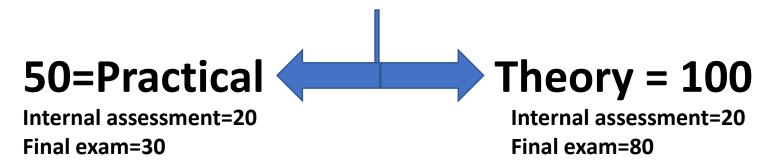
## **CHEMISTRY**



Four teachers 1h to each

- PHYSICAL CHEMISTRY; 1h, =16
- ENVIRONMENTAL CHEMISTRY; 1h=16
- INORGANIC CHEMISTRY; 1h=16
- ORGANIC CHEMISTRY; 1h=16

### **Books**

- 1. A Text book of Engineering Chemistry; By Amala Shrestha and group
- 2. A Text Book of Engineering Chemistry; By R. K. Sharm & group

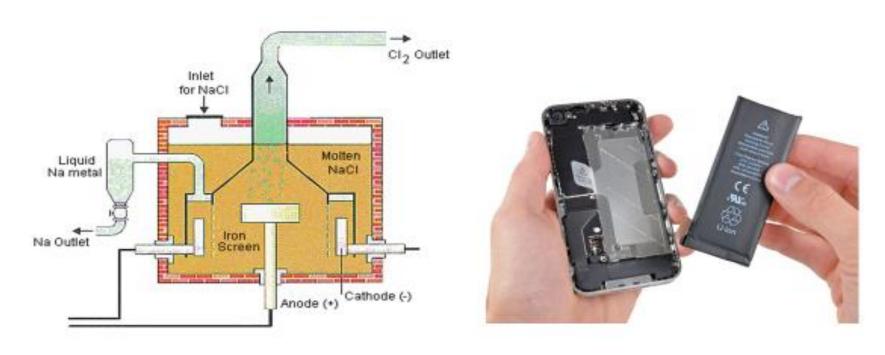
#### **For Physical Chemistry**

- 1. A Selected Topics in Physical Chemistry; By M. K. Sthapit
- 2. Essential of Physical Chemistry; By B. S. Bahl &G.D Tuli
- 2. Principles of Physical Chemistry; By Maron And Prutton

# Physical Chemistry

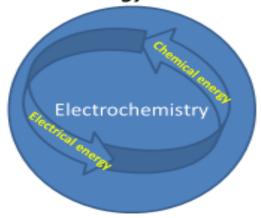
- Electrochemistry
- Buffer solution
- catalysis

## Electrochemistry



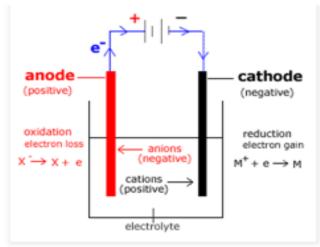
## Electrochemistry

Conversion of electrical energy in to chemical energy and vice versa



- 1. Chemical reaction due to electric energy; Electrolytic cell
- 2. Electric energy due to chemical reaction; Galvanic cell

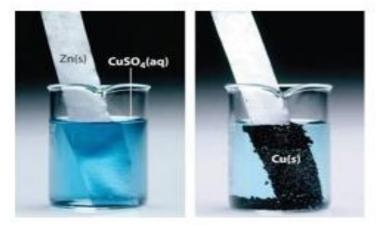
#### 1. Electrolytic cell

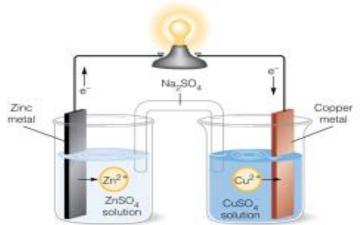


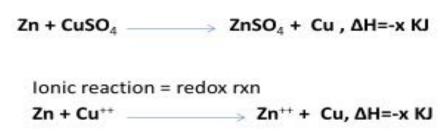
Electrolyte & non electrolyte

- 1. Electroplating
- Electrometallurgy
- 3. Nanofiber fabrication(Electrospinning)

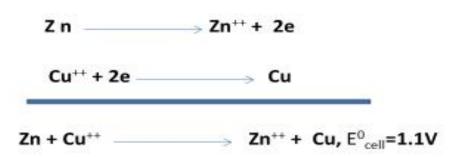
#### Concept of galvanic cell







#### Chemical Energy into heat energy



Chemical Energy into electrical energy

#### 2. Galvanic cell or voltaic cell

A. Zn-Cu cell

Mnatis Daniellcell.

