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# **CY 1020: Dynamics of Chemical Systems**

## **Basics in Electrochemistry**

# CY1020: Dynamics of Chemical Systems



**Basics in Electrochemistry:** Electrochemical principles and reactions, basic concepts of electrochemical cells, Nernst Equation, applications of EMF, conductivity of electrolyte solutions.



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# Books Recommended



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1. Principles of Physical Chemistry: Puri, Sharma, Pathania
2. Physical Chemistry: Vol- , K L Kapoor
3. Physical Chemistry: P.W. Atkins



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# Electrochemistry



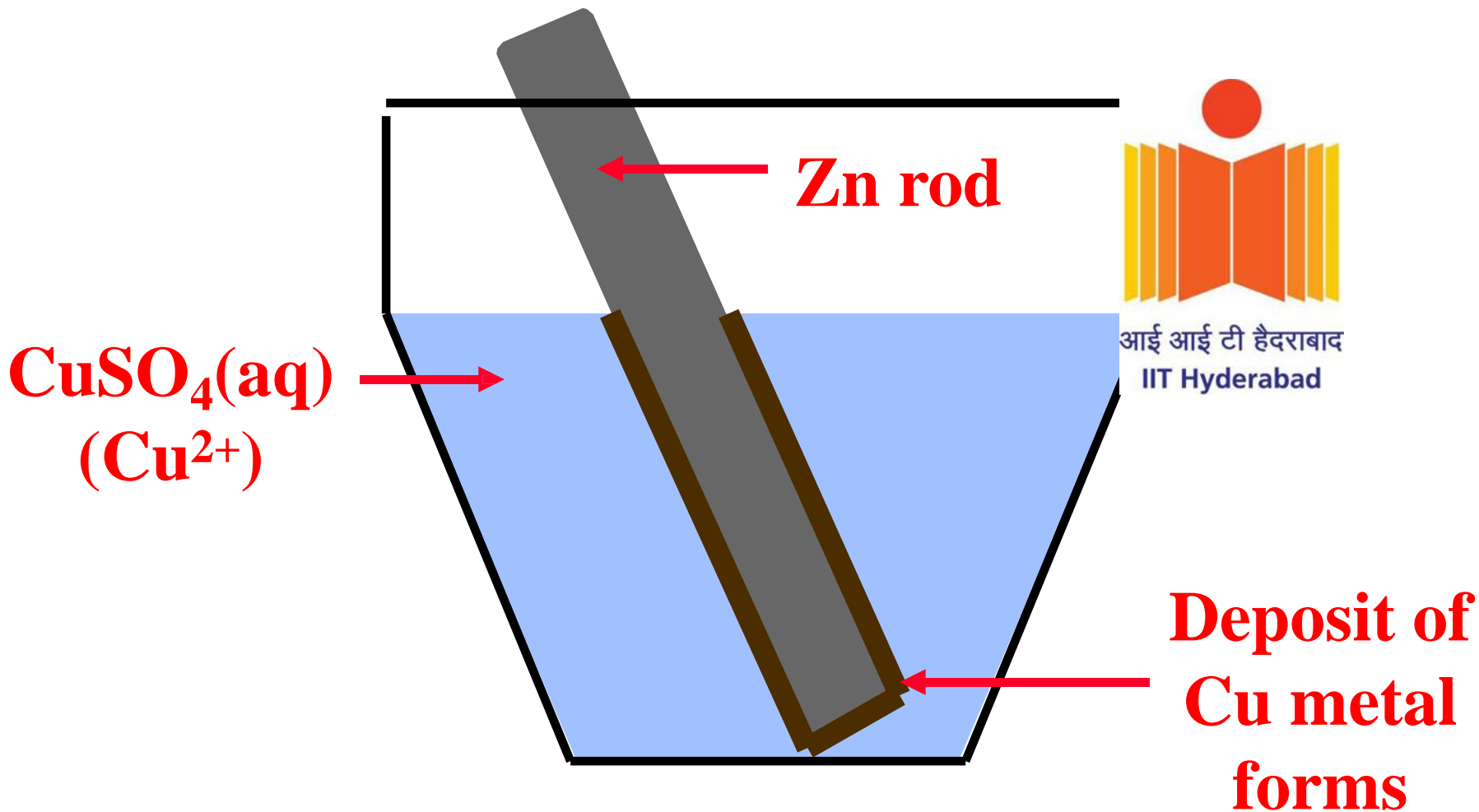
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## Electrochemistry

- ◆ deals with interconversion between chemical and electrical energy
- ◆ involves redox reactions: electron transfer reactions

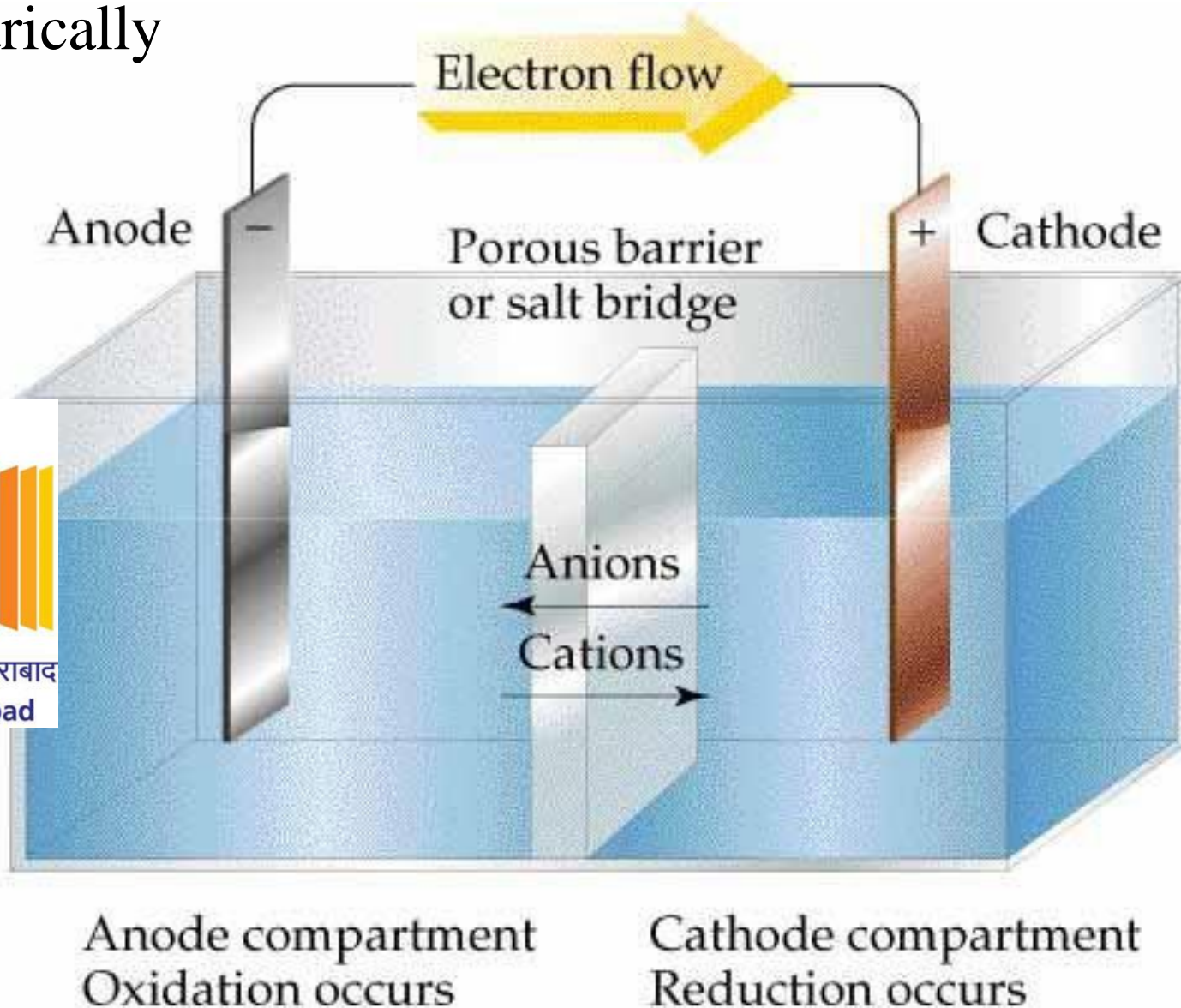
# Direct Redox Reaction

- ◆ Oxidizing and reducing agents are mixed together and reaction takes place in the same vessel

