Topic: Electrochemistry

Course: CC-1D

Semester IV

B. Sc. Chemistry

Department of Chemistry

Polba Mahavidyalaya

Electrochemistry

❑ Applications of Electrochemistry

➢ Energy storage (e.g. Battery) for different kind of electrical appliances.

➢ Fabrication of fuel cell

- A fuel cell converts the energy produced by the oxidation of fuel (e.g. H_2, MeOH) into electrical energy.
- Hydrogen fuel based vehicles is not a future concept in India anymore. It has been already launched in Pune.

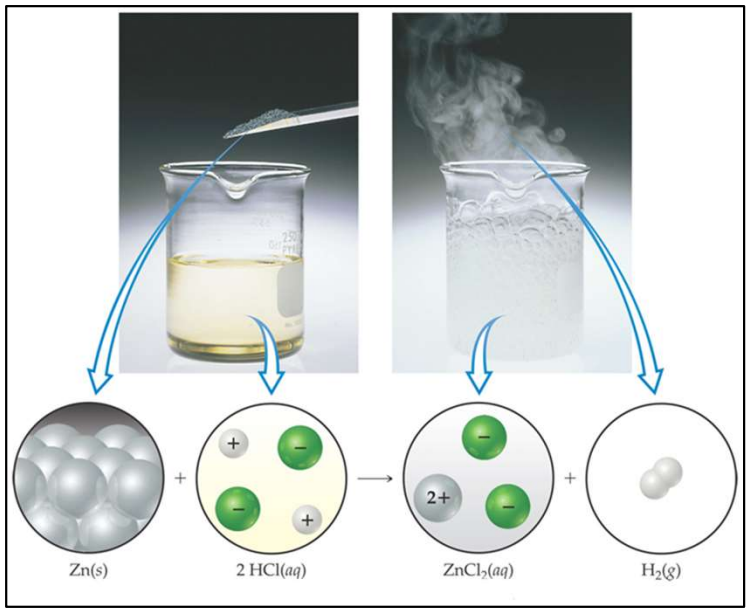
➢ Electroplating

- Electrochemical process to produce metal coating on a solid substrate through the reduction of cations via electrolysis.

Electrochemistry

❑ Few basic concepts:

- A **redox reaction** is a reaction in which there is a transfer of electrons from one species to another.



$$Zn(s) + 2\,H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

0 +1 +2 0

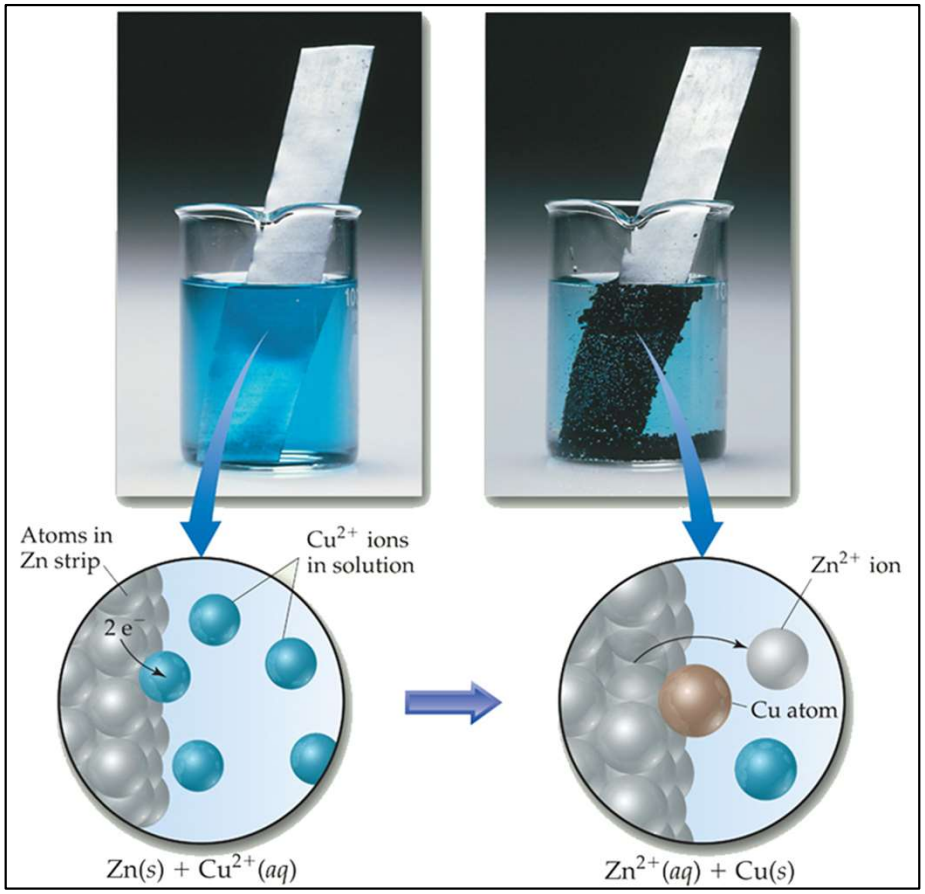
- Any **redox reaction** can be expressed as combination of two reduction **half reactions,** which are conceptual reactions showing the electron transfers.

