

ENGINEERING CHEMISTRY

Module 3- Phase equilibria



Module content:

- *Phase equilibria*
- *Gibb's phase rule*
- *Phase diagram of 1-component system*
- *Phase diagram of 2-component system*
- *Fe-C phase diagram*

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Module 3- Phase equilibria



Class content:

- *Free energy in Phase equilibria*
- *Chemical potential*
- *Phase equilibria*
 - *Phase*
 - *Component*
 - *Degree of freedom*

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Free energy in Phase equilibria

- All substances have tendency to **minimize their Gibbs energy** at constant temperature and pressure to attain stable state
- **Phase transformations** from one phase to another occur to reduce free energy of the system
- Gibb's energy is an **extensive property**

Chemical potential

- Chemical potential is defined as the **partial molar Gibb's energy** for a component i in a mixture , and is denoted by μ

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq i}$$

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Phase equilibria

- Phase equilibria between phases exist when **chemical potential of a component is equal in all the phases** in equilibrium
e.g. for water at triple point
 $\text{Solid} \rightleftharpoons \text{liquid} \rightleftharpoons \text{vapour}$

The chemical potential of water will be equal in all the three phases

- For systems not at equilibrium, the chemical potential will point to the **direction in which the system can move** in order to achieve equilibrium viz. , the system moves from higher chemical potential to lower chemical potential
- When various phases are in equilibrium with one another in a heterogeneous system, there can be **no transfer of energy or mass** from one phase to another.
- For a system at equilibrium, the various phases must have the **same temperature and pressure and their respective compositions must remain constant** all along

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Phase

A phase is defined as any **homogeneous and physically distinct part of a system** bounded by a surface and is mechanically separable from other parts of the system. It is denoted by P

- **Gaseous state :** $P = 1$ gases are completely miscible
- **Liquid state :** $P = \text{No. of layers}$ when liquids are immiscible
 $P = 1$ when liquids are completely miscible
- **Solid state :** Each solid constitutes a separate phase
Each polymorphic form constitutes a separate phase
 $P = 1$ for solid solution

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Counting the number of phases

1) Solid \rightleftharpoons liquid \rightleftharpoons vapour ; P = 3

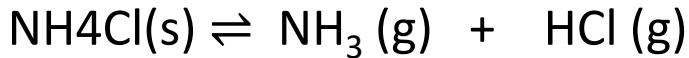
- Ice in the system is a single phase even if it is present as a number of pieces.

2) Calcium carbonate undergoes thermal decomposition



- P= 3; 2 solid phases, CaCO_3 and CaO and one gaseous phase, that of CO_2

3) Ammonium chloride undergoes thermal decomposition



- P = 2; one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl

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Components

- A component is defined as the **smallest number of independently varying chemical constituents** using which the composition of **each and every phase** in the system can be expressed
- When no reaction is taking place in a system, the number of components is the same as the number of constituents
- While expressing in terms of constituents **zero and negative values** are allowed

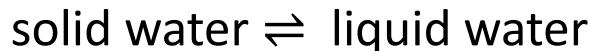
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Counting the number of components:

- **1-component system**

e.g. **Pure water ; C = 1**

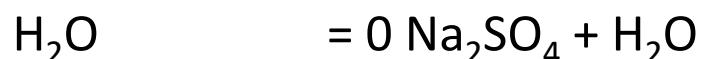
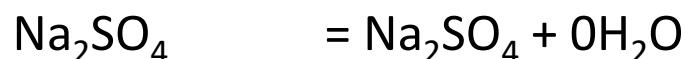
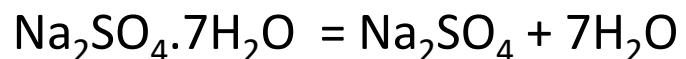
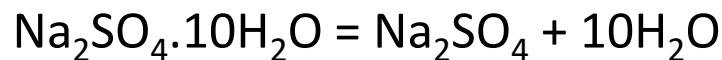


All the different phases can be expressed in terms of the single constituent water

- **2-component system**

- **Salt hydrate system**

e.g. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} ; \text{C}=2$



The composition of all the phases can be expressed in terms of 2 components

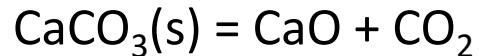
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- Thermal decomposition of solid CaCO_3 in a closed container ; $C = 2$



- Though there are 3 species present, the number of components is only two
- Phases are : $\text{CaCO}_3(s)$, $\text{CaO}(s)$ and $\text{CO}_2(g)$
- Any two of the three constituents may be chosen as the components
- If CaO and CO_2 are chosen,



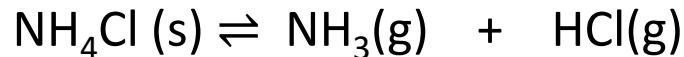
- If CaCO_3 and CO_2 are chosen,



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- Thermal decomposition of ammonium chloride in a closed system ; **C = 1**



- Phases are : solid phase of $\text{NH}_4\text{Cl}(\text{s})$ and gaseous phase of $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$



- The composition of both the solid and gaseous phase can be expressed in terms of NH_4Cl . Hence the number of components is one; C=1
- If additional HCl (or NH_3) were added to the system, then **C = 2**
- The decomposition of NH_4Cl would not give the correct composition of the gas phase
- A second component, HCl (or NH_3) would be needed to describe the gas phase, therefore C=2

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Degrees of freedom (or variance)



The degrees of freedom or variance of a system is defined as the **minimum number of intensive variables** such as temperature, pressure, concentration, which must be fixed in order to define the system completely; it is denoted by F

OR

The degree of freedom of a system may also be defined as the number of variables, such as temperature, pressure and concentration that can be **varied independently** without altering the number of phases.

Example : water system

- **Only 1 phase** (solid , liquid or gas)
 - Both temperature and pressure need to be mentioned in order to define the system; **F = 2**

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- **2 phases in equilibrium,**
 - Only one variable, either temperature or pressure need to be specified in order to define the system; $F = 1$
 - solid water \rightleftharpoons liquid water
 - If the pressure on the system is maintained at 1 atm, then the temperature of the system gets automatically fixed at 0°C , the normal melting point of ice
- **3 phases in equilibrium,**
 - No variable can be changed
 - temperature and pressure are fixed, $F = 0$
 - solid water \rightleftharpoons liquid water \rightleftharpoons water vapour
 - Three phases, ice, water, vapour can coexist in equilibrium at triple point of water at 0.0098°C and 4.6mm of Hg pressure only

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Class content:

- *Gibb's Phase rule*
- *Derivation of Gibb's Phase rule*
- *Phase diagram of a 1-component system*

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Phase rule

- It was given by **Williams Gibbs** in 1874

- **Statement of Gibb's phase rule**

Provided the equilibrium in a heterogeneous system is not influenced by external forces (gravity, electrical or magnetic forces) , the number of degrees of freedom (F) of the system is related to number of components (C) and number of phases (P) existing at equilibrium to one another by the equation

$$F = C - P + 2$$

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Derivation of the phase rule

- A system at equilibrium satisfies the following conditions:
 - **Thermal equilibrium** – Temperature is constant
 - **Mechanical equilibrium** – Pressure is constant
 - **Chemical or material equilibrium** – Chemical potential of a substance is same in all the phases
- Mathematically, $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$
- The system considered is: All C components distributed between P phases

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- Total number of intensive variables that need to be ascertained to describe the system:

Temperature 1

Pressure 1

Composition mole fraction of each component in every phase

- For each phase, the sum of mole fractions equals unity

$$\chi_1^\alpha + \chi_2^\alpha + \chi_3^\alpha + \dots + \chi_c^\alpha = 1 \quad (\text{C-1})$$

$$\chi_1^\beta + \chi_2^\beta + \chi_3^\beta + \dots + \chi_c^\beta = 1 \quad (\text{C-1})$$

$$\chi_1^\gamma + \chi_2^\gamma + \chi_3^\gamma + \dots + \chi_c^\gamma = 1 \quad (\text{C-1})$$

.

.

$$\chi_1^P + \chi_2^P + \chi_3^P + \dots + \chi_c^P = 1 \quad (\text{C-1})$$

- In each phase (C-1) mole fraction terms need to be defined
- Number of phases : P
- Number of composition variables = P(C-1)
- **Total number of intensive variables = P(C-1) + 2**

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Total number of equations(constraints) :

- At equilibrium the chemical potential of particular component is same in every phase in a system

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots \quad (\text{P-1})$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots \quad (\text{P-1})$$

$$\mu_3^\alpha = \mu_3^\beta = \mu_3^\gamma = \dots \quad (\text{P-1})$$

.

.

.

$$\mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \dots \quad (\text{P-1})$$

- For C components $C(\text{P-1})$
- **Total number of equations or constraints = $C(\text{P-1})$**

F = Total number of variables – total number of equations

$$F = P(C-1) + 2 - \{C(P-1)\}$$

$$F=C-P+2$$

which is the **Gibb's phase rule**

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Application of Gibb's phase rule $F = C-P+ 2$ to 1-component system:

Water system

When only 1 phase is present :

$C = 1, P = 1; F = 2$;Temperature and Pressure can be varied independently

Bivariant system

When 2 phases are in equilibrium:

$C = 1, P = 2; F = 1$; Temperature or Pressure can be varied independently

Univariant system

When all 3 phases are in equilibrium:

$C = 1, P = 3; F = 0$; Neither Temperature nor Pressure can be varied

Invariant system

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Phase diagram

A diagram which represents the **conditions** under which a substance exists in **different phases** in a system

Phase diagram of a 1-component system

$$F = C - P + 2$$

For a 1-component system **F = 3 – P**

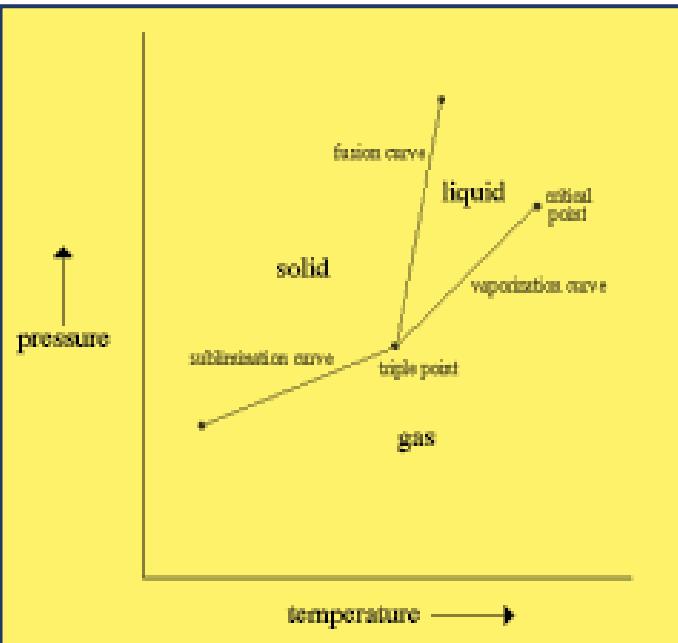
Single phase : F = 2 ; Area in a diagram

Two phases in equilibrium : F = 1 ; line in a diagram

Three phases in equilibrium : F = 0 ; point in a diagram

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High pressure, low temperature: **solid phase**

High temperature, low pressure : **vapour phase**

In between : **liquid phase**

A
R
E
A

L
I
N
E

solid \rightleftharpoons liquid

liquid \rightleftharpoons vapour

vapour \rightleftharpoons solid

POINT

Solid \rightleftharpoons liquid \rightleftharpoons vapour

Source:http://abyss.uoregon.edu/~js/glossary/triple_point.html

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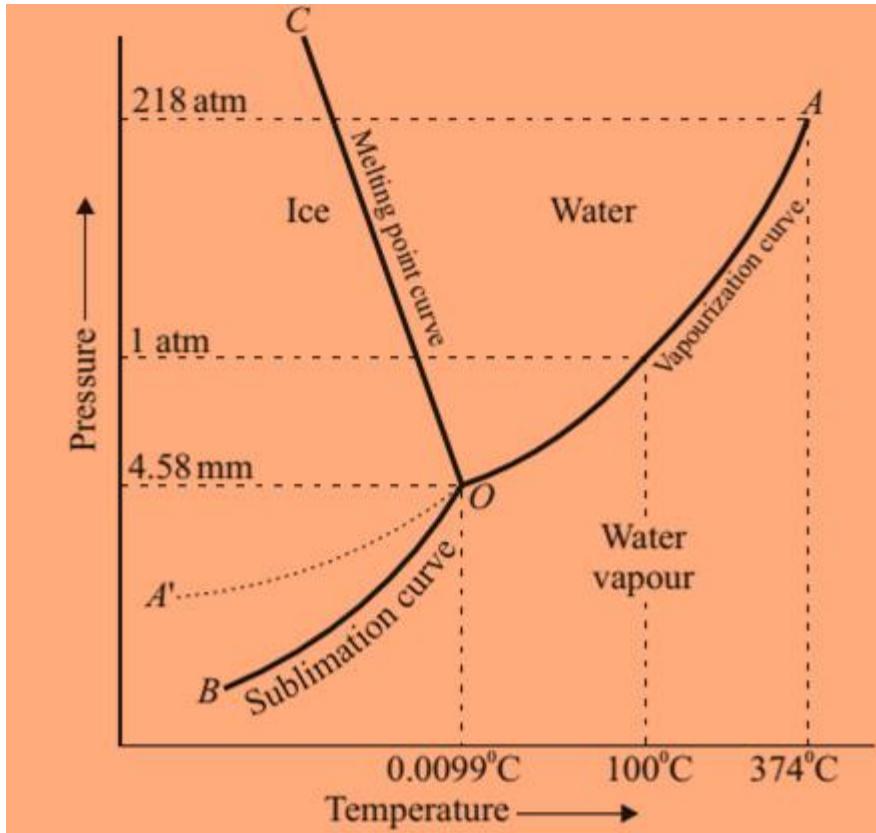
Class content:

- *Phase diagram of water*
- *Reduced phase rule for a 2-component system*

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Phase diagram of water



OC : Melting point curve

OA : Vaporisation curve

OB : Sublimation curve

O: Triple Point

A: Critical point

OA': Metastable equilibrium

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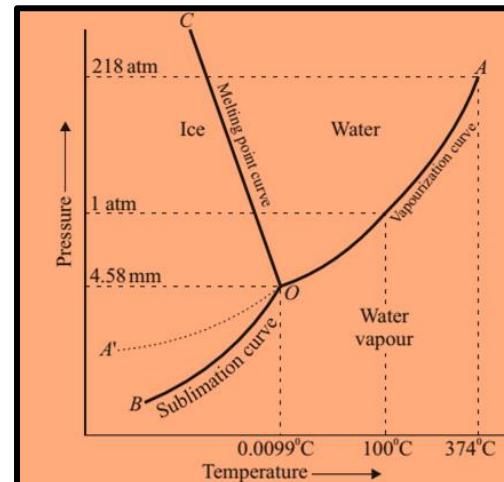
Equilibrium between solid and liquid (fusion curve OC)