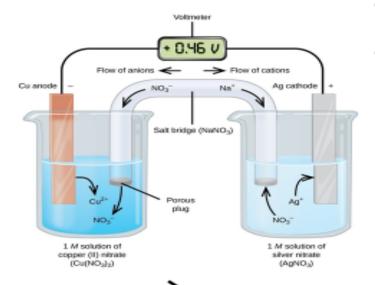


At anode (oxidation)

At cathode (reduction)

Net cell reaction; Zn + Cu $^{++}$  — Zn $^{++}$  + Cu , E $^0$ <sub>cell</sub>=1.1V

### B. Cu-Ag cell



At anode (oxidation)

At cathode (reduction)

#### Standard condition of cell

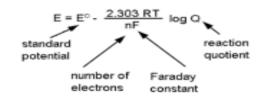
- 1. Room temperature is 25 C
- 2. Concentration of used electrolyte is 1M
- 3. If gas is used as electrode, its pressure should be 1 atm

Matis Standard Cell?

EMF measured at this condition is , E0 cell

Change of any condition; , E<sub>cell</sub>

Nernst equation



El	ements	Electron	de Reaction	E nd (volts)
A		Oxidised Form + ne' -		
Î	Li	$Li^{*}(aq) + e^{-}$	— + £i(x)	-3.05
	K	K*(aq) + e*	→ K(s)	-2.93
	Ba	${\rm He^{2*}}(ag) + 2e^-$ —	→ Ba(x)	-2.90
	Ca	Ca <sup>2+</sup> (aq) + 2c <sup>-</sup>	→ Ca(r)	-2.87
3	Na	Na*(aq) + #	→ Na(x)	-2.71
Increase	Mg	Mg2*(aq) + 2e		-2.37
2	AI	Al <sup>3+</sup> (aq) + 3e <sup>-</sup>		- 1.66
-	- Zn	Zn2*(nq) + 2e		-0.76
100	Cr	Cr3*(ag) + 3e*		-0.74
171	Fe	Fe <sup>2*</sup> (ay) + 2e <sup>-</sup> —	→ Fe(s).	-0.44
		H <sub>2</sub> O(t) + e <sup>-</sup>	$\rightarrow \frac{1}{2}H_2(g) + OH^*(\omega g)$	-0.41
200	Cd	Cif <sup>2s</sup> (aq) + 2e <sup>-</sup> —	→ Cd(s)	-0.40
8	Pb	PbSO <sub>2</sub> (x) + 2x <sup>-</sup>	→ Pb(s) + SO <sub>4</sub> <sup>3</sup> · (aq)	-031 9
Tendency for oxidation to occur Power as reducing agent	Co	Co2*(aq) + 2e	→ Co(x)	-0.28 5
	Ni	Ni <sup>2s</sup> (aq) + 2e <sup>-</sup>	→ Ni(s)	-0.25
	Sn	$Sn^{2s}(nq) + 2e^-$	→ Sn(s)	-0.14 %
	Pb	Pb <sup>2a</sup> (aq) + 2c <sup>-</sup> —	→ Pb(x)	-0.13
enden Uwer i	Ha	2H+ 2e-	→ H <sub>g</sub> (g) (standard electrode)	0.00
38	- Cu -	$-Cu^{2n}(nq) + 2e^{-}$	→ Cu(s)	+0.34 3
	I,	I <sub>2</sub> (s) + 2e <sup>-</sup>	→ 2F (aq)	+ 0.54
	Fe	Fe3+ (mp) + e	→ Fe <sup>2+</sup> (aq)	+ 0.77
	Hg	$Hg_1^{2+}(aq) + 2e^-$	+ 2Hg(I)	+ 0.79
	Ag	Ag*(uq) + e*		+ 0.80
	Hg	Hg <sup>24</sup> (nq) + 2e <sup>-</sup>	→ Hg(l)	+0.85
	N <sub>2</sub>	NO, "+4H"+3e"	→ NO(g) + 2H <sub>2</sub> O	+ 0.85
	Br,	Br <sub>2</sub> (mg) + 2e <sup></sup>	→ 2Br(aq)	+1.08
	0,	$O_2(g) + 2H_2O^4(aq) + 2q^-$		+ 1.23
	Cr	Cr <sub>2</sub> O <sub>2</sub> <sup>2-</sup> + 14H <sup>+</sup> + e <sup>-</sup> -		+1.33
	CI,	Cl <sub>2</sub> (g) + 2e <sup>-</sup>	→ 2Cl*(aq)	+1.36
	Au	Au <sup>3+</sup> (uq) + 3e <sup>-</sup>		+1.42
	Mn	MnO <sub>4</sub> <sup>-</sup> (aq) + 8H <sub>3</sub> O <sup>+</sup> (aq) + 5e <sup>-</sup> -	$\rightarrow Mn^{2n}(aq) + 12H_2O(I)$	+ 1.51
	F,	F <sub>2</sub> (g) = 2e' -		+ 2.87