- The reduced and oxidized species in a half reaction form **redox couple**. The couple is denoted as **Ox/Red**.

$$\mathbf{Ox + n}e^{-} \leftrightharpoons \mathbf{Red}$$

Electrochemistry

❑ Electron Transfer:



- In (redox) reactions, electrons are transferred and energy is released.
- Cu gains electrons and Zn loses electrons.
- This type of electron transfer doesn't allow for any useful work to be done by the electrons.

Electrochemistry

❑ Electron Transfer:

- We can use the transfer of electrons to do work if we make the electrons flow through an external device or circuit.
- It provides energy to do work.
- We can develop the idea of electrochemical cell.

Electrochemistry

❑ Electrochemical Cell:

➢ An electrochemical cell consists of two electrodes, in contact with an electrolyte (ionic conductor) . An electrode and its electrolyte comprise an electrode compartment. Various kind of electrodes are summarized in the following table:

Electrode type	Designation	Redox couple	Half-reaction
Metal/ metal ion	$M(s)\|M^+(aq)$	M^+/M	$M^+(aq) + e^- \rightarrow M(s)$
Gas	$Pt(s)\|X_2(g)\|X^+(aq)$	X^+/X_2	$X^+(aq) + e^- \rightarrow \frac{1}{2}X_2(g)$
	$Pt(s)\|X_2(g)\|X^-(aq)$	X_2/X^-	$\frac{1}{2}X_2(g) + e^- \rightarrow X^-(aq)$
Metal/ insoluble salt	$M(s)\|MX(s)\|X^-(aq)$	$MX/M,X^-$	$MX(s) + e^- \rightarrow M(s) + X^-(aq)$
Redox	$Pt(s)\|M^+(aq),M^{2+}(aq)$	M^{2+}/M^+	$M^{2+}(aq) + e^- \rightarrow M^+(aq)$

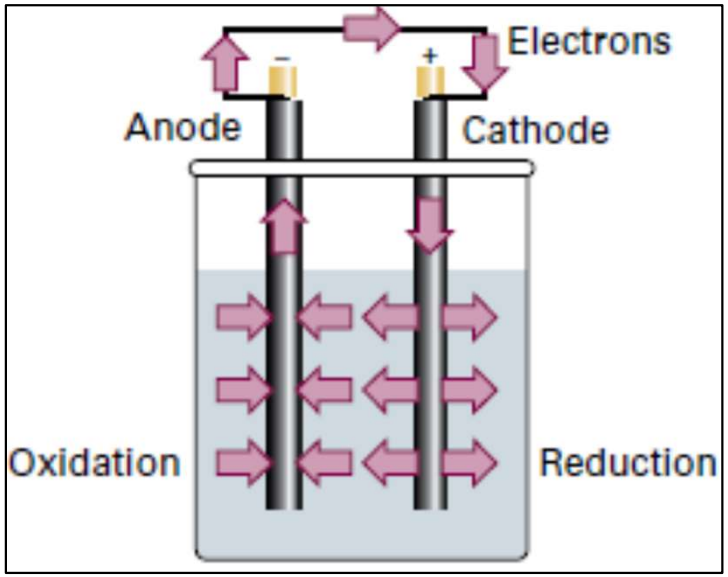
➢ If the electrolytes are different, then electrode compartments should be joined by salt bridge (eg. KCl in agar gel).