- ice \rightleftharpoons water
- F=1, monovariant system
- variation of melting point of ice with pressure
- slope is negative; as ice melts its volume decreases or density increases
- Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{Fusion}}{T\Delta V} = \text{negative}$$

Where,

ΔV = decrease in volume as ice melts is -ve; ΔH_{fusion} = endothermic, +ve



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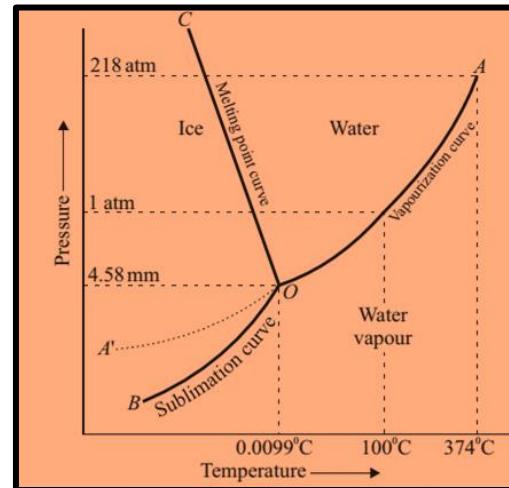
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Equilibrium between solid and vapour (sublimation curve OB)

- ice \rightleftharpoons water vapour
- F=1, **monovariant system**
- variation of sublimation temperature of ice with pressure
- **slope is positive**
- Clausius Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{sub}}{T\Delta V} = \text{positive}$$

Where ,



ΔV = Increase in volume as ice sublimates ,+ve ; $\Delta H_{sublimation}$ = endothermic reaction , +ve

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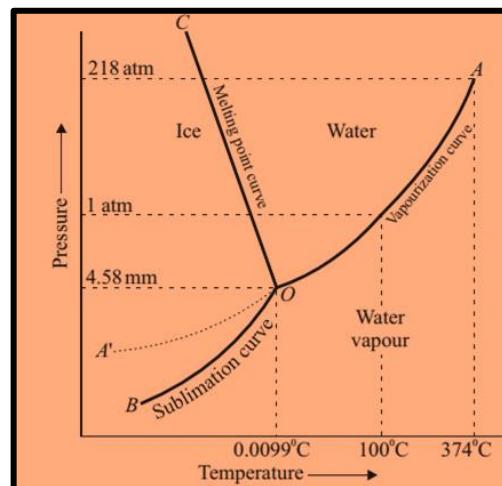
Equilibrium between liquid and vapour (vaporization curve OA)

- liquid water \rightleftharpoons vapour
- F=1, monovariant system
- variation of boiling temperature of water with pressure
- slope is positive
- Clausius - Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{Vapourisation}}{T\Delta V} = \text{positive}$$

Where,

ΔV = Increase in volume as liquid water vapourises,+ve; $\Delta H_{Vapourisation}$ = endothermic reaction,+ve



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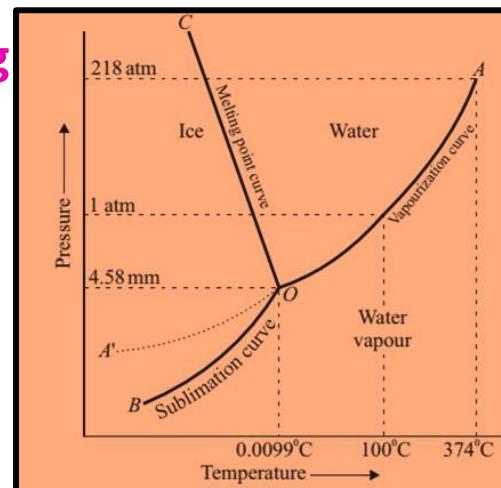
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Triple point “O”:

- Represents equilibrium between liquid, vapour and solid water (ice)
- All three phases are present together
- $F = 0$, **invariant system**
- Triple point for water lies at **0.0098 °C and 4.58 mmHg**

Critical point “A”:

- the interface between liquid water and water vapour vanishes
- a point above which water does not exist in liquid state
- Critical point lies at **374°C and 220 atm** pressure

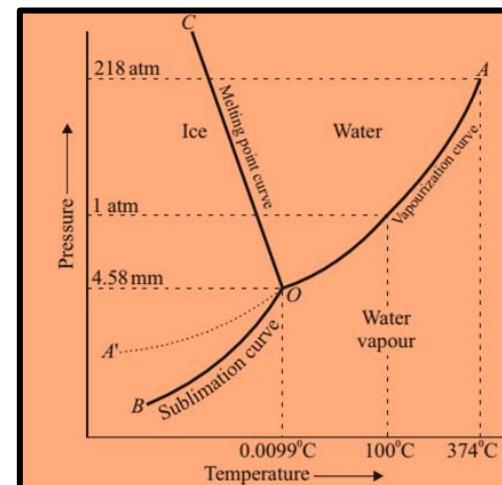


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Metastable equilibrium (OA'):

- Ice fails to form at the triple point and water continues to exist in liquid phase
- The vapour pressure of the liquid continues along OA'
- This is called **super cooled water** and represents metastable equilibrium involving liquid and vapour phases.
- Any disturbance will cause the system to go back to stable equilibrium (OB)
- The vapour pressure of the system in the metastable region is more than that of the stable system ice at the same temperature



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Phase diagram of a two component system

- The phase rule equation is $F = C - P + 2$
- For a 2 component system the ordinary phase rule cannot be used
- For a two component system, $C = 2$ then $F = 2 - P + 2 = 4 - P$
- The minimum number of phase is 1; $F = 4 - 1 = 3$
- This requires **3 dimensional space** which cannot be explained on the plane of paper
- **One of the three variables is kept constant**
- Measurements in these systems are generally carried out **at atmospheric pressure**
- Pressure may be considered constant ; degrees of freedom is reduced by 1,
- $F = C - P + 2 - 1$

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- The phase rule takes the form $F = C - P + 1$ and is known as the reduced phase rule
- Equilibria such as solid-liquid equilibria are such systems in which the gas phase is absent and hence are hardly affected by small changes in pressure
- Systems in which the gas phase is absent are called **condensed systems**
- **$F = C - P + 1$ is also known as condensed phase rule**

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Class content:

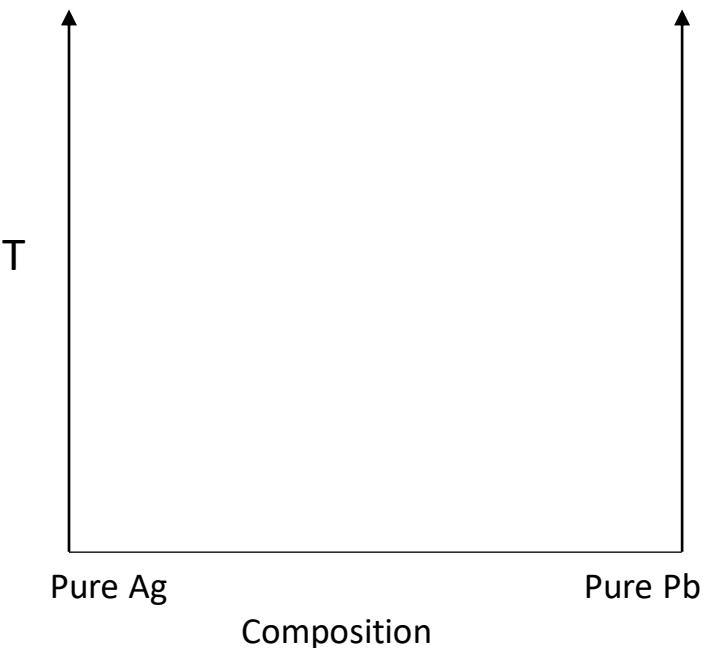
- *Phase diagram of Pb-Ag system*
- *Determination of solid-liquid equilibria*
- *Pattinson's process*

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Phase diagram of Pb-Ag system

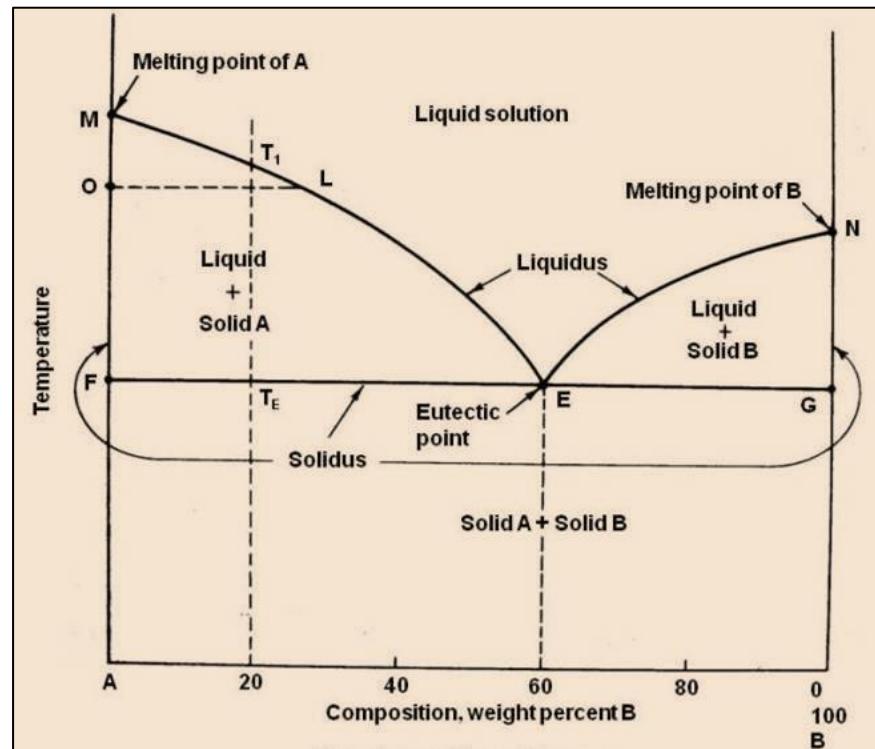
- Phase rule for a 2- component system : $F = C-P+1$
- Pressure is constant
- Plot is between Temperature and Composition
- Pb and Ag are miscible in all proportions in the liquid (molten) state
- In solid state they are completely immiscible



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Simple eutectic system



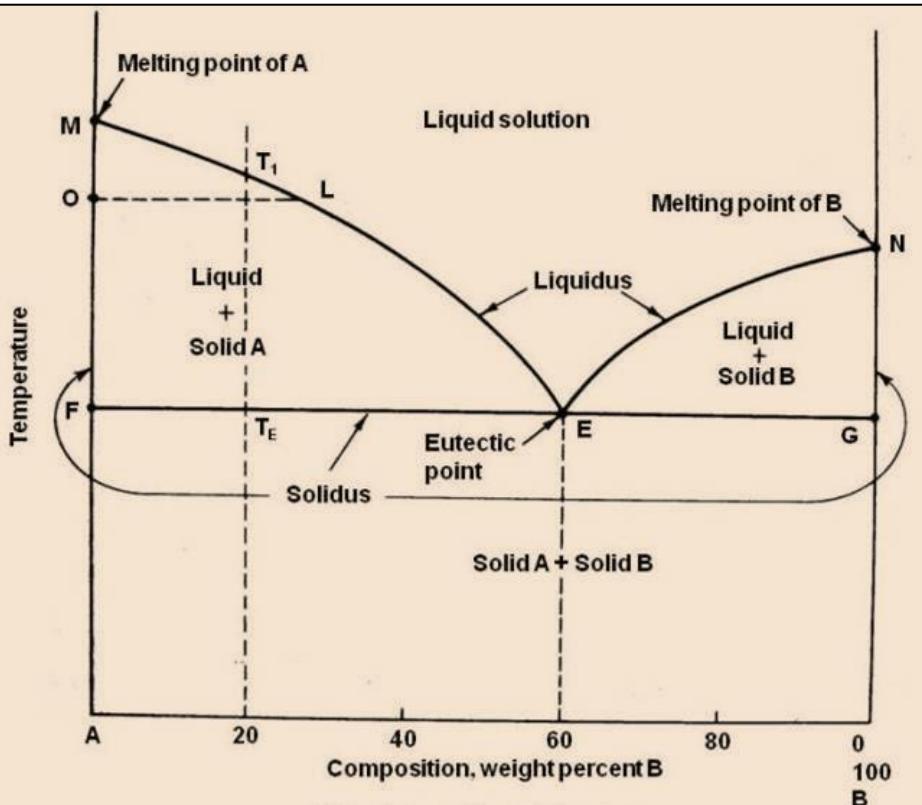
When a mixture of the 2 components is heated till the mixture melts and then cooled:

- First crystal of A if formed when f.pt. of A in the mixture is reached
- On further cooling more solid A precipitates and liquid melt becomes richer in B
- With decrease in temperature more and more solid A separates and the liquid melt moves along curve ME
- Finally when temperature reaches F, solid B also starts precipitating
- Three phases are present at E: solid A, solid B and the liquid melt
- Further cooling will just result in cooling of solid A & B

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Simple eutectic : Pb-Ag system



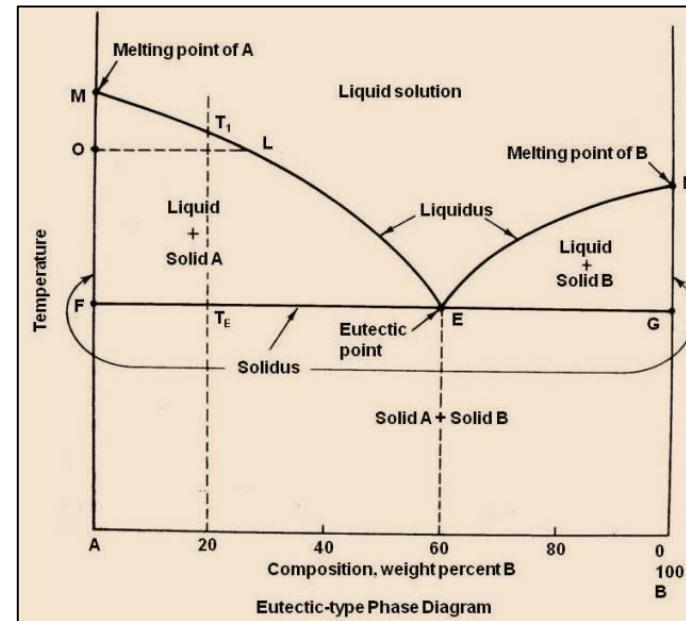
Pb-Ag system

- A : 100% Ag, M : 961°C
- B : 100% Pb, N : 327°C
- Area above MEN: Liquid melt
- Area MEF : Solid A + Liquid melt
- Area NEG : Solid B + Liquid melt
- Below FEG : Solid A + Solid B
- Eutectic point – “E”
- Curves : ME and NE