electrochemical Series

## Project for you

Application of electrochemistry in Comp Eng

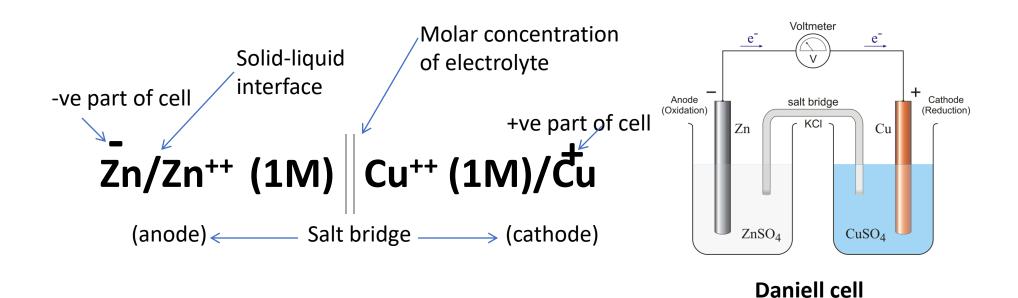
Hints; memory card energy storage device

#### **Question for examination**

- 1 . Difference between electrolytic cell and galvanic cell
- 2. What is Daniell cell?
- 3. What is standard cell?

## Cell notation

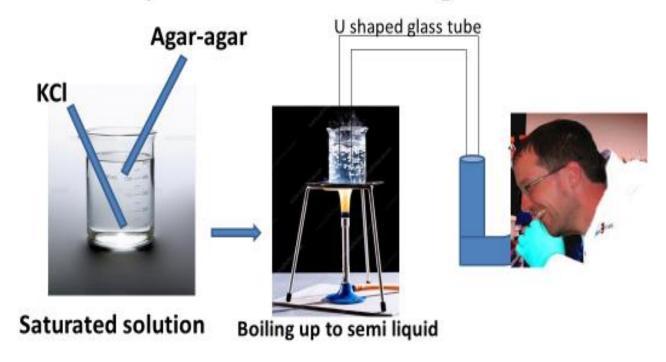
Cell notation in electrochemistry is a shorthand way of expressing a complete galvanic cell diagram in a single line

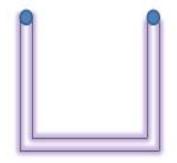


# Salt bridge

- U-shaped glass tube filled with gel of agar-agar with large amount of inert salt (KCl, NaNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>)
- Minimize liquid-liquid junction potential (Potential arises between two solutions when they are in contact with each other)
- Complete electric circuit
- Maintain flow of ions by providing aqueous medium and maintain charge balance in each half cell