➢ A Galvanic cell is an electrochemical cell that produce electricity as a result of the spontaneous reaction occurring inside it.

Electrochemistry

❑ Electrochemical Cell:

- When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in anode and collected from cathode.
- So there is a net flow of electrons which can be used to do work.
- + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the – sign of anode is where the electron leave the cell.

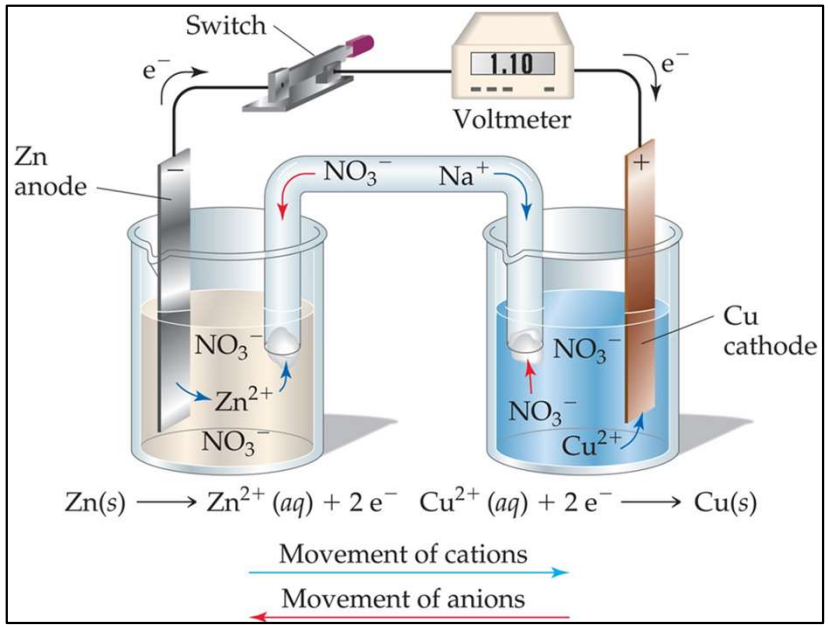


Schematic representation of galvanic cell

Electrochemistry

❑ Liquid junction potential:

- In a cell with two different electrolyte in contact, there is an additional potential difference across the interface of the two electrodes. This contribution called **liquid junction potential**.



Schematic representation of electrochemical cell with salt bridge.

❑ Notation:

- | An interface between two phase.
- ‖ An interface where liquid junction potential eliminated.
- ⋮ Liquid junction

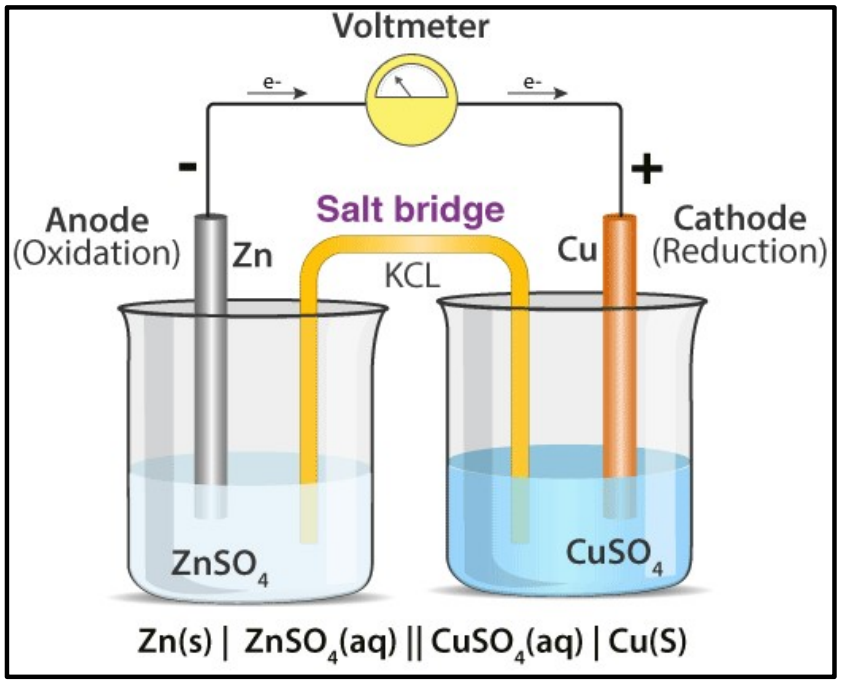
$Zn(s) \mid ZnSO_4(aq) \vdots CuSO_4(aq) \mid Cu(s)$

$Zn(s) \mid ZnSO_4(aq) \Vert CuSO_4(aq) \mid Cu(s)$

Electrochemistry

❑ Salt Bridge:

- A device used in a cell for connecting its oxidation and reduction half cells wherein a weak electrolyte is used. Salt bridge tube is a junction that connects the anodic and cathodic compartments in a cell.