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- **Eutectic mixture:** A mixture of two components which has the lowest freezing point of all the possible mixtures of the components
- It has a definite composition and a sharp melting point
- Number of phases at eutectic point = 3
- $F = C-P+1$; $C = 2$, $P = 3$, so $F = 0$; invariant point,
- Eutectic temperature: 303°C
- **Eutectic composition:** 97.4 % Pb and 2.6 % Ag



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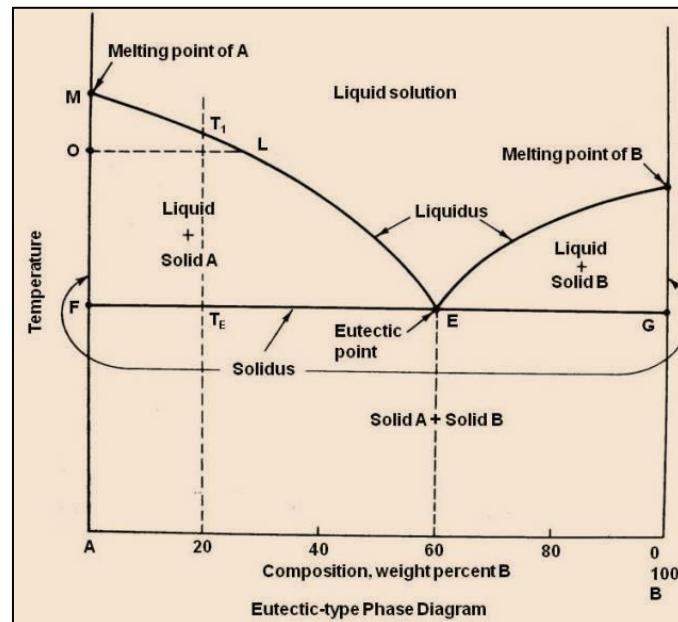
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CURVE ME : freezing point curve of Ag

- It shows decrease in freezing point / melting point of Ag due to the addition of Pb to Ag
- Solid Ag is in equilibrium with liquid melt of Pb in Ag
- Here $C = 2$ and $P = 2$, then the reduced phase rule is $F = C - P + 1 = 2 - 2 + 1 = 1$
- Hence the system is **univariant**.

CURVE NE: freezing point curve of Pb

- It shows decrease in freezing point of Pb due to the addition of Ag to Pb
- Solid Pb is in equilibrium with liquid melt of Ag in Pb
- Here $C = 2$ and $P = 2$, then the reduced phase rule is $F = C - P + 1 = 2 - 2 + 1 = 1$
- Hence the system is **univariant**



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Determination of solid-liquid equilibria

- For the determination of equilibrium conditions between solid and liquid phases – **Thermal Analysis**

Thermal analysis:

The study of the **cooling curves** of various compositions of a system during solidification

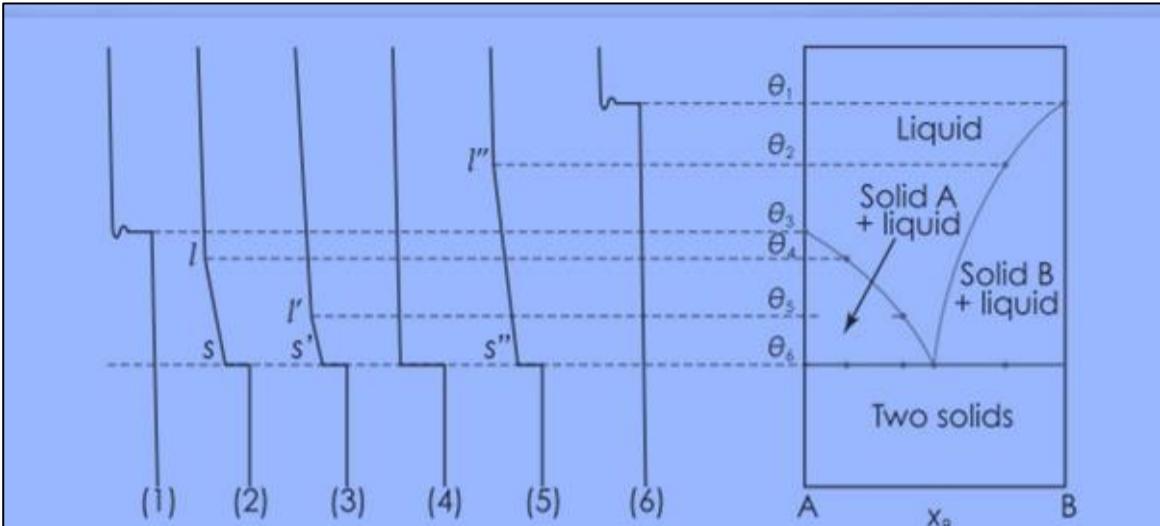
Cooling curves:

- Temperature versus time
- Freezing point** and **eutectic point** can be determined from the cooling curves

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Construction of phase diagram using cooling curves



Source:<http://www.mchmultimedia.com/PhysicalChemistry-help/clientstories/study-tips/digging-into-phase-diagrams-cooling-curves.html>

For pure solid: When the freezing point is reached, temperature remains constant until the liquid is fully solidified.

For a mixture of solids: When crystallisation of one of the components starts ,cooling curve exhibits a break. The temperature decreases continuously until the eutectic point is reached. Now the temperature remains constant, till the completion of solidification.

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Pattinson's process for the desilverisation of argentiferous lead

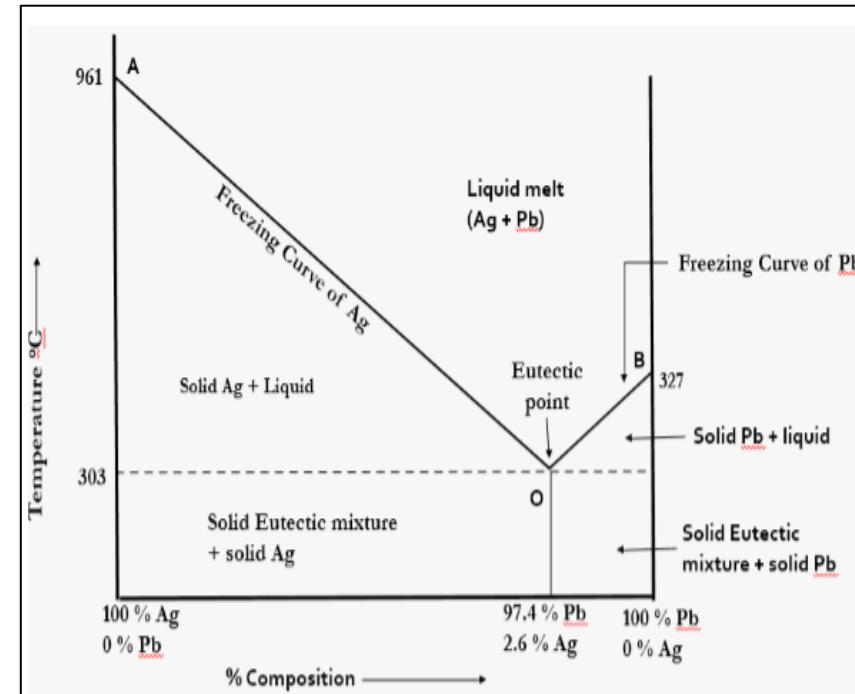
- The process of heating argentiferous lead containing a very small quantity of silver ($\sim 0.1\%$) and cooling it to get pure lead and liquid richer in silver

- Argentiferous lead is heated to a temperature above the melting point of pure lead

- The melt is allowed to cool

- Temperature of the melt reaches the freezing curve of Pb where solid lead starts separating

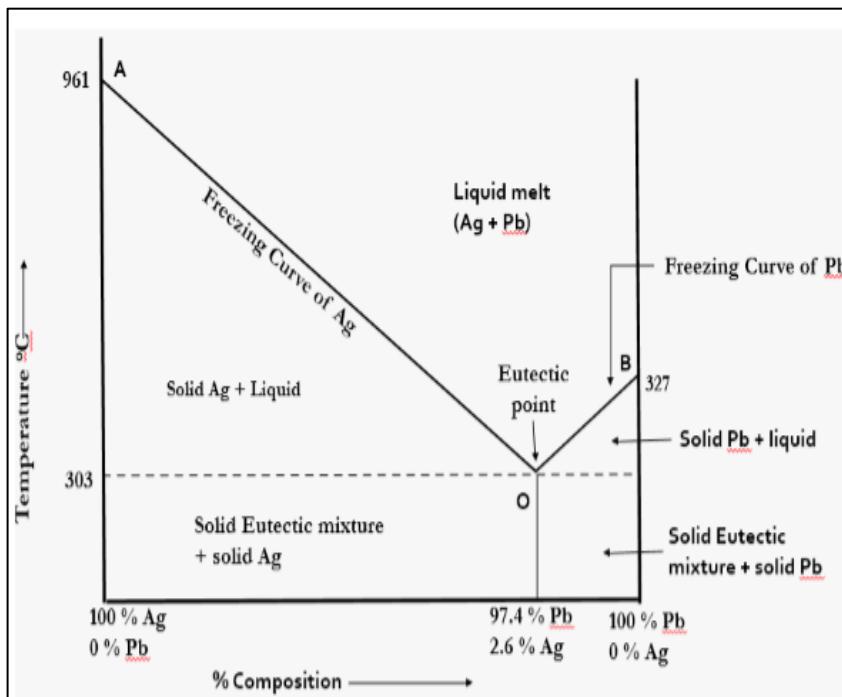
- As the system further cools, more and more lead separates and the liquid in equilibrium with the solid lead gets richer in silver



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- The lead that separates, floats and is continuously removed by ladles
- When the temperature of the liquid reaches the eutectic temperature, solid lead is in equilibrium with the liquid having the eutectic composition
- After removing the lead that separates, the liquid is cooled further when it solidifies to give a mixture of lead and silver having the eutectic composition of 2.6 % of silver
- This solid mixture of lead and silver is subjected to other processes for the recovery of silver



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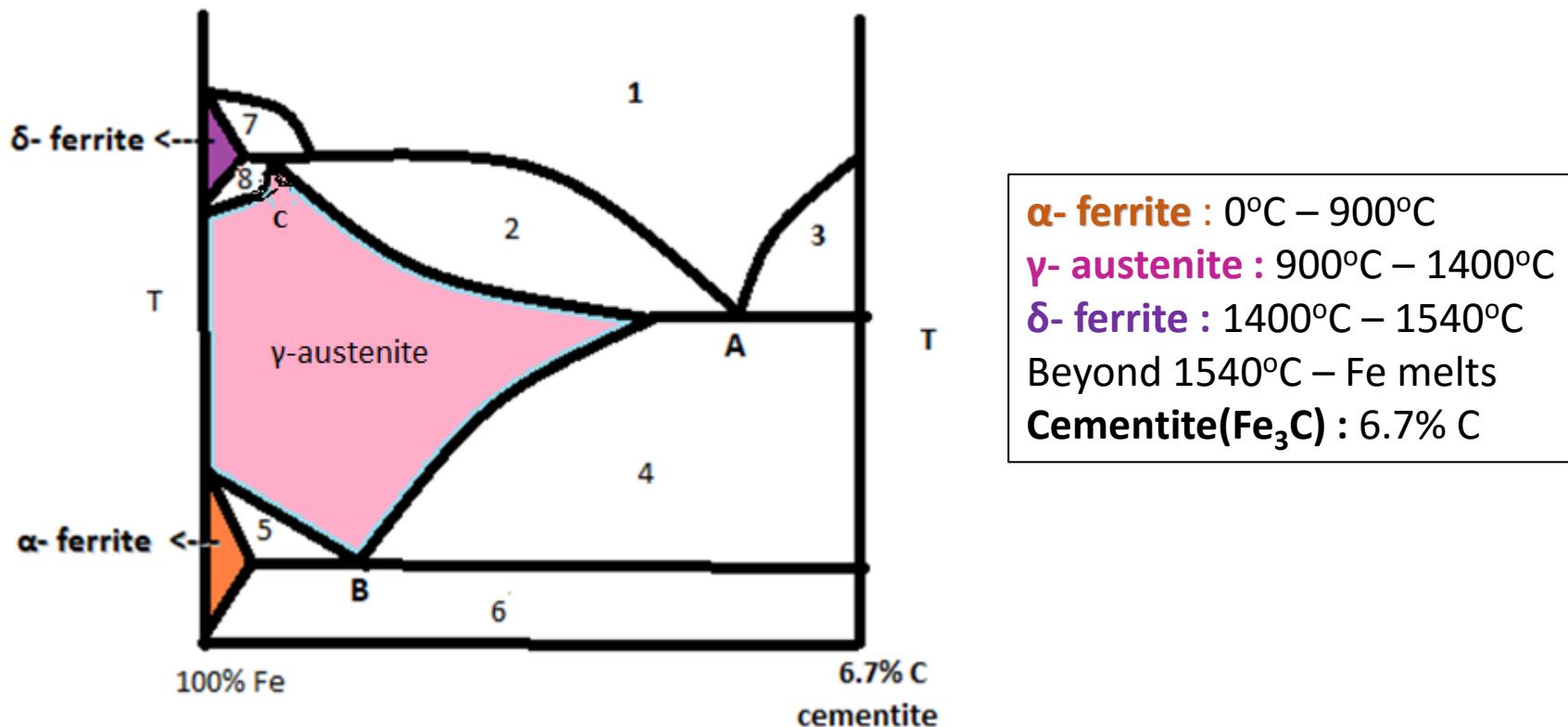
- *Fe-C phase diagram*

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Iron– Carbon (Fe–C) Phase Diagram

- Fe-C system is a 2-component system; $F = C - P + 1$
- the Fe-C phase diagram is a fairly complex one
- we consider the part of the diagram, up to around **6.7% Carbon**



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Phases in Fe–Fe₃C Phase Diagram

α -ferrite

- solid solution of C in BCC Fe
- Stable form of iron at room temperature
- Transforms to FCC γ -austenite at 900 °C

γ -austenite

- solid solution of C in FCC Fe
- Transforms to BCC δ -ferrite at 1400 °C

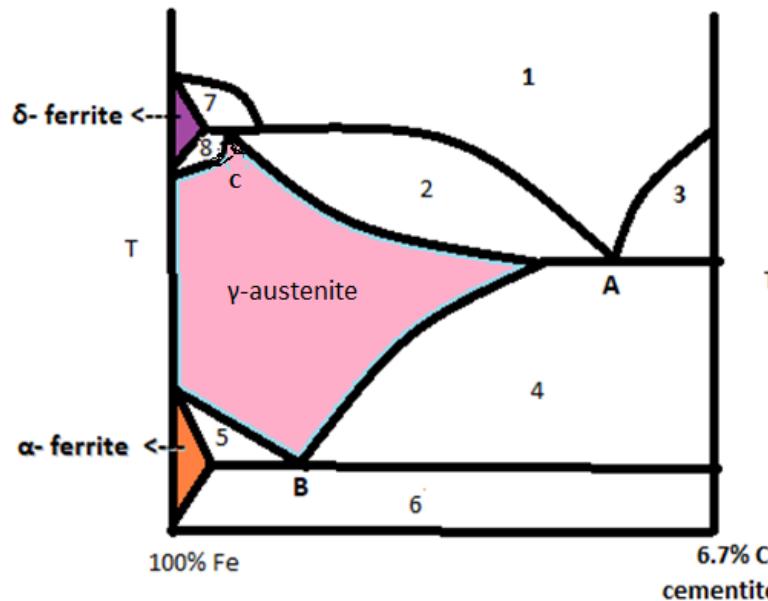
δ -ferrite

- solid solution of C in BCC Fe
- The same structure as α -ferrite
- Stable only at high T, above 1400 °C
- Melts at 1540 °C

Fe₃C (iron carbide or cementite)

- This is a intermetallic compound.

