Direct Potentiometric method

A Calibration Curve by varying the conc. of an active species may be derived and from that curve an unknown conc. of the active species is determined. pH meter is a potentiometer in which potential is measured in terms of pH.

Potentiometric titrations

change in EMF of an Daniel cell measured through the addition of a titrant

$$E = E^{\circ} - (0.0591/n) \log [Red] / [Ox]$$

Ex. AgNO_3 vs NaCl titration

A species of interest is titrated against a suitable titrant and equivalence point is obtained.

Equipment required for potentiometric measurements:-

1. Reference electrode (**SCE and Ag/AgCl**)
2. Indicator electrode (**can be of Ist kind, or 4th kind**)
3. Potential measuring device (high impedance voltmeter)

Indicator Electrode:

1. Metal Indicator Electrode (**First or 4th Kind**)
2. Membrane Electrode (e.g. **Glass electrode for measuring pH**)

In glass electrode, membrane is made up of SiO_2 , Na_2O , and CaO which is responsive to change in concentration of H^+ ions.

Review of Electrochemistry:- ^(K)

- effect of dilution. Δm , Δq , Δp
- Noyes exp. of Migration of ions
- Transport no.
- Hittorf's theoretical device.
- Conductometric titrations.
- Galvanic / electrolytic cells
- Electrodes Type
1st, 2nd, (4th) → inert
Indicator electrode, Reference electrode

CONCENTRATION CELLS

- In galvanic cells electrical energy arises from chemical reactions
- In concentration cells EMF arises not due to any chemical reaction but due to transfer of matter from one half cell to other because of the difference in concentration of the species involved.
- Concentration cell one of two types -
 - Electrode Concentration cells
 - Electrolyte concentration cells
- Electrode Concentration cells - In these cells, two like electrode at different concentrations are dipped in the same solution.

e.g. two hydrogen electrodes at unequal gas pressures immersed in the same solution of H^+ ions constitute an electrode-concentration cell.

Schematic Representation Electrode Concentration cells



Reaction is independent of the conc. of electrolyte. At moderate pressures H_2 considered as ideal gas.

So Ratio of activities = Ratio of gas pressures.

So Nernst equation --

$$E = E^\circ - (0.0591/2) \log (\text{P}_2/\text{P}_1) \text{ at } 25^\circ\text{C}$$

By definition $E^\circ = 0$

$$E = - 0.02955 \log (\text{P}_2/\text{P}_1) = 0.02955 \log(\text{P}_1/\text{P}_2)$$

When $\text{P}_2 < \text{P}_1$, EMF is +ve and the process is spontaneous equivalent to expansion of H_2 gas.

2ndexample- An amalgam with two different concentrations of the same metal.

Hg- Pb(C₁), PbSO₄ (soln.), Hg-Pb(C₂)

Electrode Reactions:

R.H.E. Pb⁺⁺ + 2e⁻ ⇌ Pb(C₂)

L.H.E. Pb(C₁) ⇌ Pb⁺⁺ + 2e⁻

Overall Pb(C₁) ⇌ Pb(C₂)

EMF of the Cell: E = E_R - E_L

$$\begin{aligned} E &= (E^0_{\text{Pb}} - 0.0591/2 \log C_2) - (E^0_{\text{Pb}} - 0.0591/2 \log C_1) \\ &= 0.0591/2 \log C_1/C_2 = 0.02955 \log C_1/C_2 \end{aligned}$$

If C₂ < C₁, EMF is positive , process spontaneous i.e. lead will go spontaneously from high conc. to low conc. amalgam.

Numerical Problem

1. Calculate the EMF of an electrode-concentration cell:

Pt; H₂(p_1), HCl, H₂(p_2); Pt

At 25 °C if $p_1 = 600$ torr and $p_2 = 400$ torr

$$E_{\text{cell}} = (0.0591/2) \log (p_1/p_2) = 0.02955 \log (p_1/p_2)$$

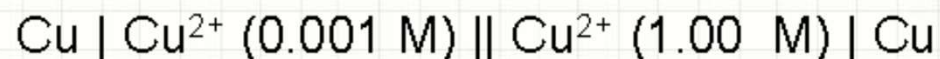
$$\text{Ans: } 5.19 \times 10^{-3} \text{ V}$$

Electrolyte Concentration Cell

Electrolyte Concentration Cell

Nernst equation demonstrates that potential depends upon concentration.

A cell made of the same materials, but with different concentrations, will also produce a potential difference.