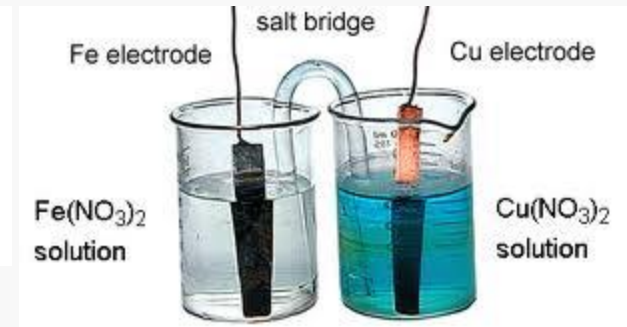
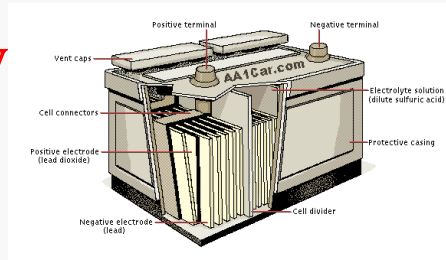


# Indirect Redox Reactions

Oxidizing and reducing agents are separated but connected electrically



- **Electrochemical cell-Voltaic Cell**
  - ◆ cell in which a spontaneous redox reaction generates electricity
  - ◆ chemical energy  $\rightarrow$  electrical energy
  - ◆ Ex: **Battery**



- **Electrolytic Cell**

- ◆ electrochemical cell in which an electric current drives a non-spontaneous redox reaction
- ◆ electrical energy  $\rightarrow$  chemical energy
- ◆ Ex: **Decomposition of water**



## **Difference between Electrochemical (Galvanic) and Electrolytic Cell**

<b>Electrochemical Cell</b>	<b>Electrolytic cell</b>
It is a device to convert chemical energy into electrical energy as a result of redox reaction taking place	It is a device to convert electrical energy into chemical energy to bring about the redox reaction
It is based upon redox reaction which is spontaneous	The redox reaction is non-spontaneous
The two electrodes may be set up in solution of the same or different electrolytes	The two electrodes are set up in the same electrolytic solution
The electrode on which oxidation takes place is called the anode and the electrode on which reduction takes place is called the cathode	The electrode which is connected to the negative terminal of the battery is called cathode, the cations migrate to it which gains electrons and hence reduction takes place here. The other electrode is called the anode
A salt bridge or a porous pot is used in this cell	No salt bridge is used in this case



# The Electrochemical Cells: Voltaic Pile

- ❖ Invented by Alessandro Volta in 1800
- ❖ Zinc and Copper with a cloth soaked in brine
- ❖ Technical Flaws:
  - ❖ Compressing of cloth created shorts
  - ❖ Short battery life



• Voltaic Pile

- **Electrodes:** are usually metal strips/wires connected by an electrically conducting wire.
- **Salt Bridge:** is a U-shaped tube that contains a gel permeated with a solution of an inert electrolyte.
- **Anode:** is the electrode where oxidation takes place.
- **Cathode:** is the electrode where reduction takes place.



- **Convention for expressing the cell:**

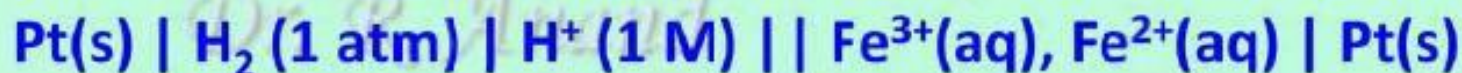


$\parallel$  represents Salt bridge

$\mid$  represents Phase boundary



The notation for a cell involving a gas has an additional vertical line because an additional phase is present. e.g.



- Electrons flow from anode to cathode.
- Anode is placed on left by convention.



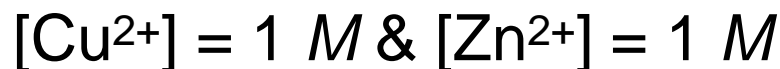
# Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- **cell voltage**
- **electromotive force (emf)**
- **cell potential**



Cell Diagram



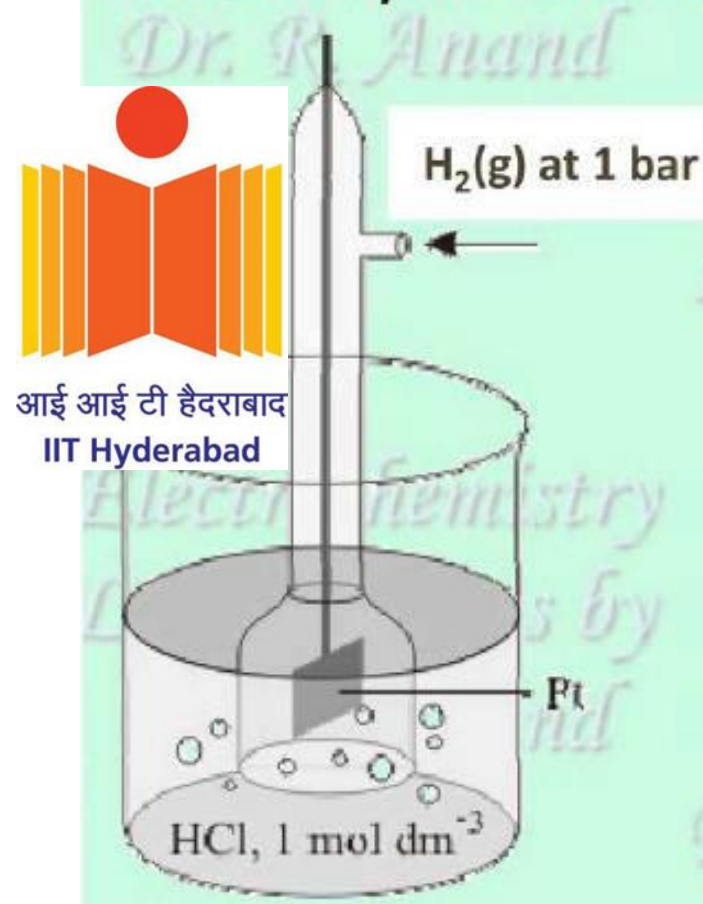
**anode**

**cathode**

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} = E_{\text{redn}} - E_{\text{ox}} \\ E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{redn}} - E^{\circ}_{\text{ox}} \end{aligned}$$

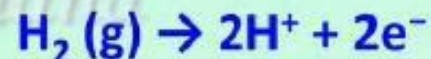
## STANDARD HYDROGEN ELECTRODE

The primary reference electrode is the standard hydrogen electrode. It consists of a platinum foil that is connected to a platinum wire and sealed in a glass tube.  $\text{H}_2$  gas at 1 atm pressure is passed through the side arm of the glass tube and bubbled through a solution of  $\text{H}^+$  ions of unit activity (e.g. 1N HCl solution) The electrode potential of SHE is zero at all temperatures.

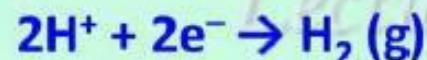


It is represented as  $\text{Pt}, \text{H}_2 (1\text{atm}) \mid \text{H}^+ (1\text{M})$

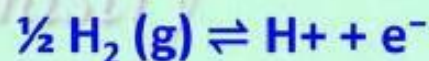
When it acts as anode the electrode reaction can be written as



When it acts as cathode the electrode reaction can be written as



The equilibrium of hydrogen electrode is represented as



●  $E^\circ = 0 \text{ V}$  (by definition)



**The electrode is reversible with respect to hydrogen ion.** Since  $\text{H}_2$  gas is non-conducting, Pt or some other metal which is not attacked by the acid and comes easily into equilibrium with  $\text{H}_2$  is used for making electrical contact in the circuit.

### **Limitations**

- It is very difficult to maintain the unit activity of hydrogen ions in solution.
- It is very difficult to pass hydrogen at 1 atm pressure uniformly.
- The deposition of impurities by adsorption on platinum foil causes hindrance in maintaining the equilibrium between hydrogen gas and hydrogen ions.
- This electrode cannot be used if some reducible ions are present in the equilibrium.
- The hydrogen electrode is readily affected by compounds of Hg, As, S and oxidizing agents like  $\text{Fe}^{3+}$ ,  $[\text{MnO}_4]^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  etc
- It cannot be used in solutions containing redox system
- The potential of the electrode is altered by changes in barometric pressure.
- It requires considerable volume of test solution.