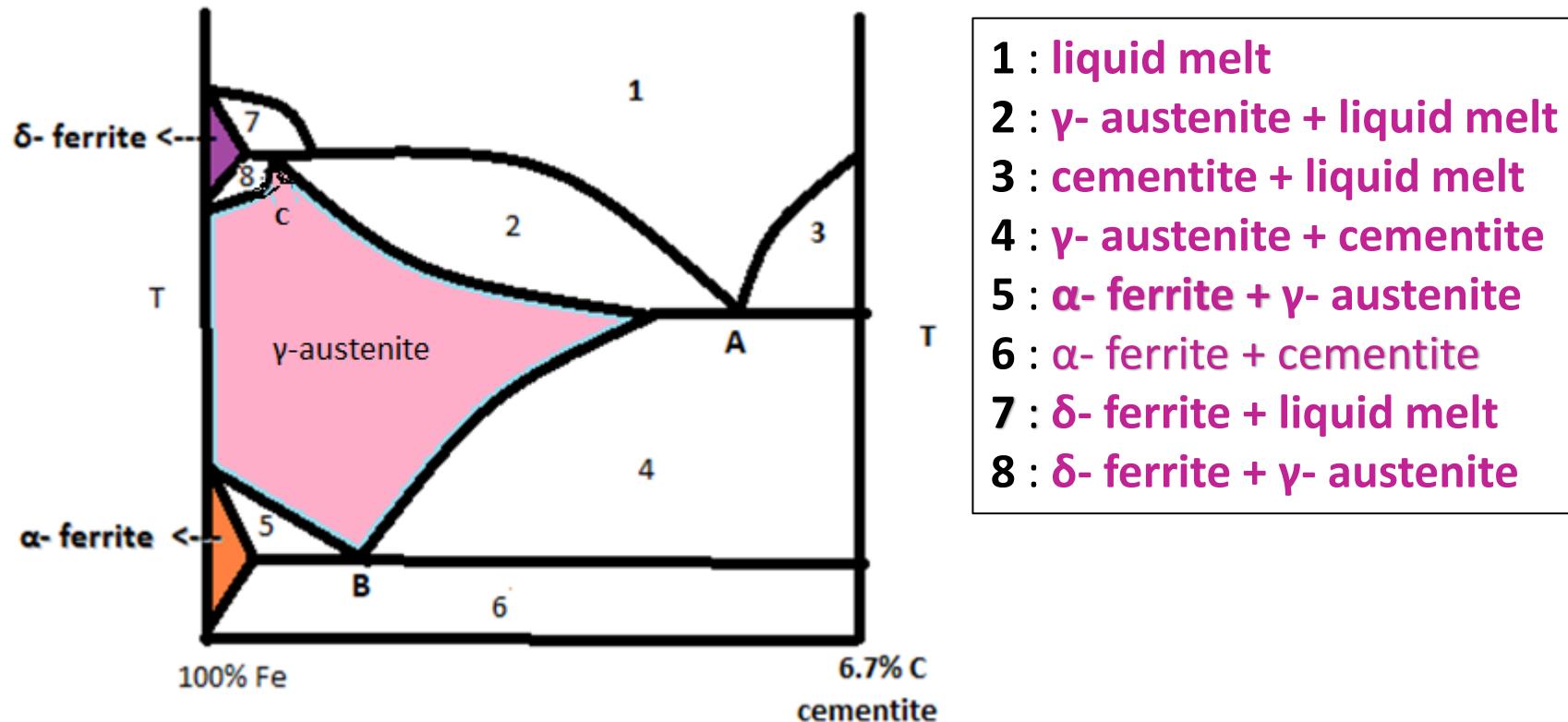
Fe-C liquid solution



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Areas in the Fe-Fe₃C phase diagram



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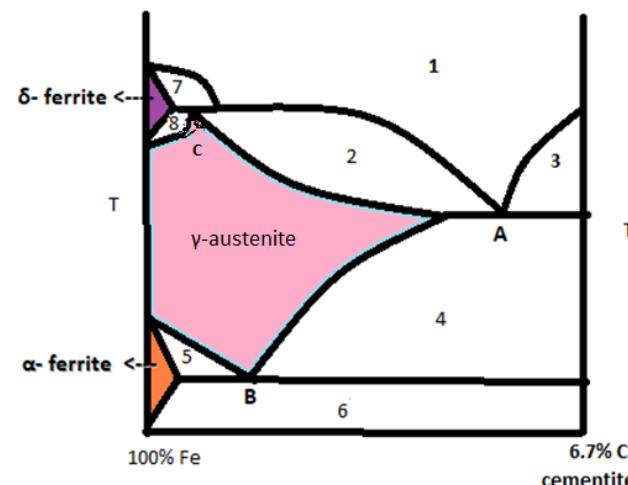
Module 3- Phase equilibria

Eutectic point A :

- liquid melt of Fe-C transforms into two different solid phases γ -austenite and cementite (Fe_3C) on cooling; $L \leftrightarrow \gamma + Fe_3C$
- corresponds to **4.3 % C, 1130 °C**
- 3 phases are in equilibrium ; **γ -austenite, cementite and liquid melt**
- $F=0$. The system is **invariant**

Eutectoid point B :

- γ -austenite phase transforms into two different solid phases α -ferrite and cementite (Fe_3C) on cooling ; $\gamma \leftrightarrow \alpha + Fe_3C$
- corresponds to **0.8 % C, 723 °C**
- 3 phases are in equilibrium; **γ -austenite, α – ferrite and cementite**
- $F=0$. The system is **invariant**

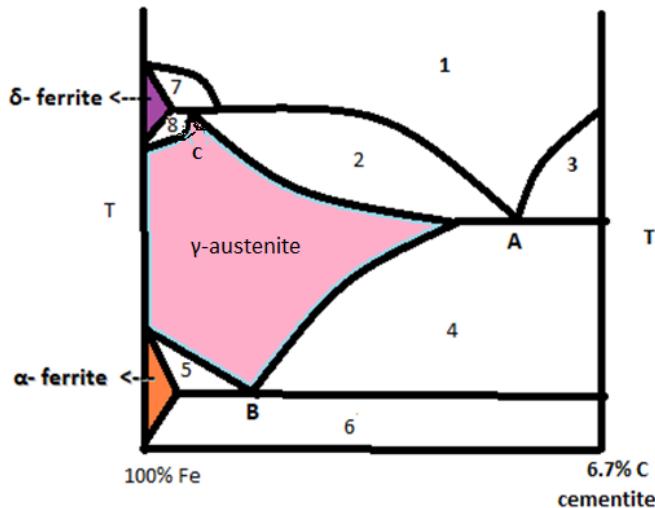


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Module 3- Phase equilibria

Peritectic point C:

- liquid melt of Fe-C transforms into two different solid phases γ -austenite and cementite (Fe_3C) on cooling: $\delta + \text{L} \leftrightarrow \gamma$
- corresponds to **0.16 % C, 1498 °C**
- 3 phases are in equilibrium ; **γ -austenite, δ - ferrite and liquid melt**
- $F=0$. The system is **invariant**



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Module 3- Phase equilibria

Three types of ferrous alloys of Fe and Carbon

Wrought Iron:

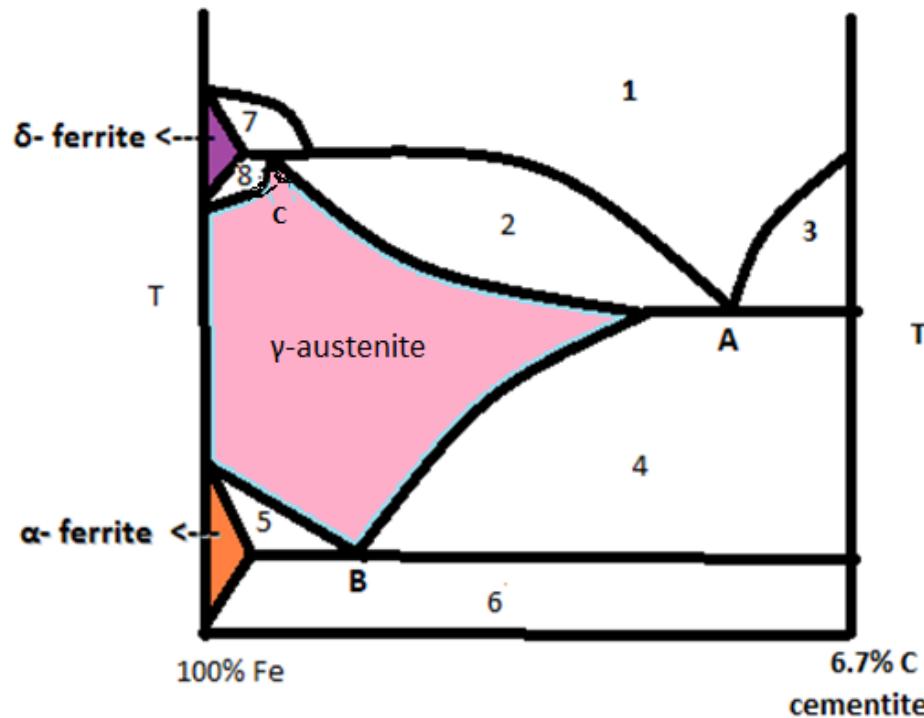
- less than 0.008 % C

Steel:

- 0.008 - 2.14 % C

Cast iron:

- 2.14 - 6.7 wt % C



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Module 4- Electrochemical equilibria



Module content:

- *Electrode potential and cell potential*
 - *Nernst Equation*
- *Types of electrodes*
- *Reference electrodes*
- *Concentration cells*
- *Ion-selective electrodes*

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Module 4- Electrochemical equilibria



Class content:

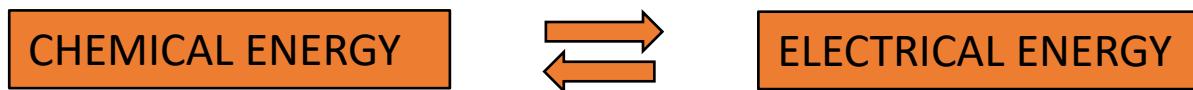
- *Origin of electrode potential*
- *Cell potential*
- *Nernst Equation*

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Module 4- Electrochemical equilibria

Electrochemistry

- Deals with the inter conversion of chemical energy and electrical energy

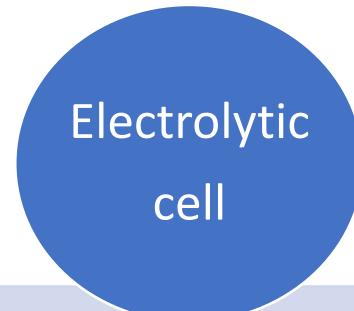


- Two types of cells:



Converts chemical energy to electrical energy

Batteries and fuel cells



Converts electrical energy to chemical energy

Cells used in electroplating

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Module 4- Electrochemical equilibria

Electrochemical studies:

- Redox reaction
- Electrodes- Anode (oxidation)
Cathode (reduction)
- Electrolytic conductance through electrolyte due to movement of ions
 - Acid, alkali or salt solutions
 - Molten electrolytes
 - Solid electrolytes

Electrode potential

- When a metal rod is dipped in a solution of its own ions, the electrical potential developed at the interface of the metal and its solution
- It is denoted by E

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Module 4- Electrochemical equilibria



Origin of Electrode potential

When a metal M is in contact with solution containing its ions M^{n+} , two reactions are possible:

1. Ionisation (Oxidation)



2. Deposition (Reduction)

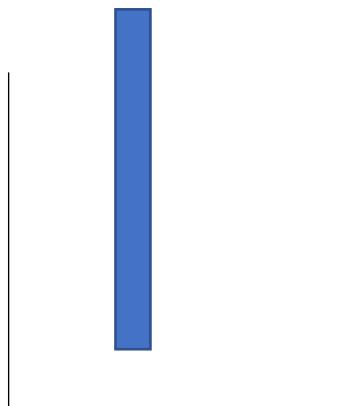


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Module 4- Electrochemical equilibria

➤ Case I : If ionization is faster than deposition

- the metal acquires net negative charge, consequently retards the rate of ionization and increases the rate of deposition. This ultimately lead to the establishment of equilibrium
- the metal electrode gets negatively charged and attracts the layer of positive ions at the interface
- an electrical double layer is formed at the interface of metal and solution known as **Helmholtz electrical double layer**