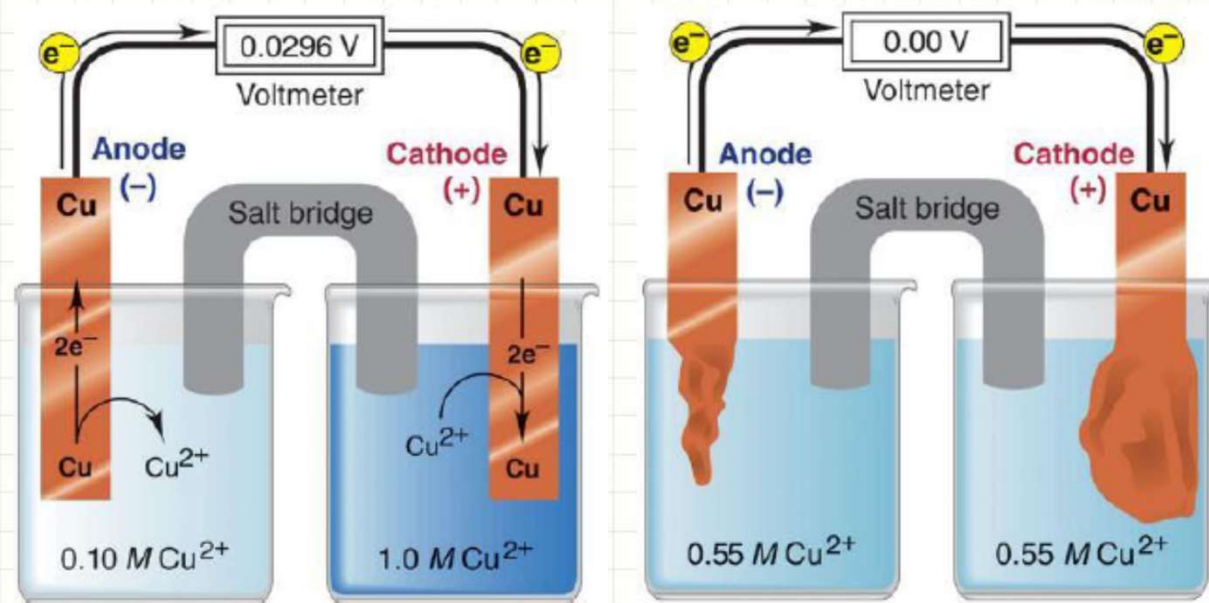


What is standard cell potential E° for this cell?

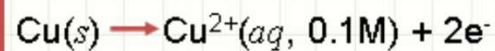
What is the cell potential E ? What is “n”, the number of electrons transferred?

Electrolyte Concentration Cell

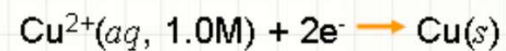
Figure 21.11 A concentration cell based on the Cu/Cu²⁺ half-reaction.



Oxidation half-reaction



Reduction half-reaction



Overall (cell) reaction



Types of Electrolyte concentration Cells---

Electrolyte conc. Cells in which solutions of the same electrolyte of different conc. are used are of two types —

1. Concentration cells without transference:

The two electrolytic solutions are not in direct contact with each other. So, transference of ions does not take place directly.

solutions are separated by salt bridge.

2. Conc. Cell with transference:

The two solutions are in direct contact.

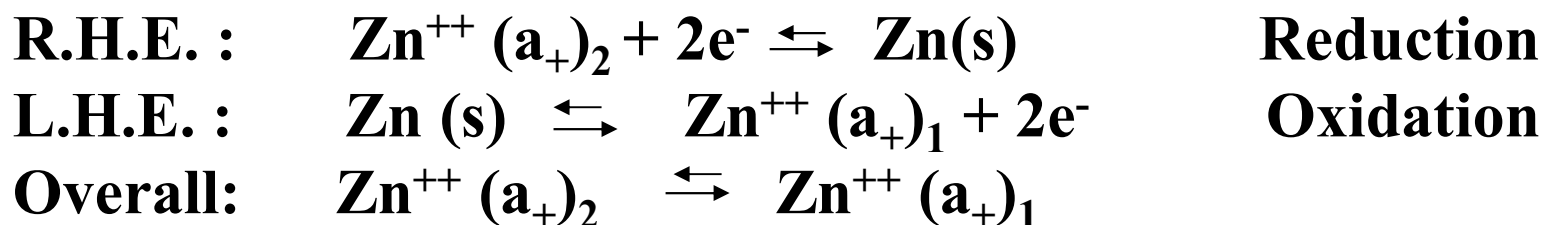
Transference of ions take place directly.