## Preparation of Salt bridge

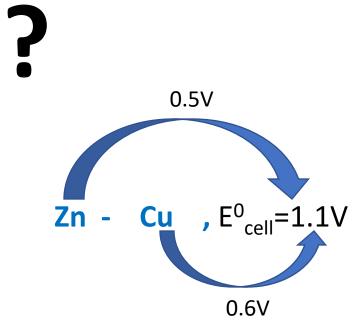




U-shaped glass tube filled with gel of Agar-Agar with large amount of inert salt

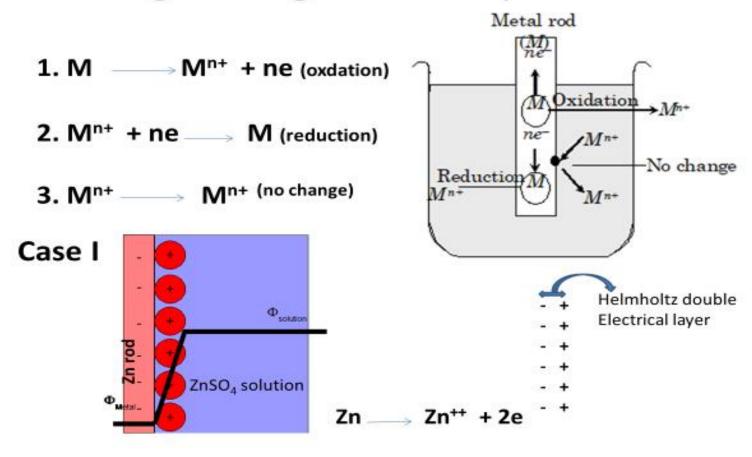
## Single electrode potential

**B. Cu-Ag cell,**  $E_{cell}^0$ =0.46V



Now single electrode potential of Zn electrode is 0.5V And that of Cu is 0.6V

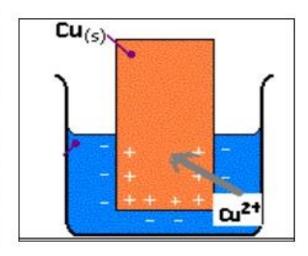
### Origin of single electrode potential



## Standard single electrode potential

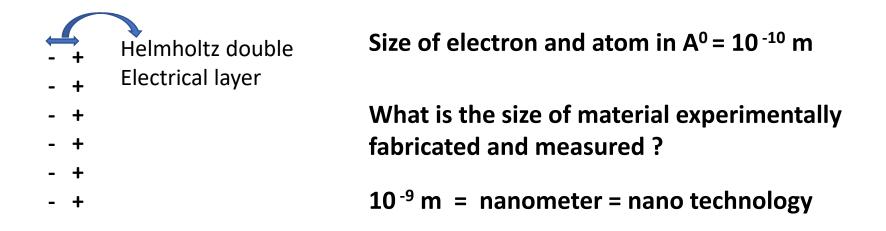
Cu rod in to M CuSO<sub>4</sub> solution at 25 degree centigrade

When Cu is placed in the solution of CuSO, the copper the solution gets deposited over the metal and the hence metal becomes positively charged. The positively charged metal attracts the negatively charged sulphate ions in the solution and hence a doubly charged layer (Helmholtz electrical double layer) is formed near the metal.



When any metallic rod is partially dipped into its soluble salt solution, there is formation of oppositely charged double electrical layer called Helmholtz double layer. Due to this oppositely charged layer, certain potential difference should be developed across the solid-liquid interface which is called single electrode potential. If it is measured at standard condition, it is called standard single electrode potential

## Measurement of single electrode potential



There is no any instrument to measure this potential difference between these opposite charged layer up to now  $$_{1.1 \rm V}$$ 

0V

Therefore need some reference Electrode having OV electrode potential

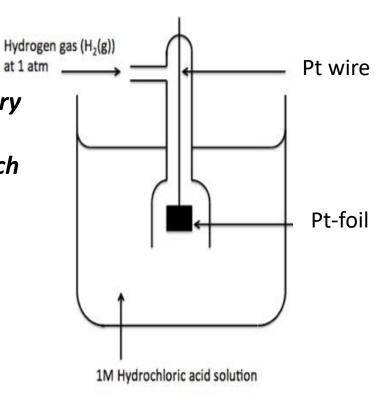
# Normal hydrogen electrode (NHE)

Normal hydrogen electrode consists of 1M HCl solution in to a beaker through which pure and dry H2 gas is passed at 1 atm. To introduce electric current through electrode system, inert metal such as Pt-foil is dipped into HCl solution. This simple system as shown in this figure at 25 degree centigrade is called NHE or SHE.

Single electrode potential of NHE is near about 0V.