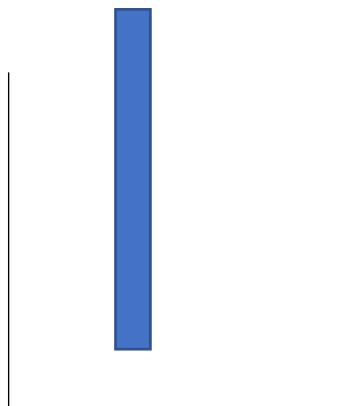


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Module 4- Electrochemical equilibria

➤ Case II : deposition is faster than ionization

- the metal acquires net positive charge, consequently retards the rate of deposition and increases rate of ionization. This ultimately lead to the establishment of equilibrium.
- The metal electrode gets positively charged and attracts the layer of negative ions at the interface,
- an electrical double layer is formed at the interface of metal and solution known as **Helmholtz electrical double layer**



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Module 4- Electrochemical equilibria

Standard electrode potential

- The potential developed at the interface of metal and solution, when the metal is in contact with a solution of its own ions having unit concentration at 298 K
- In case of gas electrodes the partial pressure of gas is maintained at 1 atmospheric pressure.
- It is represented as E°

Electrochemical Cell

Single electrode potentials cannot be measured hence two electrodes are coupled together to form a cell

Cell notation

e.g. Daniel cell:



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Module 4- Electrochemical equilibria

Cell potential

- The difference in electrode potentials of the electrodes constituting the cell
- It is denoted by E_{cell}

Standard cell potential

- E_{cell} depends on concentration of the ions in the cell, temperature and the partial pressures of any gases involved in the cell reaction.
- When all the concentrations are 1M, all partial pressures of gases are 1atm and temperature is 298K, the emf is called Standard cell potential, E°_{cell}

Calculation of E_{cell}

$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}} = E_{\text{cathode}} - E_{\text{anode}}$$

- E_{cell} represents the driving force for the cell reaction to take place

$$\Delta G = - nFE_{\text{CELL}}$$

- If reaction is spontaneous ΔG is negative, thus E_{CELL} should be positive
- If reaction is non spontaneous ΔG is positive, thus E_{CELL} should be negative

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Module 4- Electrochemical equilibria

Electrochemical Series:

- In order to predict the electrochemical behavior of an electrode – electrolyte system, elements are arranged in the order of their standard reduction potentials.
- This arrangement is known as electrochemical series.
- A negative value indicates oxidation tendency while a positive value indicates a reduction tendency.

Electrochemical series

Equilibrium (Oxidants \leftrightarrow Reductants)	E° (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

Metal Reducing Activity Increasing 

Metal Oxidizing Activity Increasing 

Source:<https://www.syedgilanis.com/2019/04/electrochemicalseries.html>

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Module 4- Electrochemical equilibria

Nernst equation for a single electrode

A quantitative relationship between electrode potential and concentration of species with which the electrode is reversible

The reaction at the electrode is



The maximum work that can be obtained is

$$-\Delta G = W_{\max}$$

For an electrochemical system, maximum work done is

$$W_{\max} = \text{Total charge available} \times \text{Energy available per unit charge}$$

- **Total charge available**, i.e., No. of moles of electrons exchanged in redox reaction (n), multiplied by charge carried per mole of electrons , $F(96,500 \text{ C/mol}) = nF$
- **Energy available per unit charge**, i.e., electrode potential because

$$\text{electrode potential} = \text{energy/unit charge} = E$$

$$\text{Therefore , } W_{\max} = nFE ; \quad \Delta G = -nFE$$

$$\text{Under standard conditions, } \Delta G^\circ = -nFE^\circ$$

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Module 4- Electrochemical equilibria



A thermodynamic equation which relates reaction quotient and decrease in free energy is given by,

$$\Delta G = \Delta G^\circ + RT \ln Q, \text{ where } Q \text{ is the reaction quotient}$$

The reaction quotient for the reaction is, $Q = [M]/[M^{n+}]$

Substituting for ΔG , ΔG° and Q , we get

$$-nFE = -nFE^\circ + RT \ln\left(\frac{[M]}{[M^{n+}]}\right)$$

Where, E° = Standard electrode potential, n = number of electrons exchanged in the redox reaction, R = Gas constant. $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, T = temp in Kelvin,
 F = Faraday 96500 C mol^{-1}

dividing throughout by $-nF$, $E = E^\circ - \frac{RT}{nF} \ln\left(\frac{[M]}{[M^{n+}]}\right)$

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Module 4- Electrochemical equilibria

since $[M] = 1$ for pure substances,

$$E = E^\circ + \frac{RT}{nF} \ln([M^{n+}])$$

at 298K,

$$E = E^\circ + \frac{0.0591}{n} \log([M^{n+}])$$

Nernst equation may also be used to calculate. emf of electrochemical cells. For the cell reaction



$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Nernst equation is

$$E = E^\circ - \frac{0.0591}{n} \log\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

n= no. of e⁻s transferred, E_{cell}° = std. emf of the cell

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Module 4- Electrochemical equilibria



Class content:

- *Types of electrodes*
 - *Metal-metal-ion electrode*
 - *Metal-insoluble salt –ion electrode*
 - *Gas electrode*
 - *Amalgam electrode*
 - *Redox electrode*
 - *Ion selective electrode*

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Module 4- Electrochemical equilibria

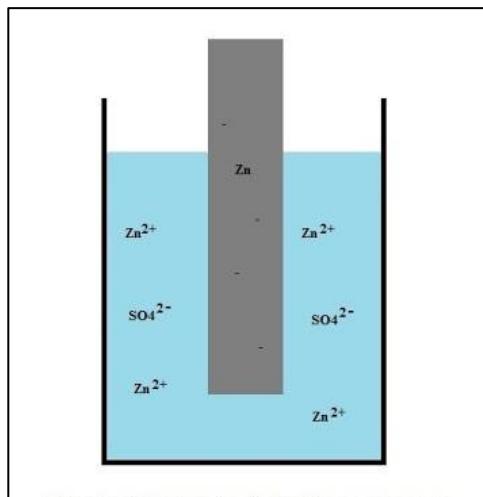
Types of electrodes

- In order to form a cell, 2 half cells or 2 electrodes are required
- Various types of electrodes are available which are constructed based on the application

1. Metal-metal ion electrode:

- Metal in contact with a solution of its own ions
e.g., Zn/Zn²⁺, Cu/Cu²⁺, Ag/Ag⁺
- $M^{n+} + ne^- \rightleftharpoons M$
- Nernst equation

$$E_{M/M^{n+}} = E_{M/M^{n+}}^{\circ} + \frac{2.303RT}{nF} \log [M^{n+}]$$



Source:[http://www.valgetal.com/physics/
Batteries/batteries.htm](http://www.valgetal.com/physics/Batteries/batteries.htm)

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Module 4- Electrochemical equilibria

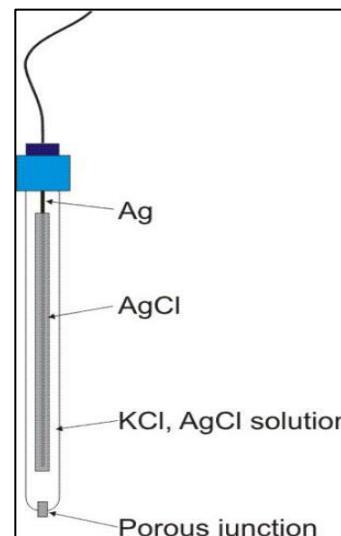
2. Metal-Metal insoluble salt- ion electrode:

- These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution of soluble salt of the same anion
e.g., Calomel electrode Hg/Hg₂Cl₂/KCl, Ag/AgCl(s)/HCl
- For silver –silver chloride electrode



- Nernst equation:

$$E_{\text{Ag}/\text{AgCl}/\text{Cl}^-} = E^{\circ}_{\text{Ag}/\text{AgCl}/\text{Cl}^-} - \frac{0.0591}{1} \log[\text{Cl}^-]$$



Source:<https://www.corrosion-doctors.org/Corrosion-Thermodynamics/Reference-Half-Cells-Silver.htm>

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Module 4- Electrochemical equilibria

3. Gas electrode:

- It consists of gas bubbling about an inert metal foil, immersed in solution containing ions to which the gas is reversible.
- The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions

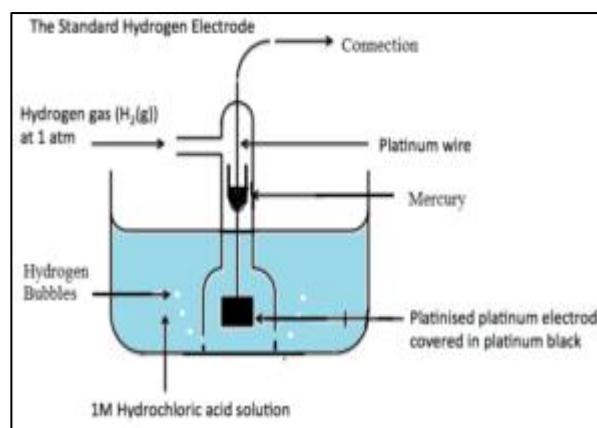
e.g., Hydrogen electrode $\text{Pt}/\text{H}_2/\text{H}^+$, Chlorine electrode $\text{Pt}/\text{Cl}_2/\text{Cl}^-$

- For a hydrogen electrode



- Nernst equation:

$$E_{\text{Pt}/\text{H}_2/\text{H}^+} = E^0_{\text{Pt}/\text{H}_2/\text{H}^+} - \frac{0.0591}{2} \log\left(\frac{p_{\text{H}_2}}{[\text{H}^+]^2}\right)$$



Source:https://thefactfactor.com/facts/pure_science/chemistry/physical-chemistry/reference-electrodes/5844/

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Module 4- Electrochemical equilibria

4. Amalgam electrode:

- It is similar to metal- metal ion electrode in which metal amalgam is in contact with a solution containing its own ions

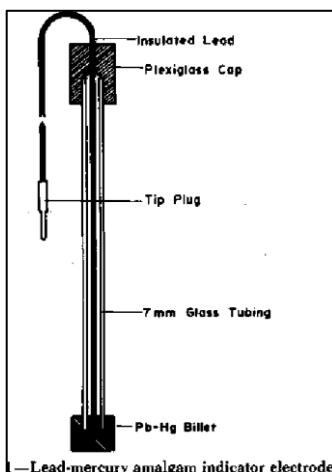
e.g., Lead amalgam electrode Pb-Hg/Pb²⁺

- For lead amalgam electrode



- Nernst equation:

$$E_{\text{Pb}^{2+}/\text{Pb-Hg}} = E^0_{\text{Pb}^{2+}/\text{Pb-Hg}} - \frac{0.0591}{2} \log\left(\frac{[\text{Pb-Hg}]}{[\text{Pb}^{2+}]}\right)$$



Source:<https://www.semanticscholar.org/paper/Potentiometric-Titration-of-Sulfate-in-Water-and-a-Robbins-Carter/c823ab0578481e876975ee707a5f8adca14c512f>

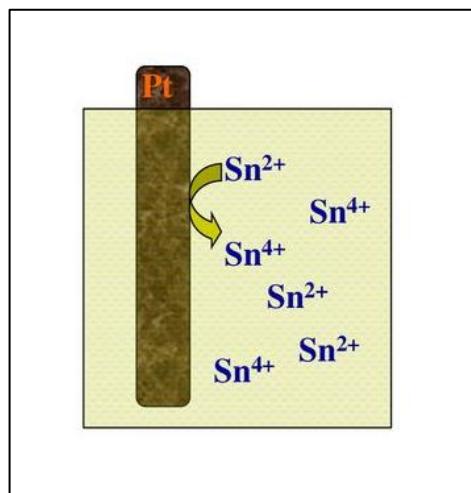
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Module 4- Electrochemical equilibria

5. Oxidation - reduction electrode :

- It consists of an inert metal such as platinum immersed in a solution containing an appropriate oxidized and reduced form of redox system.
 - The metal merely acts as electrical contact.
 - The potential arises due to the tendency of one form to change in to other form.
e.g., Pt/Fe²⁺, Fe³⁺, Pt/Ce³⁺, Ce⁴⁺, Pt/Sn²⁺, Sn⁴⁺
 - For stannous stannic electrode
- $\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$
- Nernst equation:

$$E_{\text{Pt}/\text{Sn}^{4+}/\text{Sn}^{2+}} = E^0_{\text{Pt}/\text{Sn}^{4+}/\text{Sn}^{2+}} - \frac{0.0591}{2} \log\left(\frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}\right)$$



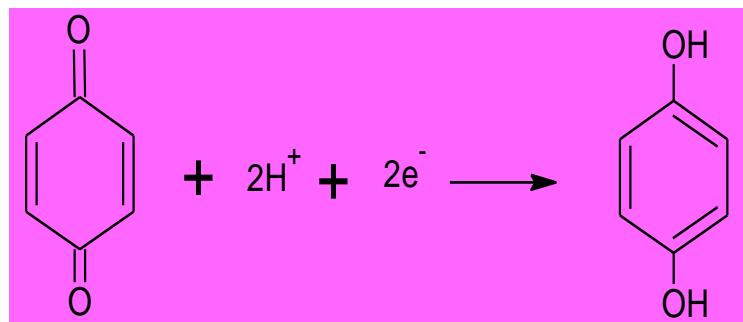
Source:<https://slideplayer.com/slide/13860805/>

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Module 4- Electrochemical equilibria

Quinhydrone electrode

- It consists of an inert metal such as platinum immersed in a solution containing quinone and hydroquinone
- The metal merely acts as electrical contact
- The potential arises due to the tendency of quinone to change to hydroquinone
- $\text{Pt}/\text{Q}, \text{QH}_2$



• Nernst equation: $E_{\text{Pt}/\text{Q}, \text{QH}_2} = E^{\circ}_{\text{Pt}/\text{Q}, \text{QH}_2} - \frac{0.0591}{2} \log\left(\frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2}\right)$

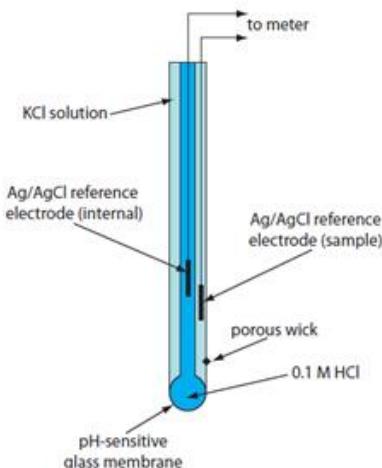
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Module 4- Electrochemical equilibria