Electrolyte Concentration cells (without transference)

In these cells two electrodes of the same metal are dipped in the solutions of metal ions of different concentrations and hence of different activities. $\text{Zn}, \text{Zn}^{++} (a_+)_1 \parallel \text{Zn}^{++} (a_+)_2, \text{Zn}$

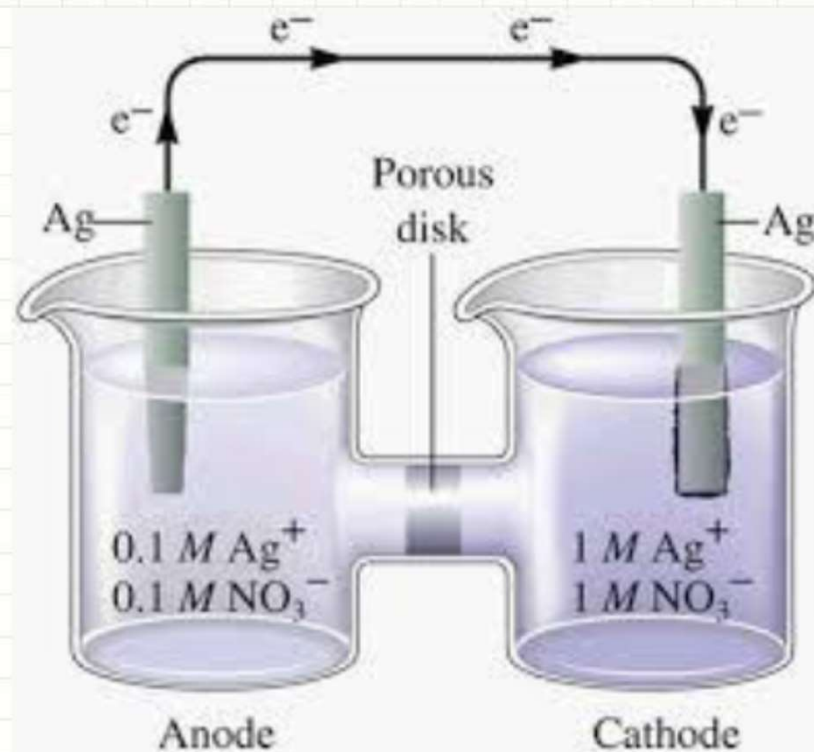
Both electrodes of zinc metal are in contact with solution of Zn^{++} ions, but the conc. and activities of ions are different. Activities of zinc ions in two electrolytes – $(a_+)_1$ and $(a_+)_2$

Reactions



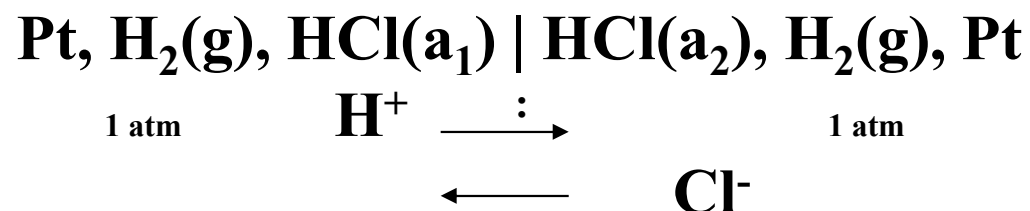
2. Electrolyte Concentration cells with transference.

- The two solutions are in direct contact.
- Transference of ions take place directly.



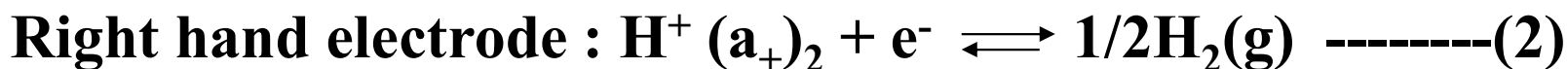
Concentration Cell with Transference.-----

Concentration cell formed by combining two hydrogen gas electrodes in contact with HCl solutions of different concentrations. The two solutions are in direct contact with each other :



The reaction on the left involves oxidation and that on the right involves reduction.