❑ Glass Tube Bridge:

- U-shaped tubes filled with electrolytes.
- NaCl, KCl, and KNO_3 are generally used electrolytes.
- The electrolyte needs to be relatively unreactive with similar migratory speeds.

❑ Glass Tube Bridge:

- It prevents or minimizes the liquid-liquid junction potential.
- A salt bridge acts as an electrical contact between two half-cells.
- A salt bridge prevents the diffusion or mechanical flow of solution from one-half cell to another.

Electrochemistry

❑ Nernst equation:

- Electrical work, associated with the transfer of electron depends on the potential difference between two electrodes.
- When the potential difference is large, a given number of electrons travelling between the electrodes can do a lot of electrical work.
- The difference of potential which causes the current to flow from the electrode of higher potential to the lower one is known as the electromotive force (emf).

$$E_{cell} = \text{Higher reduction potential} - \text{Lower reduction potential}$$

- For the process, Ox + ne ⇋ Red, the reduction potential is given by the Nernst equation as follows:

$$E = E^O + RT/nF \ ln \ (^aOx/^aRed)$$

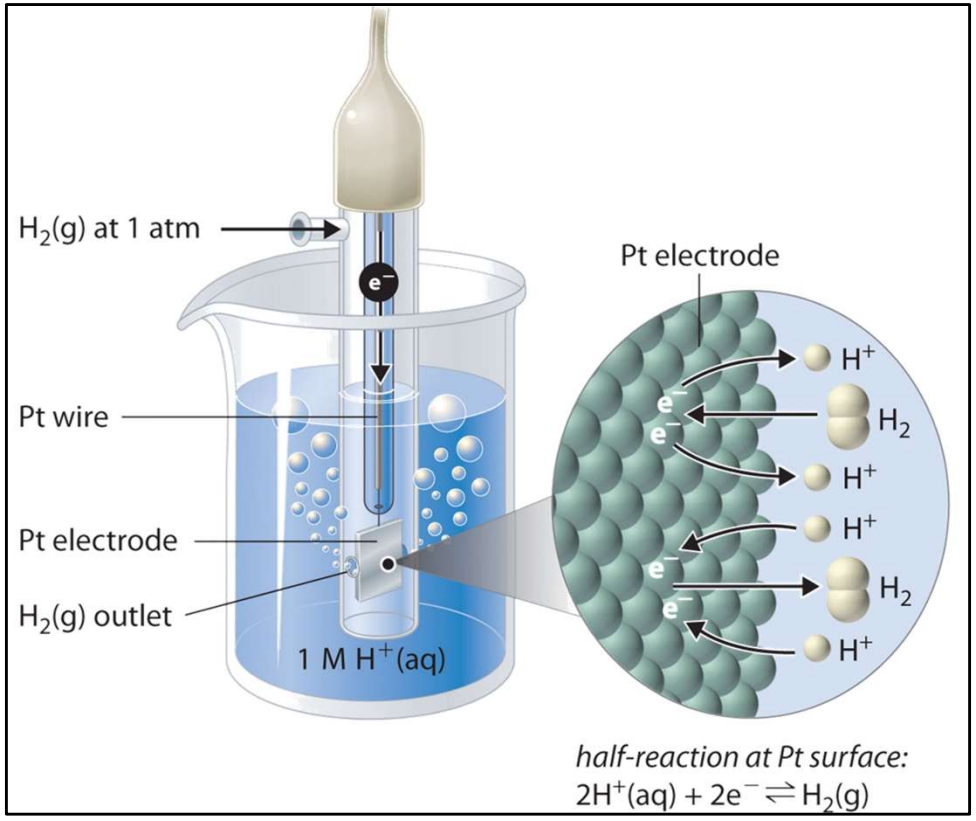
$$= E^O + 0.059/n \ log \ (^aOx/^aRed), \ (at \ 25°C)$$

- Where n is the number of moles of electrons getting transferred, F = 96,500 coulombs per mole of electron, R= 8.3 joules/degree/mole, T= temperature in Kelvin.