Therefore, it can be used as reference electrode to

Measure the single electrode potential of any electrode

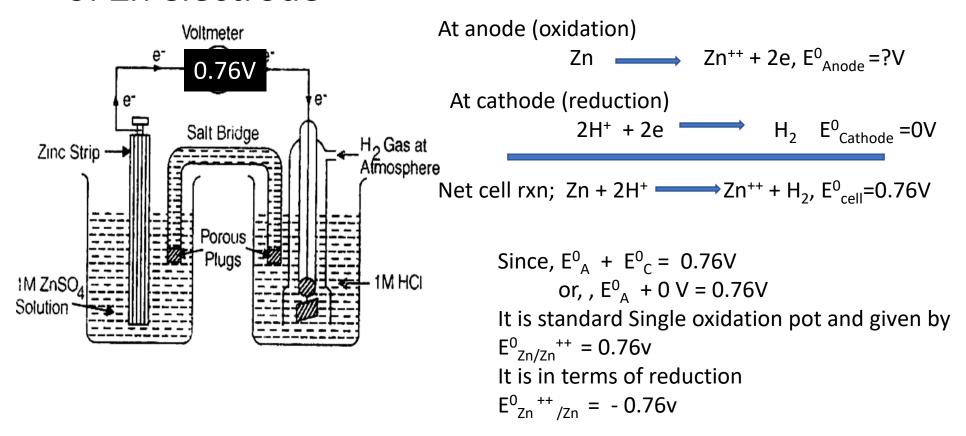


#### **Question for examination**

- 1. What is cell notation?
- 2. Write down the function of salt bridge.
- 3. What is standard single electrode potential
- 4. What is NHE or SHE?

- Standard single electrode potential
- No instrument to measure SSEP
- Need reference electrode having 0 V SSEP
- NHE is found as RE having 0 V electrode pot.
- Should make complete galvanic cell with NHE
- NHE anode, cell notation is; -Pt,H<sub>2</sub>(1atm)/H+ (1M)//
- NHE anode, cell notation is; //H<sup>+</sup> (1M)/H<sub>2</sub>(1atm)Pt <sup>+</sup>

# Measurement of single electrode potential of Zn electrode

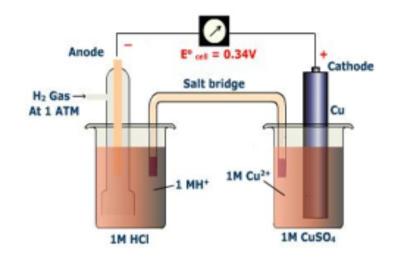


For any electrode;

Standard single reduction electrode potential = - Standard sing oxidation electrode potential

Cell notation;  $\bar{Z}n/Zn^{++}$  (1M) // H<sup>++</sup> (1M)/H<sub>2</sub> (1 atm), Pt

# Measurement of single electrode potential of Cu electrode



$$H_2 \longrightarrow 2H^+ + 2e \quad E_{Anode}^0 = 0V$$

At Cathode (reduction)

Net cell rxn; 
$$H_2 + Cu^{++} \longrightarrow H^+ + Cu$$
,  $E_{cell}^0 = 0.34V$ 

Since, 
$$E_A^0 + E_C^0 = 0..34V$$
  
or,  $E_C^0 = 0.34V$ 

It is standard Single reduction pot and given by

$$E_{Cu}^{++}/_{Cu} = 0.34V$$

It is in terms of oxidation

$$E^{0}_{Cu/Cu}^{++} = -0.34V$$

Cell notation; Pt, H2(1atm)/H+(1M) // Cu++(1M)/Cu

Foe Ag electrode, it is cathode  $E^0_{Ag}^+_{/Ag}$ = 0.80V (reduction potential)  $E^0_{Ag/Ag}^+$  = -0.80V (oxidation potential)

## Electrochemical series (ECS)

Measurement of St. Sing. Elect. Pot of each electrode With the help of NHE

Change all pot in terms of reduction and arrange them according to their increasing St Sing Red Elect Pot.