The following changes are involved for the flow of one faraday of electricity:

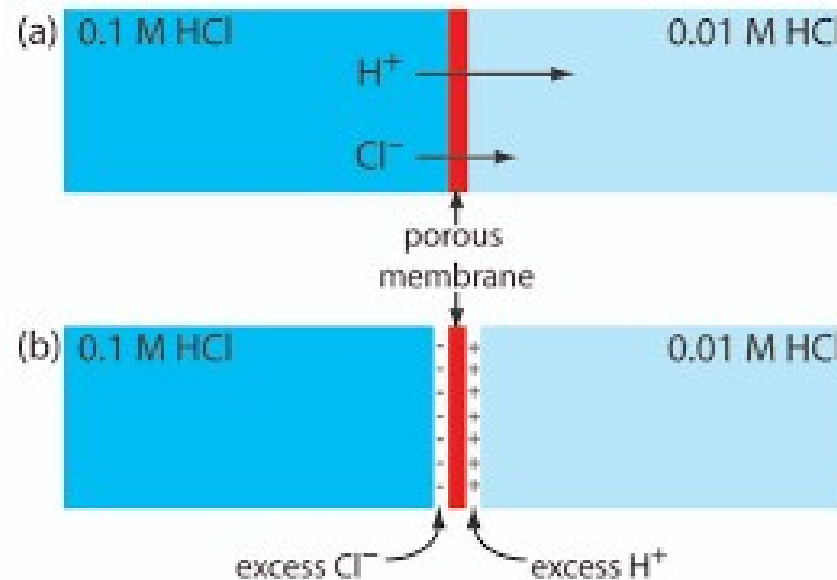


Concentration cells with transference:

- H^+ are generated at the LHE and consumed at RHE
- Cl^- will migrate in opposite direction
- Ions are free to move from one solution to other
- Hence, it is also known as cell with transference
- **A Liquid junction potential** is developed due to the migration of ions

Liquid Junction Potential

- When two salt solutions of different concentration are placed in contact with one another, the ions from the concentrated solution will tend to diffuse in to dilute one.



- The rate of diffusion of each ion is approximately proportional to the speed of the ion in electric field. Suppose positive ion moves with a greater speed than the negative ion. It means that the positive ion from the conc. solution will diffuse ahead of the -ve ion in the dilute solution.
- Thus dilute solution becomes positively charged with respect to concentrated solution.

- Suppose the negative ion moves faster. It means that negative ion will diffuse rapidly in dilute solution than the positive ion and the dilute solution gets a negative charge.
 - In both cases, an electrical double layer is set up at the junction of the two solutions and thus a potential difference is setup at this junction.
 - *This potential difference developed at the junction of two solutions of different concentration is termed as liquid junction potential (LJP).*
- (1) If two liquid moving with the same speed, there will not be any liquid – liquid junction potential.
 - (2) The liquid-liquid junction potential is due to the different migration velocities of the two ions.
 - (3) Magnitude of liquid-liquid junction potential depends on the relative speed of the ions.

How to eliminate liquid junction potential ?

- By using salt bridge
- Use high concentration of electrolyte in salt bridge
- Use electrolyte in which cations and anions have equal transport number *i.e.* difference in ionic mobilities of cation and anion is zero

Disadvantage of liquid junction potential:

It affects the accuracy of potentiometric measurements.

Reference Electrodes: The electrodes of standard (known) potential with which we can compare the potentials of an other electrode, is called a reference electrode.

Necessary conditions for an electrode to work as reference electrode: Should have a well-defined and reproducible potential, EMF shouldn't change with temperature, draws no current from cell, reversible with respect to oxidation and reduction reaction and is easy to fabricate.

e.g. SHE--- whose electrode pot. at all temp. is taken as zero.

Calomel electrode – Mercury-mercurous chloride electrode. The potential of the calomel electrode on the Hydrogen scale has been found to vary with the conc. of the KCl solution.

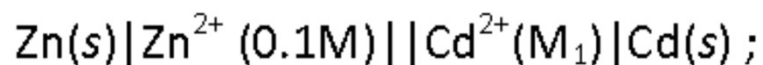
The reduction potentials for the various KCl concentration at 25°C are:

KCl conc.	0.1N	1N(none)	Saturated
E in volt.	0.3335	0.2810	0.2422

Electrode Reaction: $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq})$

Practice Problems

14. Find the concentration of Cd^{2+} ions in the given electrochemical cell:



Given: $E^\circ (\text{Zn}^{2+}, \text{Zn}) = -0.76\text{V}$; $E^\circ (\text{Cd}^{2+}, \text{Cd}) = -0.40\text{V}$; $E_{\text{cell}} = 0.33 \text{ V}$



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*All the Best with ESTs
&
Stay Safe !!*