Electrochemistry

❑ Determination of electrode potential:

- There is no way to measure the absolute value of the electrode potential.
- The value is measured with respect to some suitable reference electrode system.
- The standard hydrogen electrode (SHE) is universally used for this purpose.
- The SHE consists a strip of platinum wire in contact with an aq. soln. of 1 M H^+. The [H+] in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface



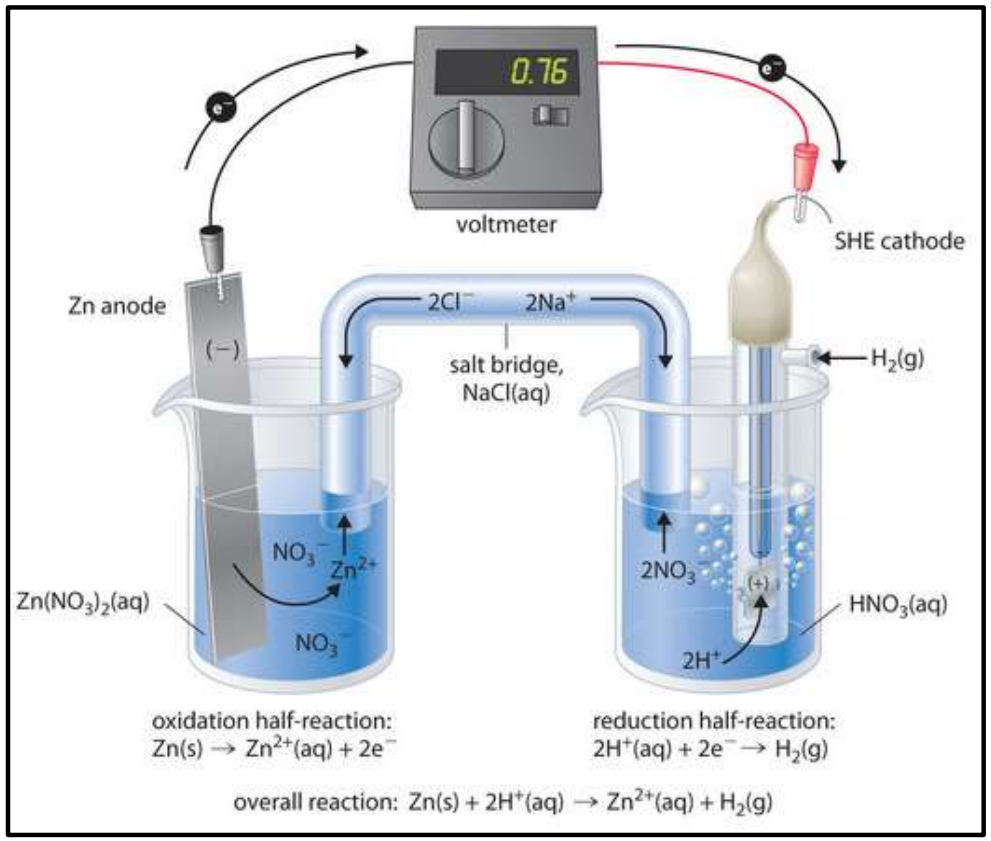
❖ Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+(aq)+2e^-\rightleftharpoons H_2(g)$$

Electrochemistry

❑ Determination of electrode potential:

- To determine the redox potential of Zn^{2+}/Zn, we can construct a galvanic cell.
- This cell consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions.
- The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment.



$Zn(s)|Zn^{2+}(aq)||H^+(aq,1M)|H^2(g,1atm)|Pt(s)$

Cathode: $2H^+(aq)+2e^- \rightarrow H_2(g)$ $E°=0V$
Anode: $Zn(s) \rightarrow Zn^{2+}(aq)+2e^-$ $E°=-0.76V$
Overall: $Zn(s)+2H^+(aq) \rightarrow Zn^{2+}(aq)+H_2(g)$

$E°_{cell}=E°_{anode}-E°_{cathode}=-0.76V$

Thank You