# Standard Electrode Potentials

- Standard Reduction Potentials,  $E^\circ$ 
  - ◆  $E^\circ_{\text{cell}}$  measured relative to S.H.E. (0 V)
    - electrode of interest = cathode
- Compare strengths of reducing/oxidizing agents.
  - ◆ the more -  $E^\circ$ , stronger the red. agent
  - ◆ the more +  $E^\circ$ , stronger the ox. agent

# Standard Reduction Potentials

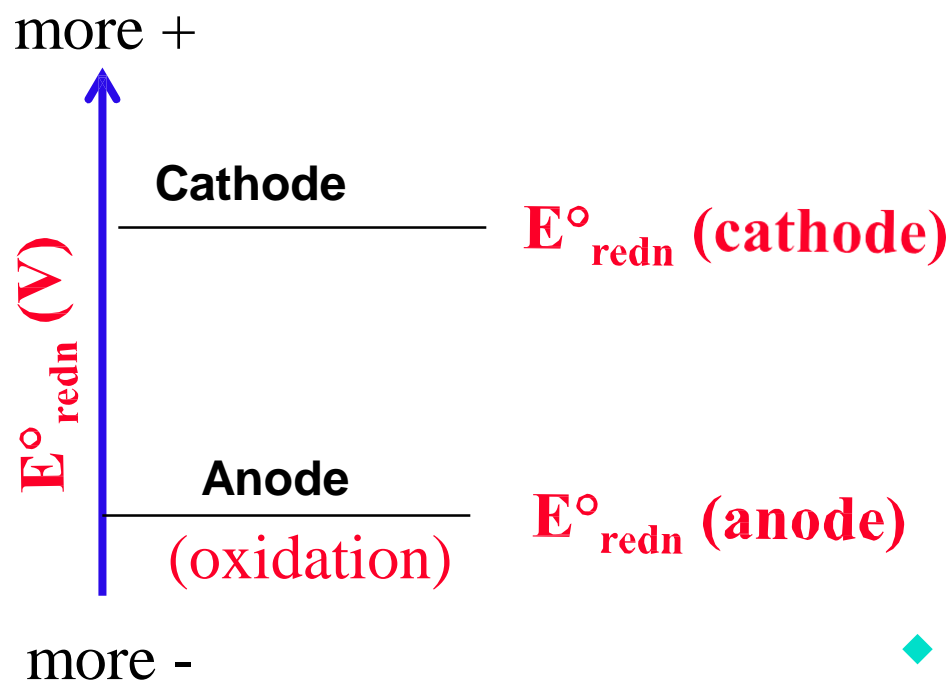
Ox. agent strength increases ↑	Reduction Half-Reaction	E°(V)	Red. agent strength increases ↓
	<b><math>\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})</math></b>	<b>2.87</b>	
	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	1.50	
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	1.33	
	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77	
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34	
	$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15	
	<b><math>2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})</math></b>	<b>0.00</b>	
	$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14	
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23	
	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44	
	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76	
	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66	
	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37	
	<b><math>\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})</math></b>	<b>-3.04</b>	



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# Uses of Standard Reduction Potentials

- Determine if oxidizing and reducing agent react spontaneously.



Spontaneous reaction if

$$E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$$

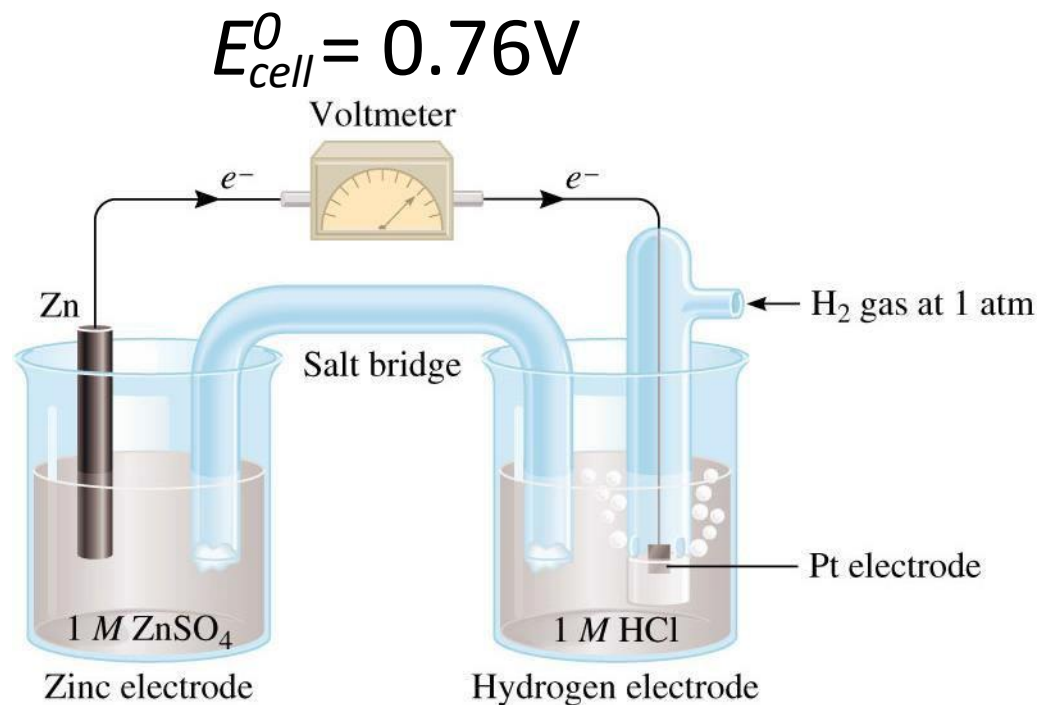
- ◆  $E^\circ_{\text{cell}} > 0$  : spontaneous redox reactions



# Standard Reduction Potentials

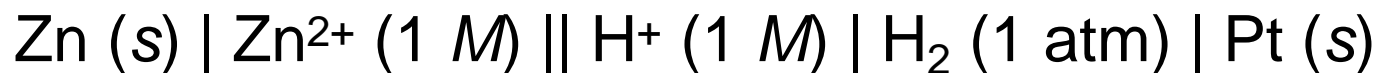


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**Standard emf ( $E_{cell}^0$ )**

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$



$$E_{cell}^0 = E_{H^+/H_2}^0 - E_{Zn^{2+}/Zn}^0$$

$$0.76 V = 0 - E_{Zn^{2+}/Zn}^0$$

$$E_{Zn^{2+}/Zn}^0 = -0.76 V$$



# Equilibrium Constants from $E_{\text{cell}}$

- Is there a relationship between  $E_{\text{cell}}$  and  $\Delta G$  for a redox reaction?

- Relationship between  $E_{\text{cell}}$  and  $\Delta G$  :

- ◆  $\Delta G = -nFE_{\text{cell}}$

- $F$  = Faraday constant = 96500 C/moles,  $n$  = #  $e^-$ 's transferred redox rxn.
- $1 \text{ J} = \text{CV}$
- $\Delta G < 0$ ,  $E_{\text{cell}} > 0$  = spontaneous

- Under standard state conditions:

- ◆  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$

And  $\Delta G^\circ = -RT \ln K$

So  $-nFE_{\text{cell}}^\circ = -RT \ln K$



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# Spontaneity of Redox Reactions

$$\Delta G = -nFE_{\text{cell}} \quad n = \text{number of moles of electrons in reaction}$$

$$\Delta G^0 = -nFE_{\text{cell}}^0 \quad F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{ C/mol}$$

$$\Delta G^0 = -RT \ln K = -nFE_{\text{cell}}^0$$

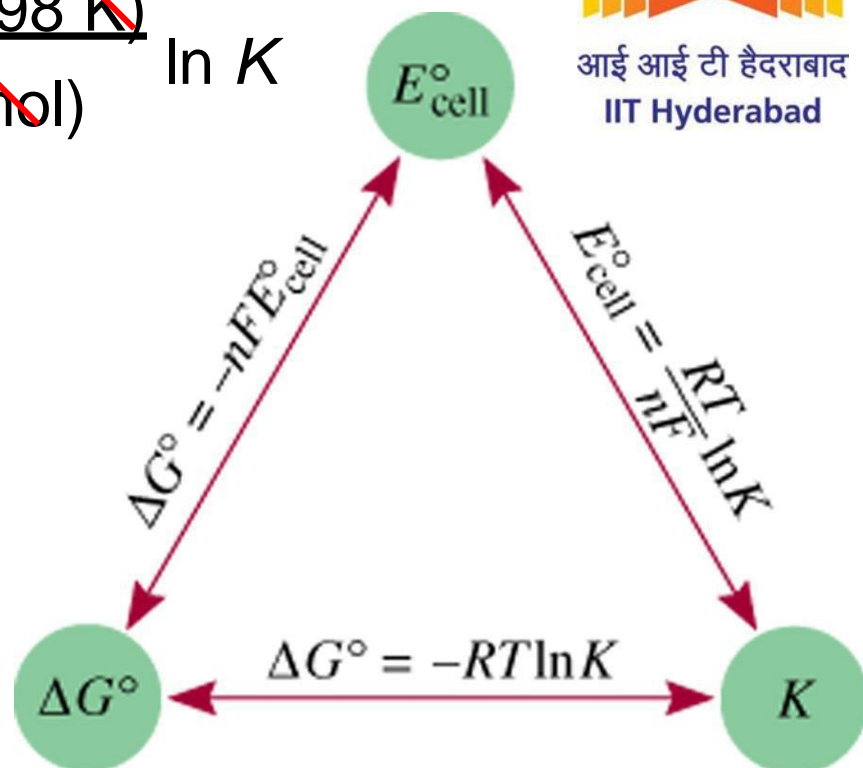
$$E_{\text{cell}}^0 = \frac{RT}{nF} \ln K = \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n (96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

$$E_{\text{cell}}^0 = \frac{0.0257 \text{ V}}{n} \ln K$$

$$E_{\text{cell}}^0 = \frac{0.0592 \text{ V}}{n} \log K$$



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# The Nernst Equation



- $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF)\ln K$  (Nernst eqn.)