6. Ion selective electrode:(membrane electrode)

- It consists of a membrane in contact with a solution, with which it can exchange ions.
e.g., **glass electrode**: selective to H^+ , Na^+ , K^+ etc.
- Equation for determining potential for pH sensitive Glass electrode

$$E_G = E_G^0 + 0.0591 \log_{10} [\text{H}^+]$$



Source:Analytical Chemistry 2.0, David Harvey,
community.asdlib.org/activelearning-textbook/

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Module 4- Electrochemical equilibria



Class content:

- ***Reference electrodes***
 - ***Primary reference electrode***
 - *Standard Hydrogen electrode*
 - ***Secondary reference electrodes***
 - *Calomel electrode*
 - *Silver – silver chloride electrode*

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Module 4- Electrochemical equilibria

Reference electrodes

- Electrodes whose potentials are accurately known, stable and with reference to which the electrode potential of any electrode can be measured
- Reference electrode is combined with indicator electrode and emf of the cell is measured
- Two types of reference electrodes:
 - **Primary reference electrodes**
 - Standard Hydrogen electrode(SHE)
 - **Secondary reference electrodes**
 - Calomel electrode
 - Silver-silver chloride electrode

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Module 4- Electrochemical equilibria

Primary reference electrode: Standard hydrogen electrode

- Electrode potential is assigned a value of 0.0 V
- Gas electrode
- Pt/H₂/H⁺
- $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$
- Used to measure potential of other electrodes

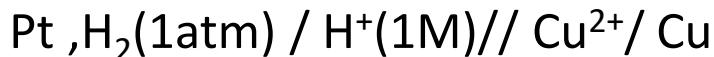
e.g.,



$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$0.76 = 0.0 - E_{\text{Zn/Zn}^{2+}}$$

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



$$E_{\text{cell}} = E_{\text{rhs}} - E_{\text{lhs}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$0.34 = E_{\text{Cu/Cu}^{2+}} - 0.0$$

$$E_{\text{Cu/Cu}^{2+}} = 0.34 \text{ V}$$

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Module 4- Electrochemical equilibria

Disadvantages of SHE:

- Maintaining concentration of H^+ ions at 1M and pressure of H_2 gas at 1 atm is difficult.
- Platinum is highly susceptible to poisoning by different impurities in gas
- It cannot be used with oxidizing and reducing environment

Secondary reference electrodes:

- Due to the limitations of standard hydrogen electrode some other electrodes whose electrode potentials are accurately known and remain stable over a long period of time and can be easily assembled. With respect to these electrodes , electrode potentials of other electrodes can be assigned

e.g., **Calomel electrode, silver silver chloride electrode**

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Module 4- Electrochemical equilibria

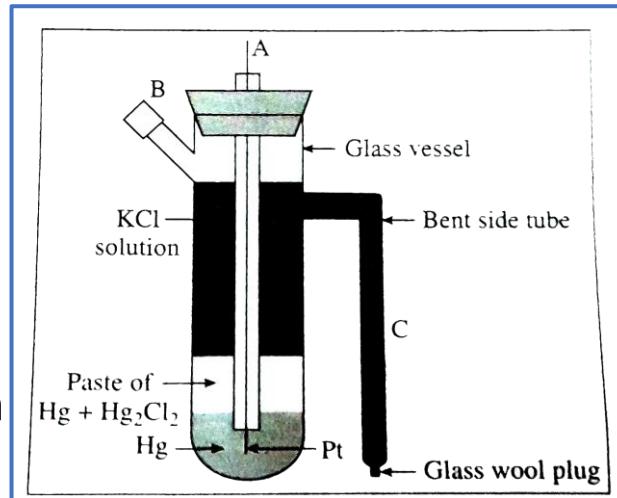
Secondary Reference electrodes:

Calomel electrode

- Most widely used reference electrode
- Metal-insoluble salt –ion electrode

Construction:

- A glass tube containing a layer of mercury over which a paste of insoluble salt Hg_2Cl_2 (calomel) + Hg and the next layer is a solution of KCl
- A Pt wire dipped in Hg provides electrical contact
- Tube is fitted with a side tube to fill KCl solution of known concentration and another side tube which connects to the salt bridge



<https://doubtnut.com/question-answer-chemistry/describe-the-construction-and-working-of-the-calomel-electrode-96607395>

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Module 4- Electrochemical equilibria

- $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s})/\text{Cl}^-$

Working :

- Can act as anode or cathode depending on the nature of the electrode with which it is coupled

As anode:



As cathode:



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Module 4- Electrochemical equilibria

Applying Nernst's equation



$$E = E^\circ - 2.303RT/2F \log [\text{Cl}^-]^2$$

at 298K

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

- Electrode is reversible to chloride ions
- Electrode potential depends on chloride ion concentration

Types of calomel electrodes:

[KCl]	Name	Electrode potential at 298K
0.1M	Decinormal electrode	0.3358 V
1M	Normal electrode	0.2824 V
Saturated solution of KCl	Saturated Calomel Electrode(SCE)	0.2422 V

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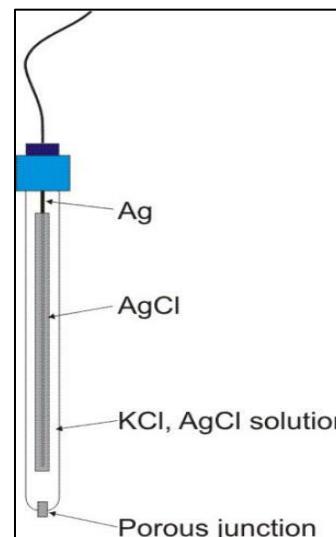
Module 4- Electrochemical equilibria

Silver-silver chloride electrode

- Widely used as reference electrode
- Metal-insoluble salt –ion electrode

Construction:

- It has a silver wire or a silver coated platinum wire, coated electrolytically with a thin layer of silver chloride which is dipped in a solution of KCl or HCl of known concentration



Source:<https://www.corrosion-doctors.org/Corrosion-Thermodynamics/Reference-Half-Cells-Silver.htm>

- Ag/AgCl/Cl⁻

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Module 4- Electrochemical equilibria

Working :

- Can act as anode or cathode depending on the nature of the electrode with which it is coupled

As anode:



As cathode:



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Module 4- Electrochemical equilibria

Applying Nernst's equation



$$E = E^\circ - 2.303RT/F \log [\text{Cl}^-]$$

at 298K

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

- Electrode is reversible to chloride ions
- Electrode potential depends on chloride ion concentration

Types of silver - silver chloride electrodes :

[KCl]	Name	Electrode potential at 298K
0.1N	Decinormal electrode	0.289 V
1N	Normal electrode	0.223 V
Saturated solution of KCl	Saturated silver-silver chloride Electrode	0.199 V

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Module 4- Electrochemical equilibria



Class content:

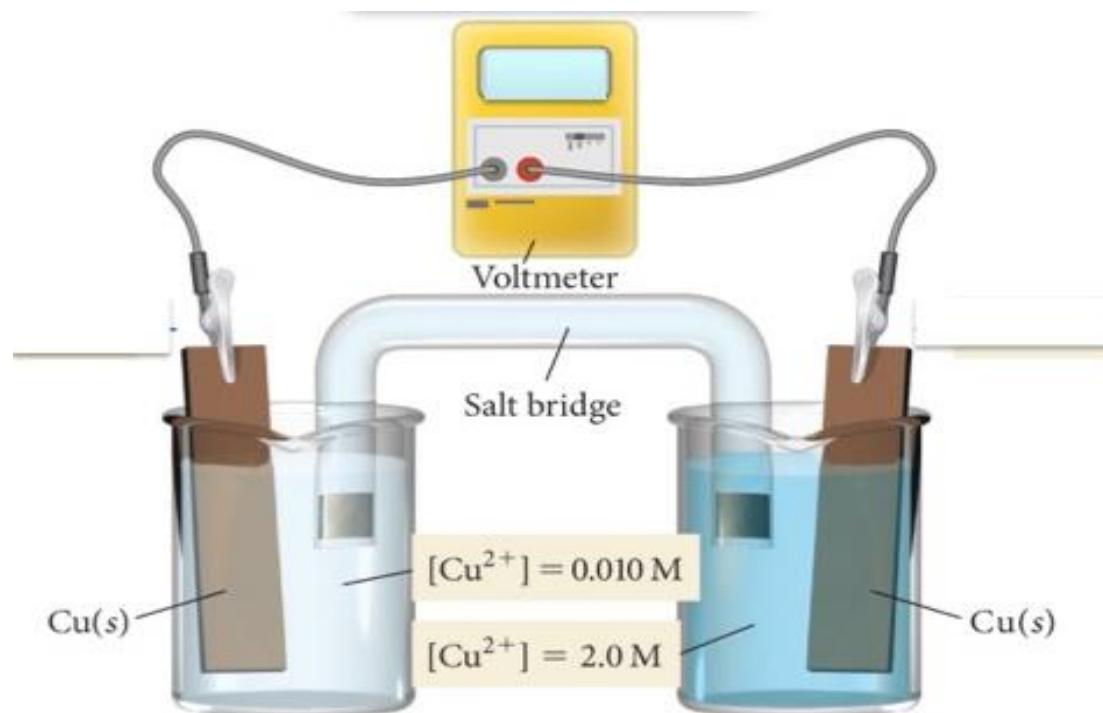
- ***Concentration cells***
 - *Types of concentration cells*
 - *Electrolyte concentration cells*
 - *Electrode concentration cells*
- ***Ion-selective electrodes***
 - *Types of ion – selective electrodes*
 - *Electrode potential for an ion-selective electrode*

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Module 4- Electrochemical equilibria

Concentration cells:

- An electrochemical cell in which identical electrodes are in contact with a solution of identical species but of different concentration



<https://chemdemos.uoregon.edu/demos/Voltaic-Cell-CuCu-concentration-cell-Demonstration>

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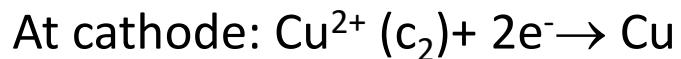
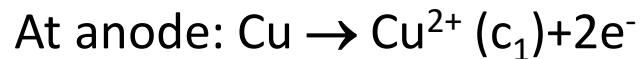
Module 4- Electrochemical equilibria

- In this cell 2 copper electrodes are immersed in copper sulphate solutions of concentration c_1 & c_2 , such that $c_2 > c_1$
- An electrolyte has spontaneous tendency to diffuse from a solution of higher concentration to a solution of lower concentration which is the **driving force** for development of potential
- Oxidation takes place at anode and reduction takes place at cathode
- e.g., $\text{Cu}/\text{Cu}^{2+}(c_1)//\text{Cu}^{2+}(c_2)/\text{Cu}$

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Module 4- Electrochemical equilibria

Reactions :



Expression for cell potential:

The emf of the cell = $E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cathode}} = E^{\circ} + \frac{2.303RT}{nF} \log c_2$$

$$E_{\text{anode}} = E^{\circ} + \frac{2.303RT}{nF} \log c_1$$

$$E_{\text{cell}} = \left(E^{\circ} + \frac{2.303RT}{nF} \log c_2 \right) - \left(E^{\circ} + \frac{2.303RT}{nF} \log c_1 \right)$$

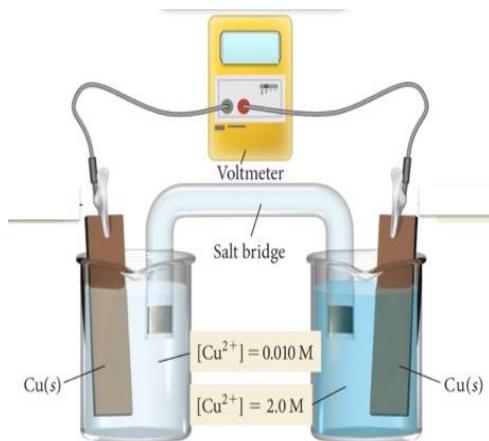
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \left(\frac{c_2}{c_1} \right)$$

$$\text{At 298K, } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{c_2}{c_1} \right)$$

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

- The emf of the cell is positive only if $c_2 > c_1$
i.e., conc of metal ion at cathode > conc. of metal ion at anode
- The emf of the cell depends upon the ratio c_2/c_1
- When $c_2 = c_1$, the emf of the cell becomes zero
- During working of the cell, concentration of ions increases at anode decreases at cathode
- When current is drawn from the cell c_1 increases and c_2 decreases
- The cell can operate only as long as the concentration terms are different



ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

Types of concentration cells:

- Electrolyte concentration cell
- Electrode concentration cell

Electrolyte concentration cell:

- Electrolyte concentration cell consists of two same electrodes that are dipped in the same electrolyte but with different concentrations of electrolytes
- $\text{Cu}/\text{Cu}^{2+}(c_1)/\text//\text{Cu}^{2+}(c_2)/\text{Cu}$
- Cell potential is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log\left(\frac{c_2}{c_1}\right)$$

Electrode concentration cell

- Electrode concentration cell consists of two identical electrodes of different activity which are dipped in the same solution of electrolyte
- $\text{Na-Hg}(c_1)/\text{Na}^+/\text{Na-Hg}(c_2)$
- Cell potential is given by

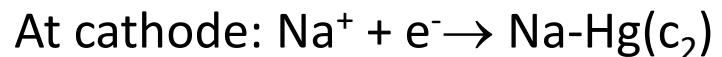
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

- $\text{Na}-\text{Hg}(c_1)/\text{Na}^+/\text{Na}-\text{Hg}(c_2)$:

Reactions are :



$$\text{Cell potential} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cathode}} = E^{\circ} - \frac{2.303RT}{nF} \log \frac{\text{Na}-\text{Hg}(c_2)}{\text{Na}^+}$$

$$E_{\text{anode}} = E^{\circ} - \frac{2.303RT}{nF} \log \frac{\text{Na}-\text{Hg}(c_1)}{\text{Na}^+}$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na}-\text{Hg}(c_1)}{\text{Na}-\text{Hg}(c_2)}$$

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Module 4- Electrochemical equilibria

- $\text{Pt}/\text{H}_2(\text{p}_1 \text{ atm})/\text{H}^+/\text{H}_2(\text{p}_2 \text{ atm})/\text{Pt}$:

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_1}{p_2}$$

- $\text{Pt}/\text{Cl}_2(\text{p}_1 \text{ atm})/\text{Cl}^-/\text{Cl}_2(\text{p}_2 \text{ atm})/\text{Pt}$:

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria



Ion selective electrodes (ISE)