Zn electrode= Anode = oxidation  
= 
$$E_{Zn/Zn}^{0}^{++} = 0.76V$$
,  $E_{Zn}^{0}^{++}/_{Zn}^{-} = -0.76V$ 

Cu electrode= Cathode, 
$$E_{Cu}^{0}^{++}$$
 /Cu = 0.34V

Ag electrode= Cathode, 
$$E_{Ag}^{0}_{/Ag}^{+} = 0.80V$$

Fe electrode= Anode = oxidation  
= 
$$E_{Fe/Fe}^{0}$$
 = 0.44V,  $E_{Cu}^{0}$  ++  $E_{Cu}^{0}$  - 0.44V

.

.

Zn =

Fe = -0.44V

- 0.76V

H = 0V

Cu = +0.34

Ag = +0.80V

. .F2

2 = +2.87V

**ECS** 

## Application of ECS

#### 1. Strength of oxidizing & reducing agent

Moving from top to down in ECS, oxidizing strength is increased where as reducing strength is decreased.

#### 2. Construction of galvanic cell

Electrode having low value of st sing red pot Is always anode and that which has high value of St sing red pot is always cathode.

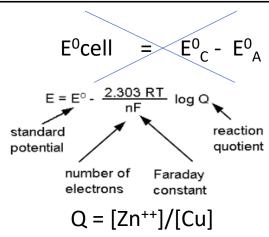
Q. Write down the cell notation of given Combination

$$E_{X/X}^{0}^{+} = -0.64VE_{M}^{0}^{++}_{/M} = +0.24V$$

Solution, M/M<sup>++</sup> // X<sup>+</sup>/X

Elements		Electro	ode Reaction	E <sup>⊕</sup> <sub>red</sub> (volts)	
A		Oxidised Form + ne -	→ Reduced Form		T
Increase	Li	Li+(aq) + e	— Li(s)	- 3.05	
	K	K*(aq) + e	— K(s)	- 2.93	I
	Ba	$Ba^{2+}(aq) + 2e^{-}$	— Ba(s)	-2.90	ı
	Ca	$Ca^{2+}(aq) + 2e^{-}$	— Ca(s)	-2.87	١
	Na	Na+(aq) + e	— Na(s)	- 2.71	
	Mg	$Mg^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Mg(s)	-2.37	ŀ
	Al	$Al^{3+}(aq) + 3e^{-}$	$\longrightarrow$ Al(s)	-1.66	ı
	Zn	$Zn^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Zn(s)	-0.76	ı
	Cr	$Cr^{3+}(aq) + 3e^-$	$\longrightarrow$ Cr(s)	-0.74	
	Fe	$Fe^{2+}(aq) + 2e^{-}$	$\rightarrow$ Fc(s)	- 0.44	ı
		$H_2O(l) + e^-$	$\rightarrow \frac{1}{2} H_2(g) + OH^-(aq)$	- 0.41	I
(a) Tendency for oxidation to occur (b) Power as reducing agent	Cd	$Cd^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Cd(s)	- 0.40	100
	РЬ	$PbSO_4(s) + 2e^-$	$\rightarrow$ Pb(s) + SO <sub>4</sub> <sup>2-</sup> (aq)	-0.31	0 01
	Co	$Co^{2+}(aq) + 2e^-$	—→ Co(s)	-0.28	HOI
	Ni	$Ni^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Ni(s)	- 0.25	duct
	Sn	$Sn^{2e}(aq) + 2e^{-}$	$\longrightarrow$ Sn(s)	- 0.14	F 16
	РЬ	Pb2+(aq) + 2e	— → Pb(s)	-0.13	bcy fe
	H <sub>2</sub>	2H+ 2e	H <sub>2</sub> (g) (standard electrode)	0.00	Tendency for reduction to occur
	Cu	Cu <sup>2+</sup> (aq) + 2e <sup>-</sup> -	$\longrightarrow$ Cu(s)	+ 0.34	(a)
	I <sub>2</sub>	$I_2(s) + 2c^-$	→ 21⁻(aq)	+ 0.54	ì
	Fe	$Fe^{3+}(aq) + e^{-}$	$\rightarrow$ Fe <sup>2+</sup> (aq)	+ 0.77	1
	Hg	$Hg_2^{2+}(aq) + 2e^-$	→ 2Hg( <i>l</i> )	+ 0.79	Ĭ
	Ag	Ag+(aq) + e	$\longrightarrow$ Ag(s)	+ 0.80	-
	Hg	Hg <sup>2+</sup> (aq) + 2e <sup>-</sup> -	$\longrightarrow$ Hg( $l$ )	+ 0.85	
	N <sub>2</sub>	NO <sub>3</sub> -+ 4H <sup>+</sup> + 3e <sup>-</sup>		+ 0.97	
	Br,	Br <sub>2</sub> (aq) + 2e <sup>-</sup> -		+1.08	-
	0,	$O_2(g) + 2H_3O^*(aq) + 2e^-$		+ 1.23	
	Cr	Cr <sub>2</sub> O <sub>2</sub> <sup>2</sup> + 14H <sup>+</sup> + e <sup>-</sup> -	11160070	+ 1.33	
	CI <sub>2</sub>	Cl <sub>2</sub> (g) + 2e <sup>-</sup> -		+1.36	
	Au	Au <sup>3+</sup> (aq) + 3e <sup>-</sup> -		+ 1.42	V
	Mn	$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^-$		+ 1.51	1
	F <sub>2</sub>	F <sub>2</sub> (g) + 2e <sup>-</sup> -		+ 2,87	