- ◆ At 298 K (25°C)

$n$  = number of moles of electrons in reaction

$$F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{ C/mol}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n (96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

so

- $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0257/n) \ln K$

or

- $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592/n) \log K$

**Nernst Equation**

# Application of Gibb's – Helmholtz equation

## Calculation of enthalpy change for the cell reaction (galvanic cell)

If a cell yields  $nF$  Columbus of electricity in a reversible manner, it must equal to the decrease in the free energy, then

$$-\Delta G = nFE^o \quad (1)$$

Where  $n$  = no. of electrons involved in the process

$F$  = Faraday = 96,500 coulombs

$E^o$  = Energy in volts

Gibb's – Helmholtz equation

Substituting,  $-\Delta G = nFE^o$

$$E^o = -\frac{\Delta H}{nF} + T \left( \frac{\partial E^o}{\partial T} \right)_P$$

$$\Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P$$

$$-nFE^o = \Delta H + T \left( \frac{\partial (-nFE^o)}{\partial T} \right)_P$$

$$-nFE^o = \Delta H - nFT \left( \frac{\partial E^o}{\partial T} \right)_P$$

$$\Delta H = -nFE^o + nFT \left( \frac{\partial E^o}{\partial T} \right)_P \quad (2)$$

$$\Delta H = -nF \left[ E^o - T \left( \frac{\partial E^o}{\partial T} \right)_P \right] \quad (3)$$



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# Application of Gibb's – Helmholtz equation (cont.)



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## Calculation of EMF of the cell

Diving eqn. (2) by  $nF$

$$\Delta H = -nFE^o + nFT \left( \frac{\partial E^o}{\partial T} \right)_p \quad (2)$$

$$E^o = -\frac{\Delta H}{nF} + T \left( \frac{\partial E^o}{\partial T} \right)_p \quad (4)$$

Calculation of entropy change

$\Delta H$  and  $\Delta S$  are related by eqn.

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

But,  $-\Delta G = nFE^o$  and  $\Delta H$  can be calculated from eqn. (3). Using these values  $\Delta S$  can be calculated from eqn. (5)

$$\Delta H = -nF \left[ E^o - T \left( \frac{\partial E^o}{\partial T} \right)_p \right] \quad (3)$$

Gibb's – Helmholtz equation is applicable to all process occurring at constant pressure. It is used to calculate  $\Delta H$  from values of free energy change at two different temperature.

# Factors affecting the battery performance

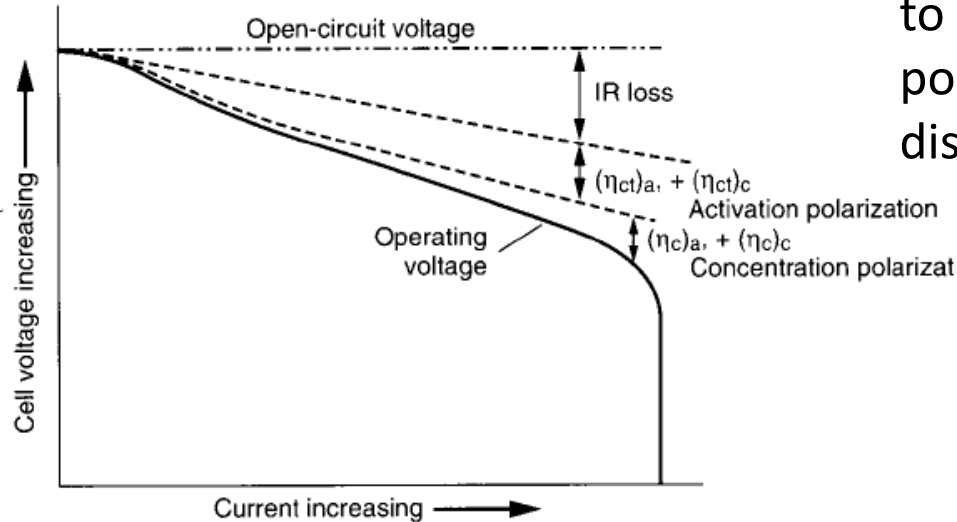
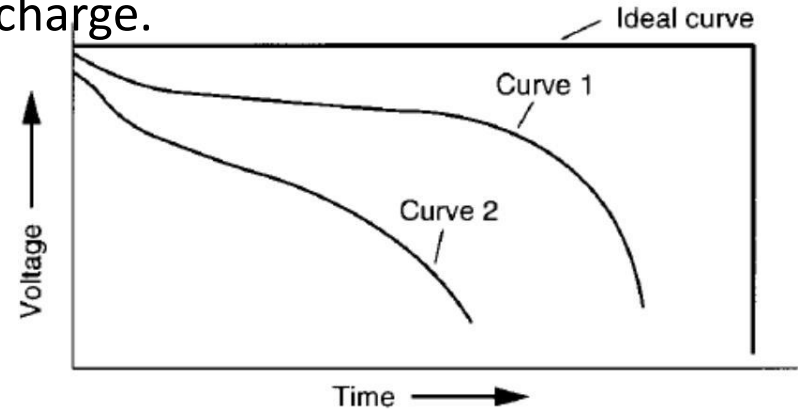


FIGURE 2.1 Cell polarization as a function of operating current.

The difference is caused by IR losses due to cell (and battery) resistance and polarization of the active materials during discharge.



The voltage also drops during discharge as the cell resistance increases due to the accumulation of discharge products, activation and concentration, polarization, and related factors.

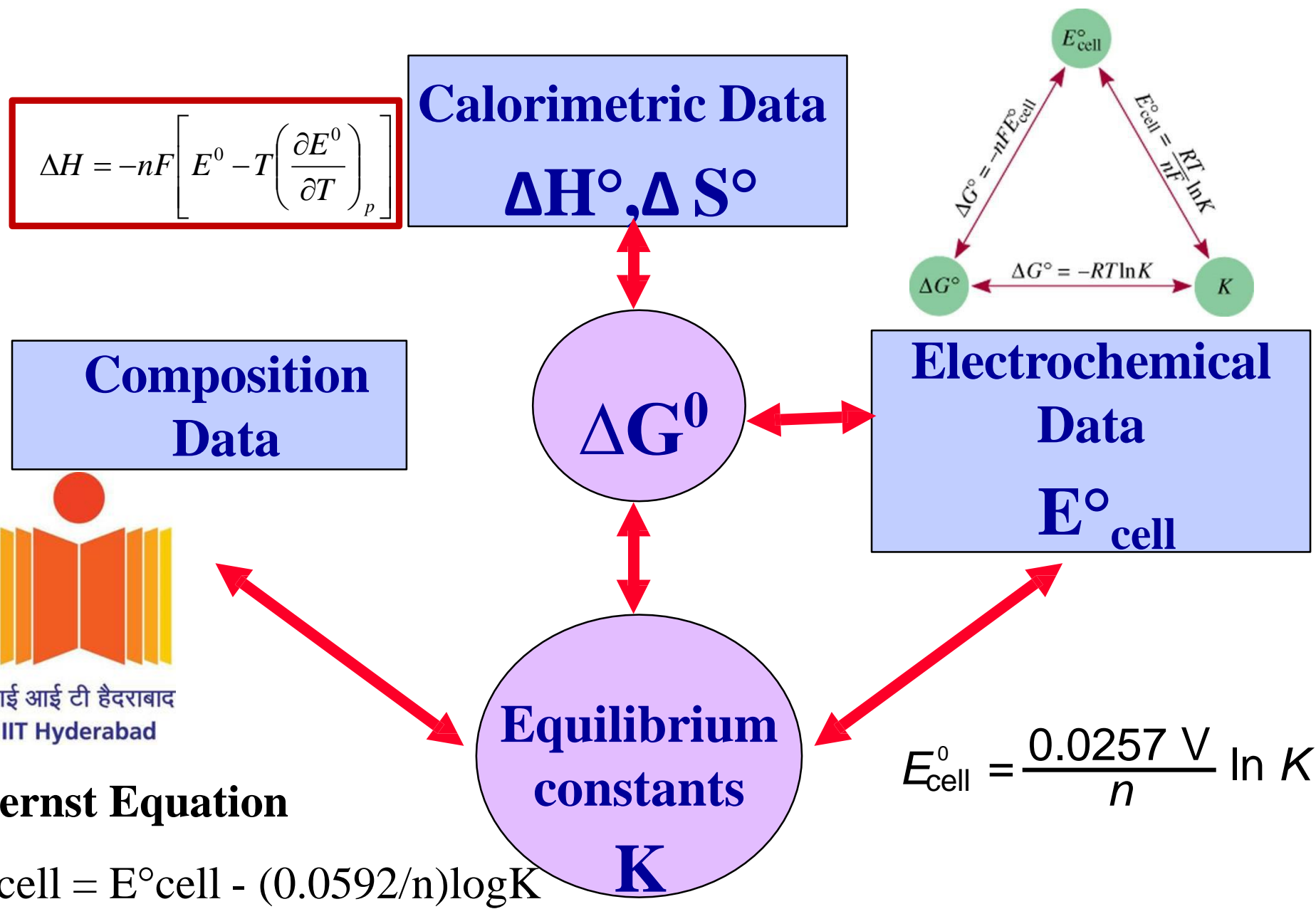
When connected to an external load  $R$ , the cell voltage  $E$  can be expressed as

$$E = E_0 - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i = iR \quad (2.1)$$

where  $E_0$  = electromotive force or open-circuit voltage of cell  
 $(\eta_{ct})_a, (\eta_{ct})_c$  = activation polarization or charge-transfer overvoltage at anode and cathode  
 $(\eta_c)_a, (\eta_c)_c$  = concentration polarization at anode and cathode  
 $i$  = operating current of cell on load  
 $R_i$  = internal resistance of cell