- Selectively respond to a **specific ion** in a mixture
- Potential developed is a function of concentration of that ion
- Have a membrane which is capable of exchanging the specific ion with solution with which it is in contact
- **Membrane electrodes**
e.g., glass electrode

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Module 4- Electrochemical equilibria

Types of Ion selective electrodes :

Electrodes are classified based on the membrane material

- **Crystalline / solid state membrane electrodes:**

Single crystal LaF_3 selective to F^-

Polycrystalline such as Ag_2S selective to S^{2-}

- **Non-crystalline membrane electrodes:**

e.g., Glass membrane selective to H^+ , Na^+

- **Liquid membrane electrodes:**

An ion-exchanger is dissolved in a viscous organic liquid membrane; used for Ca^+ , K^+

- **Immobilised liquid in a rigid polymer:**

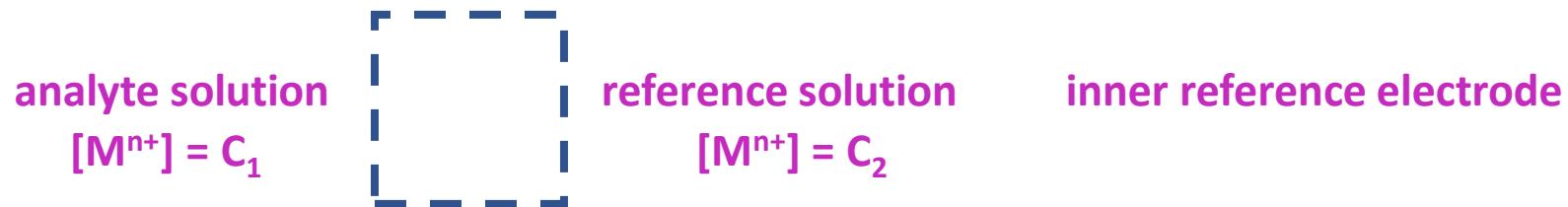
e.g., immobilized ion exchanger in PVC matrix ; used for Ca^+ , NO_3^-

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Module 4- Electrochemical equilibria

Electrode potential of an ion-selective electrode

Schematic representation:



boundary potential is

$$E_j = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$$

since concentration of reference solution C_2 is constant

$$E_j = \frac{2.303RT}{nF} \log C_1 + K$$

where

$$K = -\frac{2.303RT}{nF} \log C_2$$

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Module 4- Electrochemical equilibria

Overall potential of the membrane electrode is given by

$$E_M = E_j + E_{ref}$$

since $E_j = \frac{2.303RT}{nF} \log C_1 + K$

$$E_M = \frac{2.303RT}{nF} \log C_1 + K + E_{ref}$$

$$E_M = E^o_M + \frac{2.303RT}{nF} \log C_1 \quad \text{where} \quad E^o_M = K + E_{ref}$$

At 298K, $E_M = E^o_M + \frac{0.0591}{n} \log C_1$

Membrane electrode is coupled with an external reference electrode

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Module 4- Electrochemical equilibria

External ref. electrode/Analyte/membrane/ ref. solution/Internal ref. electrode

Cell potential = $E_{\text{cathode}} - E_{\text{anode}}$

$E_{\text{cell}} = E_{\text{membrane}} - E_{\text{ext.ref.electrode}}$

E_{cell} can be measured, $E_{\text{ext.ref.electrode}}$ is known

E_{membrane} can be determined

Since $E_M = E^{\circ}_M + \frac{0.0591}{n} \log C_1$, C_1 can be determined

The disadvantage of an ion-selective electrode is that the **membrane offers very high resistance** so ordinary potentiometers cannot be used; special type of potentiometers have to be used.

Applications :

Used to determine concentration of number of cations and anions such as H^+ , Li^+ , Na^+ , K^+ , Pb^{2+} , Cu^{2+} , Mg^{2+} , CN^- , NO_3^- , F^- etc

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria



Class content:

- ***Glass electrode***
 - ***Construction***
 - ***Working***
 - ***Determination of pH***

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Module 4- Electrochemical equilibria

Glass electrode

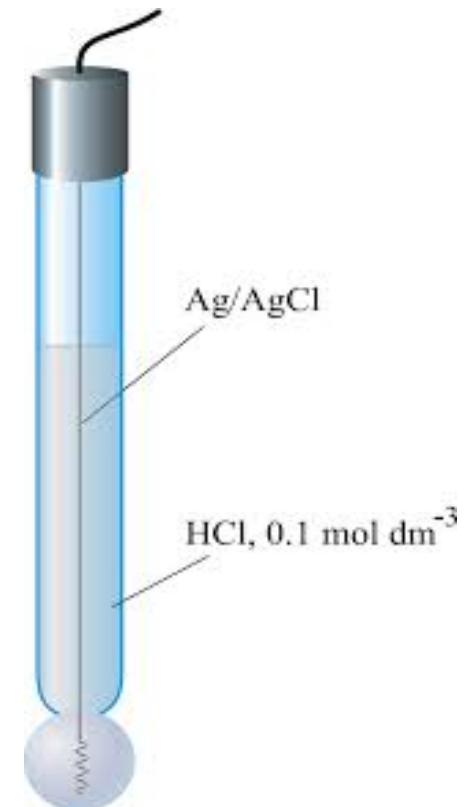


- Ion-selective electrode
- Responds to Hydrogen ion
- pH sensitive; can be used to determine pH of a solution
- Consists of a glass membrane which is capable of exchanging H^+ ions

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Module 4- Electrochemical equilibria

- Construction:
- Glass tube , the end of which is a bulb of **very thin glass membrane**
- Glass bulb is made up of special type of glass, CORNING 015
- The glass bulb is filled with **solution of known pH** which is the reference solution
- A **silver - silver chloride electrode** is dipped inside the reference solution serves as internal reference electrode and also provides external electrical contact
- The electrode is immersed in a **solution containing H⁺** which is the analyte
- **Ag/AgCl/HCl/glass**



Source:<https://glossary.periodni.com/glossary.php?en=glass+electrode>

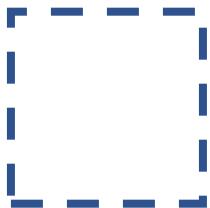
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Module 4- Electrochemical equilibria

Working:

analyte solution

$$[H^+] = C_1$$



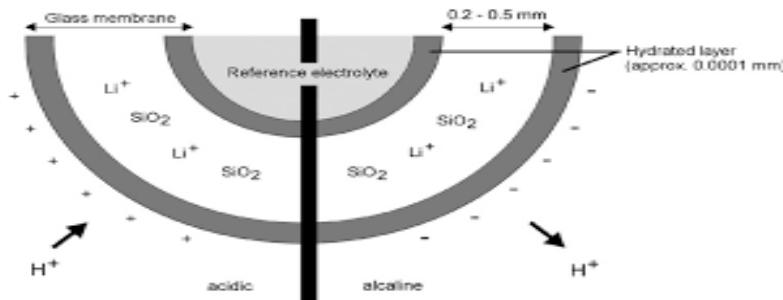
reference solution

$$[H^+] = 0.1\text{M HCl} = C_2$$

Ag-AgCl electrode



- The inner and outer surfaces of the glass membrane can exchange H^+ ions with the solution they are in contact with



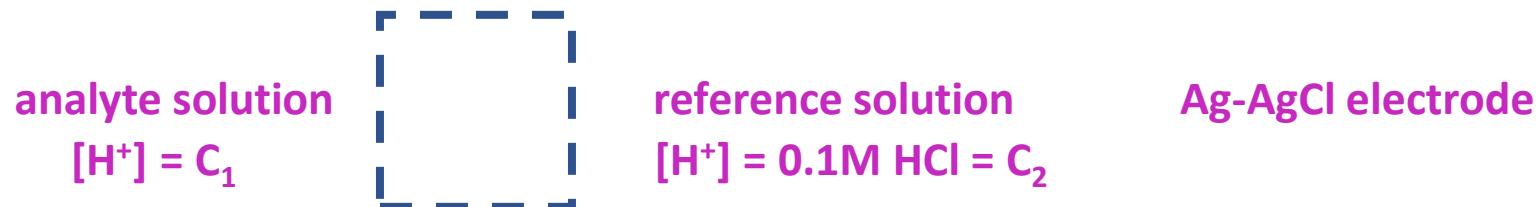
Source:http://www.metrohmsiam.com/teachingresearch/TRL_25/TRL25_95520780155013.pdf

- The hydrated glass membrane brings about ion exchange reaction between singly charged cations in the interstices of glass lattice and protons from the solution
- A potential is developed, which is a function of H^+ of the solution

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

Electrode potential of a glass electrode :



boundary potential is $E_b = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$

since concentration of reference solution, C₂ is constant

$$E_b = L' + \frac{2.303RT}{nF} \log C_1 \quad \text{where} \quad L' = -\frac{2.303RT}{nF} \log C_2$$

At 298K, $E_b = L' + \frac{0.0591}{n} \log[H^+]$ since for H⁺, n = 1

$$E_b = L' - 0.0591 \text{pH}$$

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

The glass electrode potential has 3 components

1. The boundary potential
2. The potential of internal reference electrode
3. Asymmetric potential

$$E_G = E_b + E_{\text{ref}} + E_{\text{asymmetric}}$$

- Asymmetric potential arises due to difference in responses of inner and outer surfaces of the glass bulb, due to differing conditions of stress on two glass surfaces

$$\begin{aligned} E_G &= E_b + E_{\text{ref}} + E_{\text{asymmetric}} ; \quad E_b = L' + \frac{0.0591}{n} \log[H^+] \\ &= L' + \frac{0.0591}{n} \log[H^+] + E_{\text{ref}} + E_{\text{asymmetric}} \\ &= E_G^0 + 0.0591 \log [H^+] \quad \text{where } E_G^0 = L' + E_{\text{ref}} + E_{\text{asymmetric}} \\ E_G &= E_G^0 - 0.0591 \text{pH} \end{aligned}$$

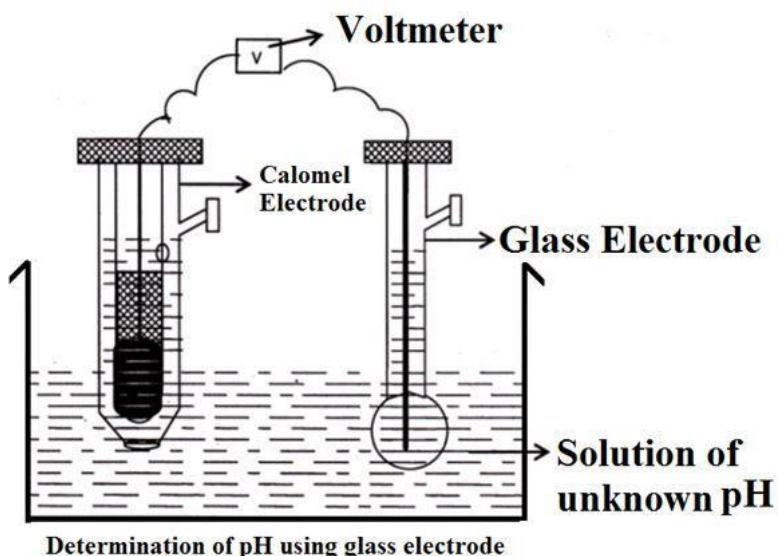
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Module 4- Electrochemical equilibria

Determination of pH using glass electrode:

- Glass electrode is combined with an external reference electrode

Hg/Hg₂Cl₂/Cl⁻//analyte solution/glass/0.1N HCl/AgCl/Ag



Source:<https://utkarshiniedu.wordpress.com/2016/12/22/lecture-1-108-ion-selective-electrodes/>

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

Determination of pH using glass electrode:

- The emf of the cell is determined potentiometrically

$$E_{\text{cell}} = E_G - E_{\text{calomel}} ; \quad E_G = E^0_G - 0.0591\text{pH}$$

$$= E^0_G - 0.0591\text{pH} - E_{\text{calomel}}$$

$$\text{pH} = \frac{E^0_G - E_{\text{calomel}} - E_{\text{cell}}}{0.0591}$$

- To evaluate E^0_G the glass electrode is dipped in a **solution of known pH(buffer solution)** and combined with calomel electrode, the emf of the cell is measured from which E^0_G can be evaluated

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Module 4- Electrochemical equilibria

Applications of glass electrode:

Used extensively in chemical, industrial, agricultural and biological labs

Advantages of glass electrode :

- Can be used in oxidizing and reducing environments and metal ions
- Does not get poisoned
- Can be used for very small volumes
- Accurate results can be obtained between pH 1 to 9 by ordinary electrodes. However by using special glass electrodes pH 1 to 14 can be measured with accuracy
- Simple to operate and can be used with portable instruments

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Module 4- Electrochemical equilibria

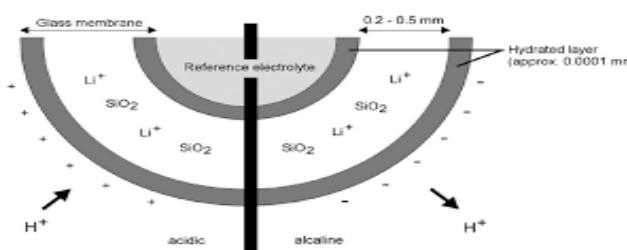
Disadvantages of glass electrode:

- Because of high resistance of glass, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements
- Glass membrane is very delicate, hence has to be handled carefully
- At very high pH levels usually over a pH of 9 , **Alkaline error** is observed



When the Sodium ion level is relatively high, some of the H^+ ions in the gel layer around the sensitive electrode membrane are replaced by Na^+ ions

The electrode may eventually respond to Na^+ instead of H^+ ions, giving a false lower pH value than the actual value



ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria



Class content:

- ***Fluoride - ion electrode***
 - ***Construction***
 - ***Working***
 - ***Determination of $[F^-]$***

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Module 4- Electrochemical equilibria

Fluoride-ion electrode

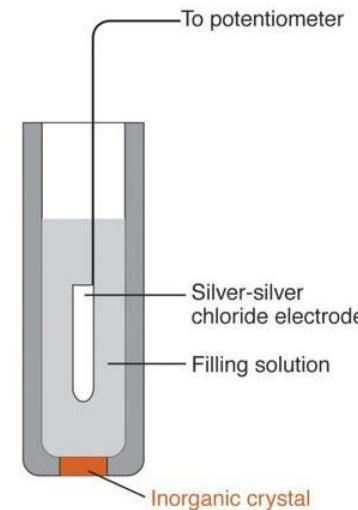


- Ion-selective electrode
- Responds to Fluoride ion
- Example: lanthanum fluoride electrode
- Consists of a **lanthanum fluoride (LaF_3) membrane** which is capable of exchanging F^- ions