#### 3. Calculation of EMF of cell at standard condition



Use; At anode (oxidation)

$$Zn = Zn^{++} + 2e, E^{0}_{Oxidation} = 0.76V$$

At cathode (reduction

$$Cu^{++} + 2e = Cu, E_A^0 = 0.34V$$

Net rxn, 
$$Zn + Cu^{++} = Zn^{++} + Cu, E^0cell = E_A^0 + E_C^0$$

#### 4. Spontaneity of redox reaction

If EMF of cell is +ve, the given redox rxn towards forward direction is spontaneous And if it is –ve, the redox rxn is nonspontaneous (not feasible)

#### 5. Slow and fast redox reaction

Larger the distance between two electrode faster will be the redox reaction

1. 
$$Zn + Cu^{++} = Zn^{++} + Cu$$
,  $E^0$ cell = 1.1V (fast rxn)

2. 
$$Cu + 2Ag^{+} = Cu^{++} + 2Ag$$
,  $E^{0}$ cell = 0.46V (slow rxn)

#### **6.** Calculation of ΔG and Keq of reaction

$$\Delta G = - nFE$$

$$\Delta G = -RT \ln Keq$$

7. Only those metal having upper position in ECS can displace another metal from soluble salt which is below in the ECS

Fe vessel can not be used to store CuSO4 solution but it can be used to store ZnSO4 solution

8. Metals above the Hydrogen in ECS can produce H2 gas from nonoxidising acid but metals below H2 could not

# Calculation of emf of cell or electrode potential at nonstandard condition (Nernst equation)

Standard condition; (1) Temperature 25° C

- (2) Concentration of electrolyte 1M
- (3) If gas is used as electrode, its pressure 1 atm

For given cell, calculate the emf at standard condition

Cu + Ag<sup>+</sup> = Cu<sup>++</sup> + Ag  
Given, 
$$E^0_{Cu/Cu}^{++}$$
 = -0.34V ,  $E^0_{Cu}^{++}_{/Cu}$  = +0.34 V  
 $E^0_{Ag}^{+}_{/Ag}$  = +0.80V

Solution; 
$$E^{0}_{Cell} = E^{0}_{C} + E^{0}_{A}$$
  
 $E^{0}_{Cell} = 0.80 - 034$   
 $= 0.46V$ 

$$Cu \longrightarrow Cu^{++} + 2e, E^{0}_{Cu/Cu} = -0.34V$$

At cathode (reduction)

$$2 \text{ Ag}^+ + 2 \text{e} \longrightarrow 2 \text{Ag}, E^0_{\text{Ag/Ag}} = +.080 \text{V}$$

Net rxn; Cu+2 Ag<sup>+</sup>
$$\longrightarrow$$
 Cu<sup>++</sup>+2Ag, E<sup>0</sup><sub>cell</sub>=0.46v

$$E_{cell} = E_{cell}^{o} - \frac{RT}{nF} \ln Q$$
 Q = [Cu + +] [Ag]<sup>2</sup>/[Cu] [Ag +]<sup>2</sup>