# Equilibrium Constant from $E_{\text{cell}}$



# Schematic presentation of a Li-ion cell

## Cathodes

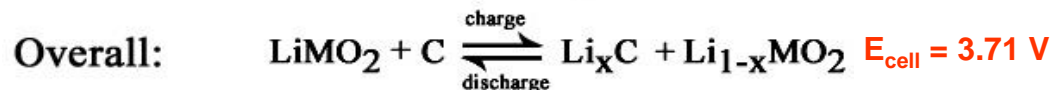
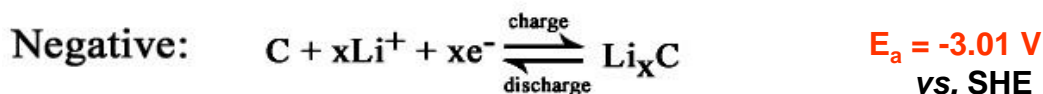
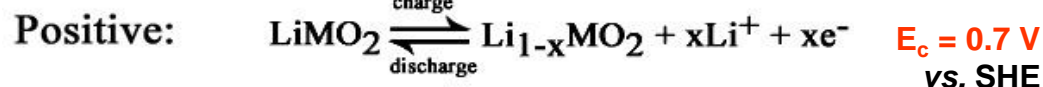
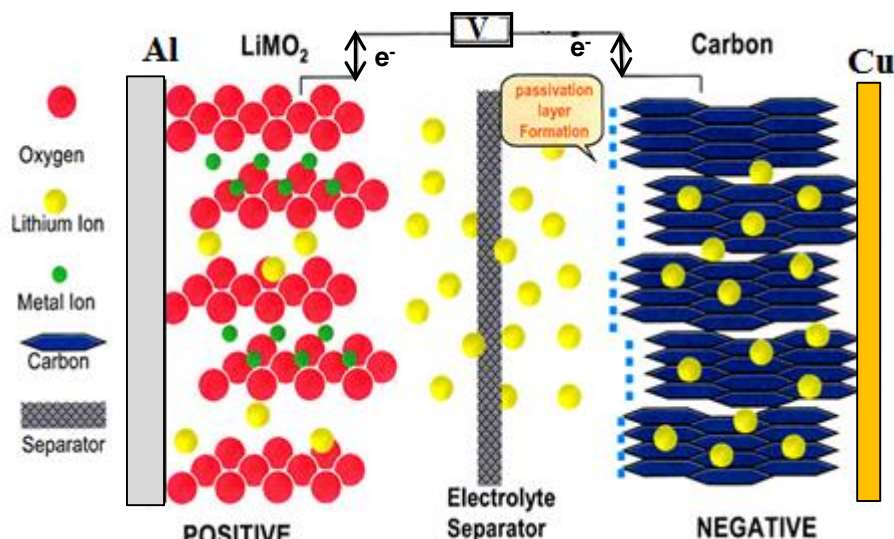
(Layered):  $\text{LiCoO}_2$  (3.7 V)

(Spinel):  $\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{O}_4$  (4.7V)

(Olivine):  $\text{LiFePO}_4$  (3.4V)



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**Electrolyte: EC:DMC (1:2) /  $\text{LiPF}_6$  (1 M)**

## Anodes

$\text{LiC}_6$  (0.1-0.2V)

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  (1.55V)

Next gen: **Si-C** (0.1-0.2V)

Sn based anodes

## Composite Cathodes for Li-ion batteries

**Positive active mass:**  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$

❖ **Conductive additive** (e.g. Carbon, carbon nanofibers, graphenes, graphites)

❖ **Binder:** PVDF,

❖ **Current collector** (Al)

## Composite Anodes for Li-ion batteries

**Negative active mass:**  $\text{LiC}_6$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$

❖ **Conductive additive** (e.g. Carbon, carbon nanofibers, graphenes, graphites)

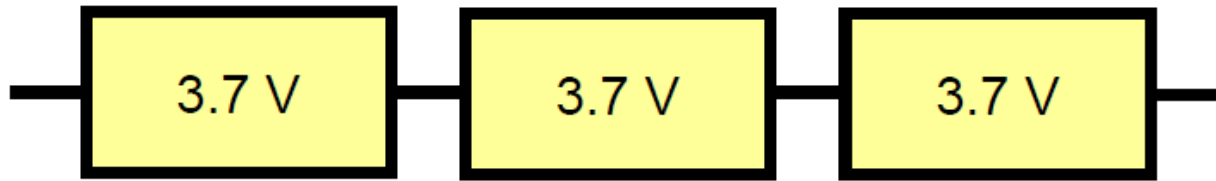
❖ **Binder:** PVDF, SMC, Teflon

❖ **Current collector** (Cu)

# Lithium Ion Batteries

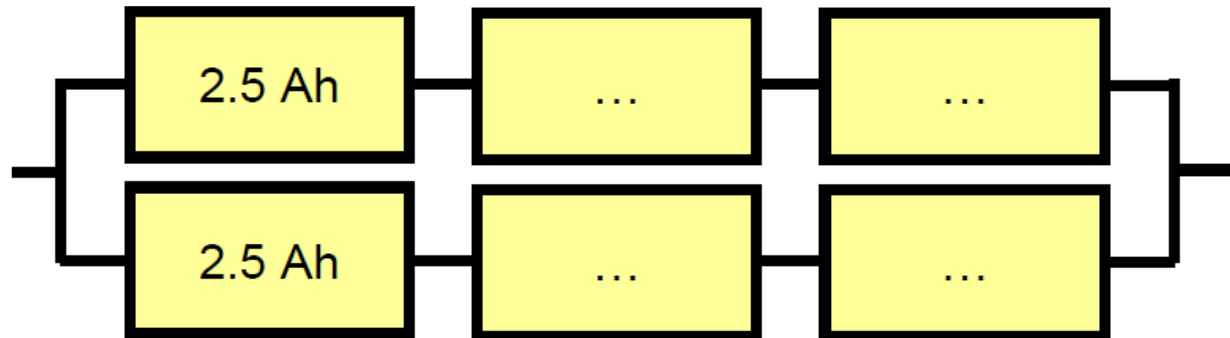
## How to combine Li-ion cells?