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

- **Construction:**
- A tube to which the sensing membrane is bonded at one end
- Membrane is a **single crystal of Lanthanum fluoride(LaF_3) doped with Europium fluoride (EuF_2)** to improve conductivity
- Doping creates **fluoride ion vacancies** which allows F^- ions to migrate across the membrane
- The tube is filled with the reference solution **containing 0.1 M NaF and 0.1M NaCl**
- A **silver - silver chloride electrode** is placed in the reference solution which acts as the internal reference electrode and also serves for external electrical contact
- The electrode is immersed in a **solution containing F^- ions** which is the analyte
- **Ag/AgCl/NaCl,NaF/LaF₃**



Source:[https://slideplayer.com/
slide/14040224/](https://slideplayer.com/slide/14040224/)

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Module 4- Electrochemical equilibria

Working:

analyte solution



reference solution

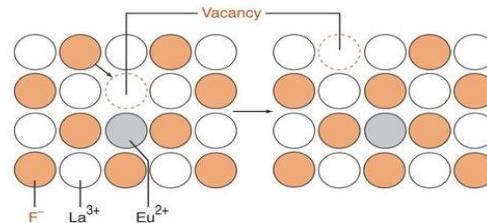
$$[F^-] = C_1$$

$$[F^-] = C_2$$

Ag-AgCl electrode



- The inner and outer surfaces of the membrane can exchange F^- ions with the solution they are in contact with
- The F^- ions migrate through the membrane by jumping through the lattice vacancies
- As transference of charge through the crystal is almost exclusively due to fluoride ion, the electrode is highly specific to fluoride ion
- The only ion which significantly interferes is hydroxide (OH^-) ion



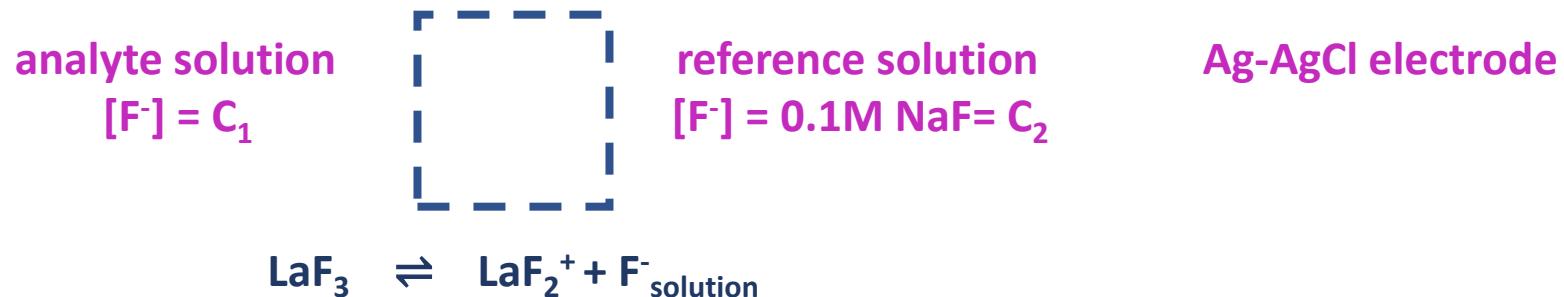
Migration of F^- through LaF_3 doped with EuF_2 .

Source:<https://slideplayer.com/slide/14040224/>

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

Electrode potential of a Fluoride ion electrode :



boundary potential is

$$E_b = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$$

Since n is -1 for F^- ion,

$$E_b = \frac{2.303RT}{F} \log\left(\frac{C_2}{C_1}\right)$$

since concentration of reference solution, C_2 is constant

$$E_b = K' - \frac{2.303RT}{F} \log C_1 \quad \text{where} \quad K' = \frac{2.303RT}{F} \log C_2$$

At 298K,

$$E_b = K' - 0.0591 \log[F^-]$$

$$E_b = K' + 0.0591 pF$$

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Module 4- Electrochemical equilibria

The fluoride ion electrode potential is given by

1. The boundary potential
2. The potential of internal reference electrode

$$E_F = E_b + E_{ref}$$

$$E_b = K' - 0.0591 \log[F^-]$$

since

$$E_F = K' - 0.0591 \log[F^-] + E_{ref}$$

$$= E^0_F - 0.0591 \log[F^-] \quad \text{where} \quad E^0_F = K' + E_{ref}$$

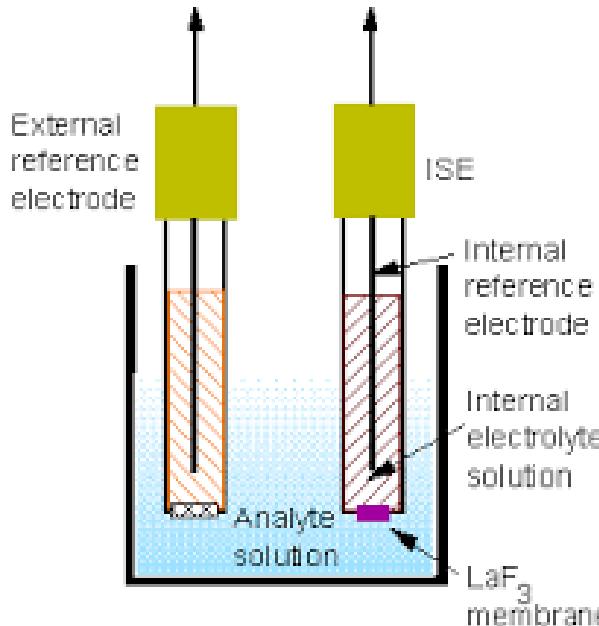
$$E_F = E^0_F + 0.0591 pF$$

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Module 4- Electrochemical equilibria

Determination of pF using Fluoride ion electrode:

- Fluoride ion electrode is combined with an external reference electrode



Source:<http://elchem.kaist.ac.kr/vt/chem-ed/echem/ise.htm>

ENGINEERING CHEMISTRY

Module 4- Electrochemical equilibria

Determination of pF using Fluoride ion electrode:

- The emf of the cell is determined potentiometrically

$$E_{\text{cell}} = E_F - E_{\text{calomel}} ; \quad E_F = E^0_F + 0.0591pF$$

$$= E^0_F + 0.0591pF - E_{\text{calomel}}$$

$$pF = \frac{E_{\text{cell}} - E^0_F + E_{\text{calomel}}}{0.0591}$$

- To evaluate E^0_F the fluoride ion electrode is dipped in a **solution of known F⁻ ion concentration** and combined with calomel electrode, the emf of the cell is measured from which E^0_F can be evaluated

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Module 4- Electrochemical equilibria

Applications of Fluoride ion electrode:

- To determine concentration of F^- ion in water pollution studies
- To determine concentration of F^- ion in toothpaste

Advantages of Fluoride ion electrode :

- Can be used for very small volumes
- Very sensitive ; can determine $[\text{F}^-]$ upto 10^{-6}M

Disadvantages of Fluoride ion electrode:

- Because of high resistance of the membrane, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements
- The presence of OH^- ions interferes with measurement of F^- ions ;shows best results between pH 5 and 8.Hence the $[\text{OH}^-]$ is kept constant using a buffer

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Module 4- Electrochemical equilibria



End of Module 4- Electrochemical equilibria

End of Unit II

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Module 4 – Electrochemical Equilibria



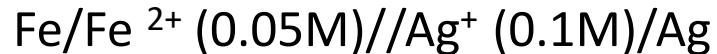
Class content:

- *Numericals on electrochemistry*
 - *Nernst equation*
 - *Ion selective electrode*

ENGINEERING CHEMISTRY

Module 4 – Electrochemical Equilibria

1. For the given cell:



- (i) Write the overall cell reaction
- (ii) Calculate E_{cell}° and E_{cell} at 25°C
(Given : $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44\text{V}$; $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.80\text{V}$)

Sol. Anode : $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathode : $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$

Overall reaction : $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag}$

$$E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 0.80 + 0.44 = 1.24\text{V}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}][\text{Ag}]^2}{[\text{Fe}][\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 1.24 - \frac{0.0591}{2} \log \left(\frac{[0.05]}{[0.1]^2} \right)$$

$$E_{\text{cell}} = 1.2193\text{V}$$

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Module 4 – Electrochemical Equilibria

2. For the following concentration cell:



Calculate potential of the cell at 25°C.

Sol.

$$E_{cell} = \frac{0.0591}{n} \log \frac{p_{H_2(anode)}}{p_{H_2(cathode)}}$$

$$E_{cell} = \frac{0.0591}{n} \log \frac{8}{2}$$

$$E_{cell} = 0.01779\text{V}$$

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Module 4 – Electrochemical Equilibria

3. A decinormal calomel electrode as cathode is coupled with a saturated calomel electrode as anode to form a cell. Write the cell representation and calculate the concentration of Cl^- ion in the saturated calomel electrode, if the cell potential measured is 0.0988 V at 25°C.

Sol.



$$E_{\text{cell}} = E_R - E_L$$

$$= [E^0 - 0.0591 \log (0.1)] - [E^0 - 0.0591 \log(x)]$$

$$\frac{0.0988}{0.0591} = \log \frac{x}{0.1}$$

$$1.6717 - 1 = \log(x)$$

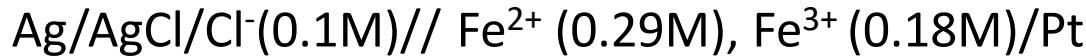
$$x = \text{Antilog}(0.6717)$$

$$x = 4.69\text{M}$$

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Module 4 – Electrochemical Equilibria

4. For the following cell:

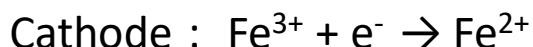


(i) Write the half cell reactions and overall cell reaction.

(ii) Calculate E_{Cell}° and E_{Cell} at 298 K

(Given: $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V}$, $E_{\text{Calomel}}^{\circ} = 0.222 \text{ V}$, $R = 8.314 \text{ J/K/mol}$, $F = 96500 \text{ C/mol}$)

Sol. (i) Anode: $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$



(ii) $E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 0.77 - 0.222 = \mathbf{0.548\text{V}}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \left[\frac{[\text{Fe}^{2+}]}{([\text{Fe}^{3+}][\text{Cl}^-])} \right]$$

$$E_{\text{cell}} = 0.548 - \frac{0.0591}{1} \log \left[\frac{[0.29]}{[0.18] \times [0.1]} \right]$$

$$E_{\text{Cell}} = \mathbf{0.4767\text{V}}$$

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Module 4 – Electrochemical Equilibria

5. Calculate the EMF of the following cell at 25°C.



(Given : R = 8.314 J/K/mol, F = 96500 C/mol)

Sol.

$$E_{cell} = \frac{0.0591}{n} \log \frac{[\text{M}^{n+}(\text{cathode})]}{[\text{M}^{n+}(\text{anode})]}$$

$$E_{cell} = \frac{0.0591}{n} \log \left[\frac{(0.12)}{0.05} \right]$$

$$n = 3 ,$$

$$E_{cell} = 0.00749\text{V}$$

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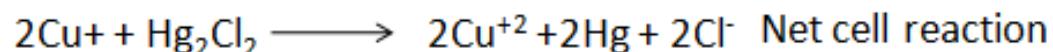
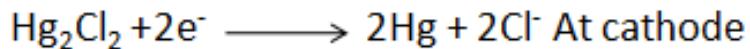
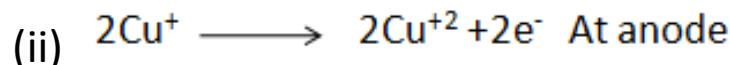
Module 4 – Electrochemical Equilibria

6. A decinormal calomel electrode is used to determine the potential of the following redox electrode : Pt/Cu²⁺(0.58 M),Cu⁺(0.08M)

- (i) Write cell representation.
- (ii) Write the reactions at the electrodes
- (iii) Calculate E⁰_{cell} and E_{cell} at 298 K.

(Given : E⁰_{Hg/Hg₂Cl₂/Cl⁻} = 0.281V , E_{Cu²⁺/Cu} = 0.153 V)

Sol. (i) Pt/Cu²⁺(0.58 M),Cu⁺(0.08M)//Cl⁻(0.1 M)/Hg₂Cl₂/Hg



(iii) $E_{cell}^0 = E_C^0 - E_A^0 = 0.281 - 0.153 = 0.128 \text{ V}$

$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log \left[\frac{([Cl^-]^2 [Cu^{2+}]^2)}{([Cu^+]^2)} \right]$$

$$E_{cell} = 0.1362 \text{ V}$$

$$E = E_{cell}^0 - \frac{0.0591}{2} \log \frac{0.58^2 \times 0.1^2}{0.08^2}$$

ENGINEERING CHEMISTRY

Module 4 – Electrochemical Equilibria

7. For the following cell:



- i. Write the half cell reactions.
- ii. Calculate E_{cell}° and E_{cell} at 298K .

(Given $E_{\text{Au}^{+3}/\text{Au}}^{\circ} = 1.52\text{V}$, $E_{\text{Fe}^{+2}/\text{Fe}}^{\circ} = -0.44\text{V}$, $R = 8.314 \text{ J/K/mol}$, $F = 96500\text{C/mol}$)

Sol. i) Half cell reactions



(ii) $E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 1.52 + 0.44 = 1.96 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \left[\frac{[\text{Fe}^{+2}]^3}{[\text{Au}^{+3}]^2} \right]$$

$$E_{\text{cell}} = 1.96 - \frac{0.0591}{6} \log \left[\frac{[0.1]^3}{[0.5]^2} \right]$$

$$E_{\text{cell}} = 1.9836 \text{ V}$$

ENGINEERING CHEMISTRY

Module 4 – Electrochemical Equilibria

8. A glass electrode is coupled with saturated calomel electrode to measure unknown pH. The cell potentials measured are 0.215V and 0.385V in contact with a solution of pH = 7 and with solution of unknown pH respectively. Calculate the pH of unknown solution.

Given $E_{SCE} = 0.244\text{V}$

Sol.
$$\begin{aligned} E_G^0 &= E_{cell} + 0.0591\text{pH} + E_{SCE} \\ &= 0.215 + 0.0591 \times 7 + 0.244 \\ &= 0.8727 \text{ V} \end{aligned}$$

$$pH = \frac{E_G^0 - E_{SCE} - E_{cell}}{0.0591}$$

$$pH = \frac{0.8727 - 0.244 - 0.385}{0.0591}$$

$$\text{pH} = 4.12$$