→ **Connect your battery (3.7 V, 2.5 Ah) in series**



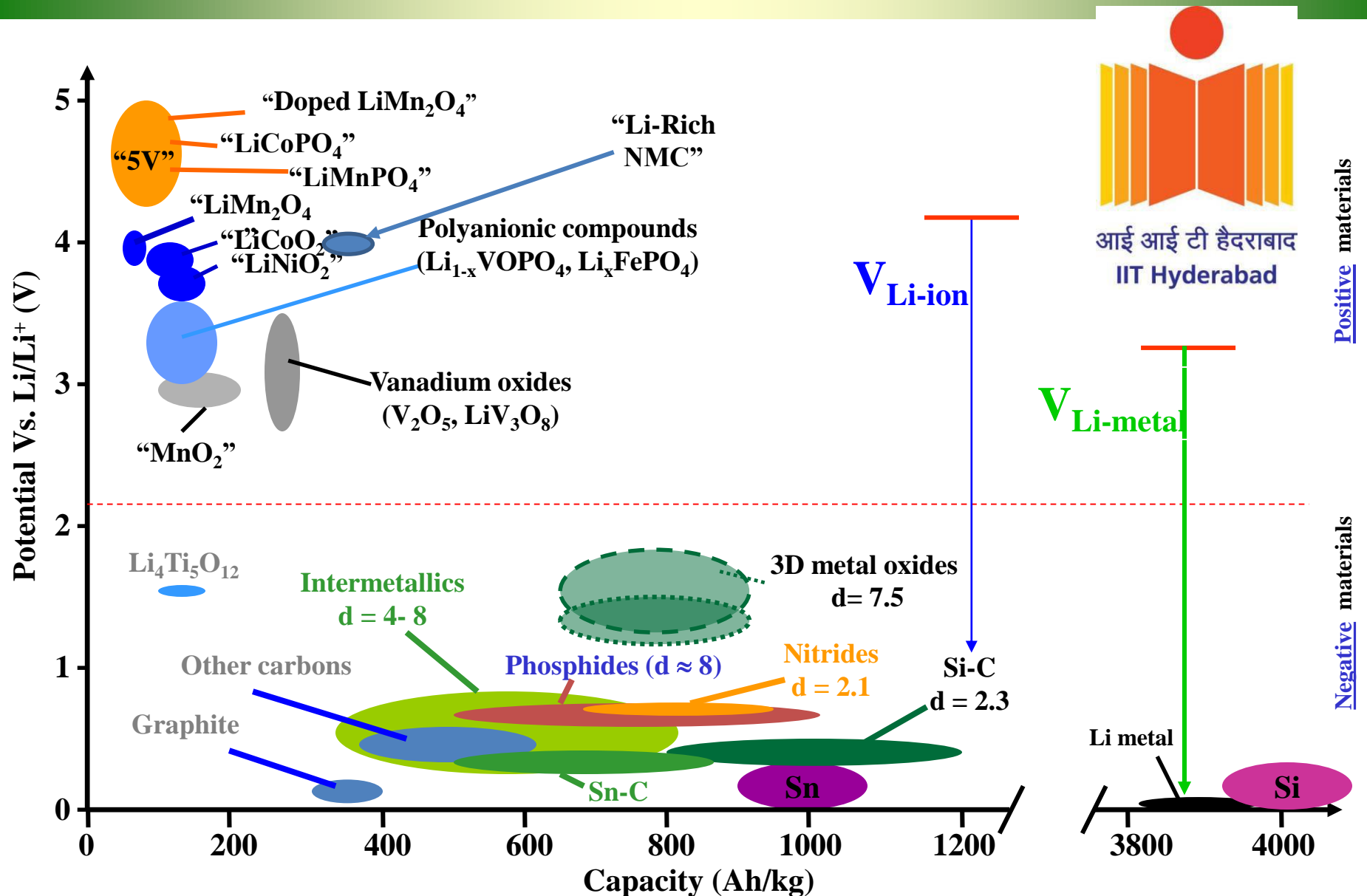
→ 3 times 3.7 V gives you 11.1 V (you get the voltage you need)

→ **Connect your battery (3.7 V, 2.5 Ah) in parallel**

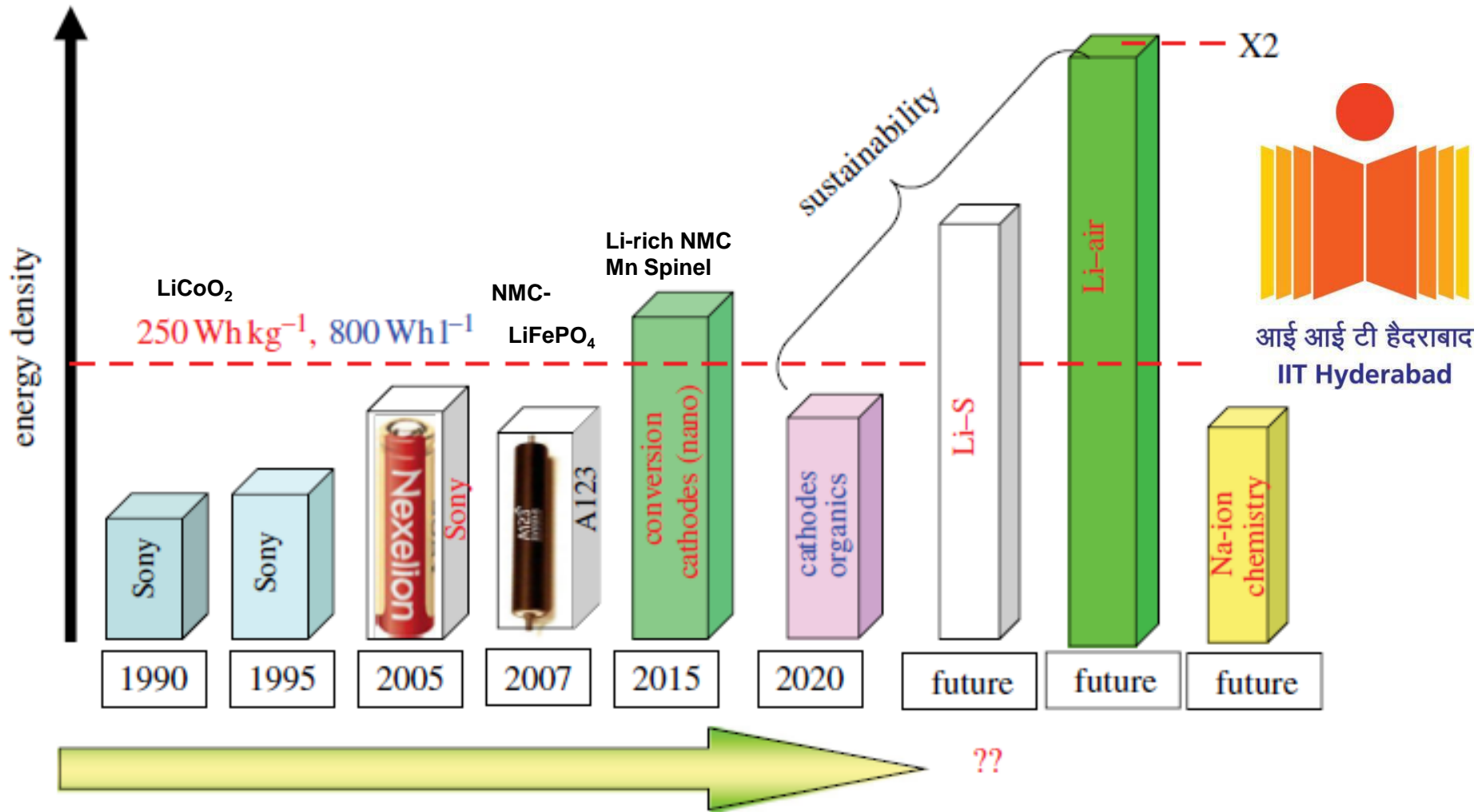


2 times 2.5 Ah gives you 5 Ah (you get the capacity you need)

# Current status of cathode and anode Materials



# The lithium battery cathode technology landscape



Cathode materials are detrimental to the performance and safety of Li-ion batteries.



# Electrochemistry of Lead-Acid Battery



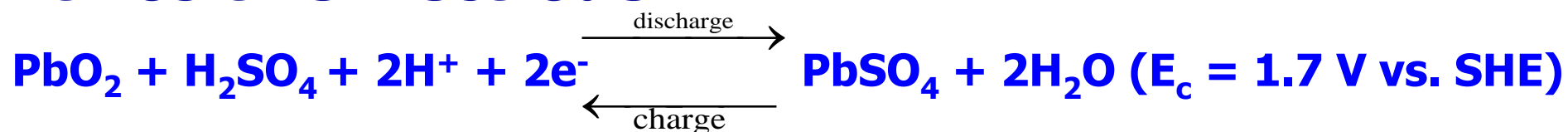
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**Negative Electrode: Lead**

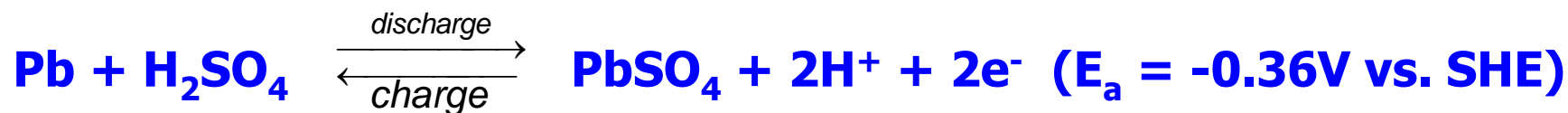
**Positive Electrode : Lead dioxide**

**Electrolyte : Sulfuric acid**

## At Positive Electrode



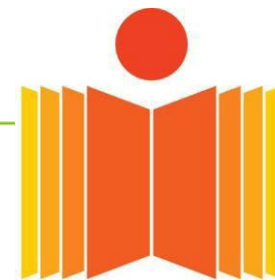
## At Negative Electrode



## Net Cell Reaction



# Lead-Acid Batteries for Start-Stop Applications



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## How does a Start-Stop system work?



**STOP** at red  
traffic light  
→ Engine off



Battery is  
**DISCHARGED**



**START** at green  
traffic light  
→ Engine crank



Battery is  
**DISCHARGED**



Driving phase



Battery is  
**RECHARGED**

# CELLS AND BATTERIES

**1.The anode or negative electrode**—the reducing or fuel electrode—which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

**Anode should have following properties:**

- 1.Efficiency as a reducing agent,
- 2.high coulombic out put (Ah/ g),
- 3.good conductivity,
- 4.stability, ease of fabrication, and low cost.

Practically, metals are mainly used as the anode materials.

Ex: Lithium



**2.The cathode or positive electrode** —the oxidizing electrode—which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

**Cathode should have following properties:**

1. The cathode must be an efficient oxidizing agent,
2. be stable when in contact with the electrolyte,
3. Have a useful working voltage.



The most of the common cathode materials are **metallic oxides**. Other cathode materials, such as the **halogens** and the **oxyhalides, sulfur and its oxides**, are used for special battery systems

# Separator:

Physically the anode and cathode electrodes are electronically isolated in the cell to prevent internal short-circuiting, but are surrounded by the electrolyte.

The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity.

In some cases the electrolyte is immobilized for a non-spill design.

Electrically conducting grid structures or materials may also be added to the electrodes to reduce internal resistance.

**The electrolyte—the ionic conductor** —which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode.

❖ The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalis to impart ionic conductivity.

❖ Some batteries use solid electrolytes, which are ionic conductors at the operating temperature of the cell.

The electrolyte must have **good ionic conductivity but not be electronically conductive, as this would cause internal short-circuiting.**

Other important characteristics are non-reactivity with the electrode materials, little change in properties with change in temperature, safety in handling, and low cost.

Most electrolytes are aqueous solutions, but there are important exceptions as, for example, in thermal and lithium anode batteries, where molten salt and other non-aqueous electrolytes are used to avoid the reaction of the anode with the electrolyte.

# Electrolytic conductance

- ❖ Electrolytic conductance occurs when a voltage is applied to the electrode dipped into an electrolyte solution, ions of the electrolyte move and electric current flows through the electrolytic solution.
- ❖ This power of the electrolyte to conduct electricity is known as conductance or conductivity.
- ❖ Electrolytic solution also obey Ohm's Law just like metallic conductor.





# Difference between electronic & electrolytic conductors

Electronic conductors	Electrolytic conductors
(1) <b>Flow of electricity take place without the decomposition of substance.</b>	(1) <b>Flow of electricity takes place by the decomposition of the substance.</b>
(2) Conduction is due to the flow of <b>electron</b>	(2) Flow of electricity is due to the <b>movement of ions</b>
(3) <b>Conduction decreases with increase in temperature</b>	(3) <b>Conduction increases with increase in temperature</b>

The conductivity of a solution of water is highly dependent on its concentration of dissolved salts and sometimes other chemical species which tend to ionize in the solution.

Electrical conductivity of water samples is used as an indicator of how salt free or impurity free the sample is; the purer the water, the lower the conductivity.

Solution	Electric Conductivity (Sm <sup>-1</sup> )
Seawater	5
Drinking water	0.0005 to 0.05
De-ionized water	$5.5 \times 10^{-6}$



# What is electrolyte?

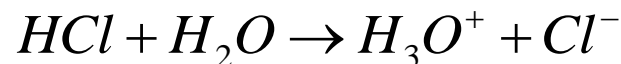
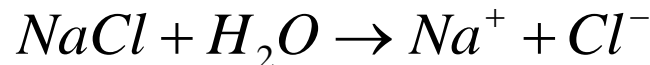
- Any substance that produce ions when dissolved in a solvent (usually water) is an electrolyte.

Dissociate in a solvent to give two or more particles.

Consequently, the total number of particles increases in solution

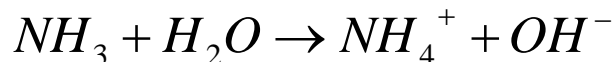
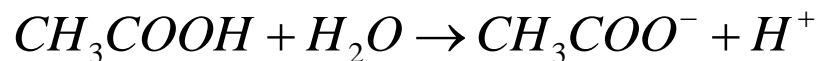
## Types of electrolytes

### ❖ Strong electrolyte

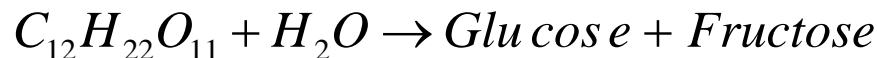


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### ❖ Weak electrolyte



### ❖ Non-electrolyte



Solutions of cane sugar, glucose, urea etc.

# Degree of dissociation

**It is defined as the fraction of total substance that undergoes dissociated into ions.**

$$\alpha = \frac{\text{No. of moles of substance dissociated}}{\text{Total no. of moles of the substance taken}}$$

$$\alpha = \frac{C_{\text{dissociated}}}{C_{\text{Total}}} = \frac{N_{\text{dissociated}}}{N_{\text{Total}}}$$

$$\text{Percent (\% )of dissociation} = \frac{[\text{HA}]_{\text{dissociated}}}{[\text{HA}]_{\text{Initial}}} \times 100$$

Or Degree of dissociation can be written as  $\alpha = \frac{i - 1}{m - 1}$

**where m is the number of particles in solution, i is Van't Hoff factor**

For example: the electrolytes of the type AB, such as KCl, NaCl, etc., the number of particles in solution  $m = 2$

Then  $\alpha = i - 1$



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**Van't Hoff factor 'i'** to express the extent of association or dissociation of solutes in solution.

$$i = \frac{\text{normal molar mass of the solute}}{\text{observed molar mass of the solute}}$$

- ❖ In case of association, observed molar mass being more than the normal, the factor 'i' has a value less than 1.
- ❖ In case of dissociation, the Van't Hoff factor is more than 1 because the observed molar mass has a lesser value.

For most ionic compounds dissolved in water, the van 't Hoff factor is equal to the number of discrete ions in a formula unit of the substance (Ex: NaCl, KCl etc.  $i = 1+1=2$ ).

- ❖ In case of solutes which do not undergo any association or dissociation in a solvent. Van't Hoff factor 'i' will be equal to 1 because the observed and normal molar masses will be same.

**Example:** For most non-electrolytes dissolved in water, the van' t Hoff factor is essentially 1.

- ❖ The deviation for the van 't Hoff factor tends to be greatest where the ions have multiple charges.

# According to the Degree of dissociation ( $\alpha$ ) electrolytes can be classified into the following:

- **strong electrolytes** are compounds that dissociate to a large extent ( $\alpha > 30\%$ ) into ions when dissolved in water. For example, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HI, NaOH, KOH, KCl.
- **medium strong electrolytes**  $\alpha = 2 - 30\%$ . H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub>.
- **weak electrolytes** are compounds that dissociate to only a small extent  $\alpha < 2\%$ . For example, NH<sub>4</sub>OH, H<sub>2</sub>S, HCN, H<sub>2</sub>CO<sub>3</sub>.
- **nonelectrolytes**  $\alpha = 0$  are compounds that don't dissociate when dissolved in water. Example: alcohols, H<sub>2</sub>O



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# Activity and Concentration



- ❖ Activity – “**effective concentration**” of a species in a mixture
- ❖ The activity of an ion is particularly influenced by its surroundings.
- ❖ Activity is treated as a **dimensionless quantity**
- ❖ The activity of **pure substances in condensed phases** (solid or liquids) is normally taken **as unity**.
- ❖ Activity depends on **temperature, pressure and composition** of the mixture
- ❖ For gases, the effective partial pressure is usually referred to as **fugacity**.

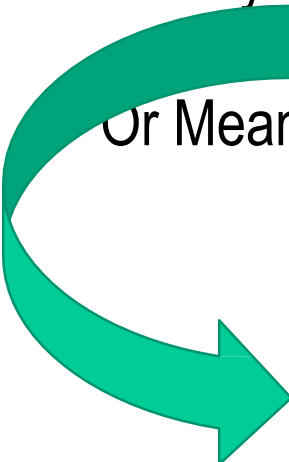


# Activity and Mean Ionic Activity of Electrolytes

- ❖ We take into account of **activity of Individual ions**
- ❖ There is no expt. method by which activities of individual ions can be determined. Because it is not possible to have solutions of one kind of ion.
- ❖ Therefore **activity or mean ionic activity  $a_{\pm}$  of the electrolyte** is considered.

**For uni-univalent electrolyte:** Ex: HCl (  $H^+=a_+$  and  $Cl^-=a_-$  )

Activity  $a = a_+ a_-$



Or Mean ionic activity =  $a_{\pm} = \sqrt{a_+ a_-}$

Squaring  $\Rightarrow (a_{\pm})^2 = a_+ a_-$

$$\Rightarrow (a_{\pm})^2 = a$$

# Mean Ionic Activity of Electrolytes

Consider an electrolyte  $A_xB_y$  ionizing as



Then activity  $a = (a_+)^x(a_-)^y = (a_{\pm})^{x+y}$



## Activity coefficient of the electrolyte

- ❖ Ion-ion and ion- $H_2O$  interactions (hydration shell) cause number of ions available to react chemically ("free" ions) to be less than the number present.
- ❖ Concentration can be related to activity using the **activity coefficient**  $\gamma$ , where  $[a] = \gamma (m)$

Until now we have assumed that **activity,  $a$ , is equal to concentration,  $m$** , by Setting  **$\gamma = 1$**  when dealing with dilute aqueous solutions...

# Activity coefficient of the electrolyte

The activity coefficient of the electrolyte  $A_xB_y$  is given by

$$a = (\gamma_+ m_+)^x (\gamma_- m_-)^y = (\gamma_+ x m)^x (\gamma_- y m)^y = x^x y^y (m \gamma_{\pm})^{x+y}$$

$$(\gamma_{\pm})^{x+y} = \gamma_+^x \gamma_-^y$$

For uni-univalent electrolyte:

HCl,  $x=1$ ,  $y=1$

$$a = (a_{\pm})^2 = (\gamma_{\pm} m)^2$$

For uni-bivalent electrolyte: Ex:  $\text{Na}_2\text{SO}_4$ ,  $x=2$  and  $y=1$ .

$$\text{Hence } a = (a_{\pm})^3 = 2^2 \times 1 (\gamma_{\pm} m)^3 = 4m^3 \gamma_{\pm}^3$$

The value of  $\gamma$  depends on:

- Concentration of ions and charge in the solution
- Charge of the ion



# Ionic strength

The ionic strength of a solution is a **measure of the concentration of ions** in that solution.

The **total electrolyte concentration** in solution will affect important properties such as the **dissociation** or the **solubility** of different salts.

The ionic strength,  $I$ , of a solution is a function of the concentration of all ions present in that solution.

$$I = \frac{1}{2} \sum_{i=1}^n m_i z_i^2$$



$m_i$  the **molal concentration of ion  $i$**  (M, mol/Kg),  $z_i$  is the **charge number of that ion**, and the sum is taken over all ions in the solution.

For a 1:1 electrolyte such as sodium chloride, the ionic strength is given by

$$I = \frac{1}{2} (m_{Na^+} z_{Na^+}^2 + m_{Cl^-} z_{Cl^-}^2) = \frac{1}{2} (m_{Na^+} 1^2 + m_{Cl^-} 1^2) = \frac{1}{2} (m_{Na^+} + m_{Cl^-})$$

Calculate the ionic strength of 0.15 molal KCl solution

# Debye-Hückel theory of strong electrolytes

For evaluation of mean ionic activity coefficient



## Assumptions

The Debye-Hückel theory is based on three assumptions of how ions act in solution:

- ❖ Electrolytes completely dissociate into ions in solution.
- ❖ Ions of electrolytes interact with themselves according to the electrostatic's law.
- ❖ The nature of solvent influences on the interaction between ions.
- ❖ A central ion is surrounded by the ion's atmosphere (ions of opposite charge) .
- ❖ The size of the central ion is like a point charge.



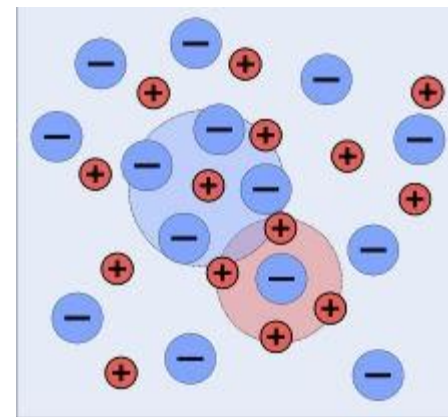
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## Debye–Hückel theory continuing....

The ions are shown as spheres with unit electrical charge.

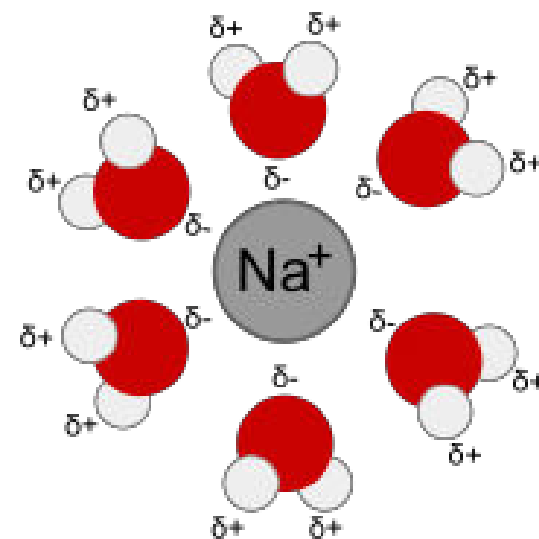
Ions of charge  $z_1e^+$  and  $z_2e^-$ , where  $z$  can be any integer.



The principal assumption is that departure from ideality is due to electrostatic interactions between ions, mediated by Coulomb's law: the **force of interaction between two ions**, separated by **a distance,  $r$**  in a medium of relative permittivity  $\epsilon_r$  is given by

$$Force = \frac{z_1 z_2 e^2}{4\pi \epsilon_r \epsilon r^2}$$

❖ If the solvent has high dielectric constant the electrostatic between ions will be small.





## Debye–Hückel theory continuing....

2. Solutions of Electrolytes are **very dilute**, on the order of 0.01 M. Solution is very dilute, the distance between the ions will be large.

3. Each ion is surrounded by **ions of the opposite charge**, on average.

Activity coefficient of single ion  $i$  in dilute solution of strong electrolyte

$$\log \gamma_i = -A z_i^2 \sqrt{I}$$

$$\text{where } I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + \dots + m_i z_i^2)$$

$$\text{where } A = \frac{e^3}{4.606(DkT)^{3/2}} \times \sqrt{\frac{8\pi N_A \rho}{10^3}}$$

$T = 298\text{K}$  and water as a solvent,

$D = \text{dielectric constant} = 78.3$

$\rho = 1 \text{ g/cc}$ ,

$N_A = \text{Avogadro's number} = 6.023 \times 10^{23}$ ,

$k = \text{Boltzmann constant} = 1.38 \times 10^{-16} \text{ erg/K}$



## Debye–Hückel theory continuing....



Putting these values:  $A = 0.51$  at 298K.

$$\log \gamma_i = -0.51 z_i^2 \sqrt{I}$$

Mean ionic activity coefficient of strong electrolytes in dilute solution containing the electrolyte  $A_xB_y$  in general is given by.

$$\log \gamma_{\pm} = -A z_+ z_- \sqrt{I}$$

$$\log \gamma_{\pm} = -0.51 z_+ z_- \sqrt{I}$$

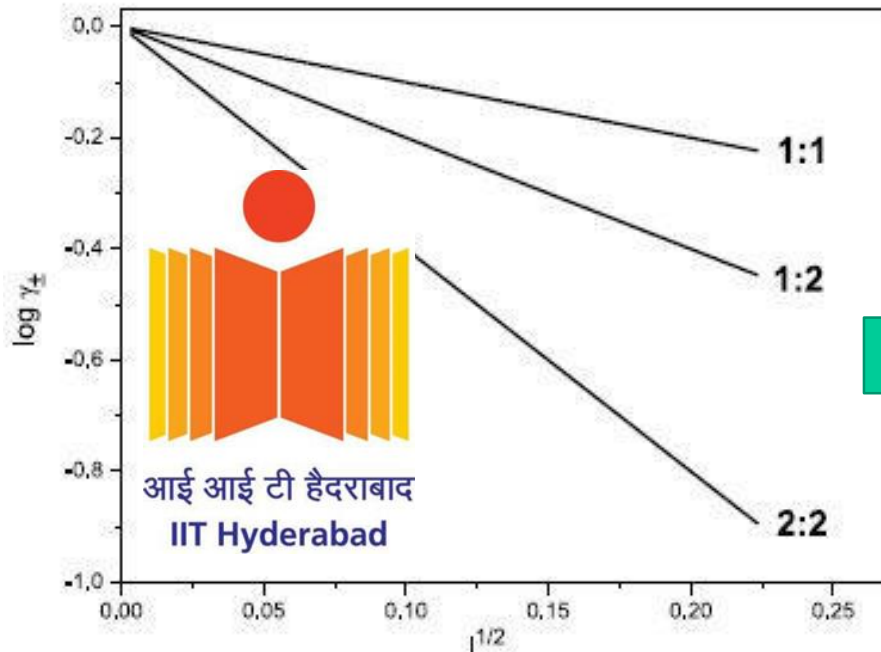
**Debye–Hückel limiting law and used to calculate mean ionic activity coefficient of the strong electrolytes in dilute solution.**

***The activity coefficient of the electrolytes depends only upon the ionic strength of the solution.***

## Debye–Hückel theory continuing....

Negative value means mean ionic activity coefficient is less than 1.

According to Debye–Hückel equation if  $z_+$  and  $z_-$  are same, the activity coefficient varies with ionic strength of the solution and not with nature of the electrolytes.



Thus all electrolytes of same valency type should have equal activity coefficient at the same ionic strength.

- ❖ All the electrolytes should give st. line passing through origin.
- ❖ All slopes depends on  $Z_+Z_-$ .
- ❖ For uni-univalent= slope = 0.51
- ❖ Bi, Uni-bi, bi-univalent = 2 X 0.51

Predictions of Debye-Huckel limiting law