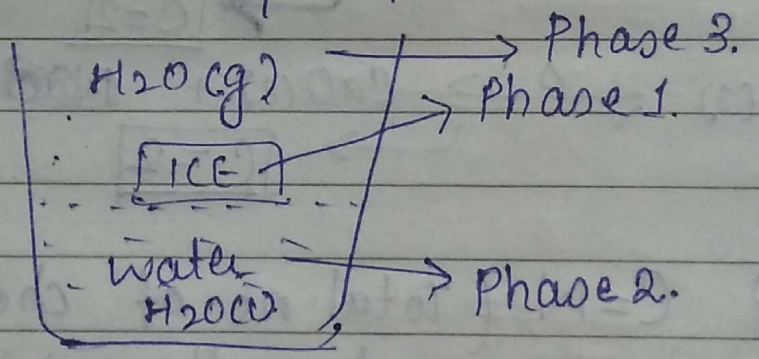
Physical Chemistry - D.1 . H.P. Kalyek.

(i) Phase Equilibria
(ii) Corroision and its Control.
(iii) Electrochemistry.

PHASE EQUILIBRIA

Phase: Any homogeneous part ~~of~~ & physically distinct part of a system with definite boundary as well as mechanically seperable.



Examples:- ① A mixture of N_2 and H_2.
$P = 1$

② Aqueous Solution Nacl. $P = 1$
③ Mixture of cely and H_2O. $P = 2$
④ $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. $P = 3$
(As 2 solids cannot give homo. mix)

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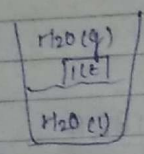
Component : Minimum number of chemical constituents required to define a system Completely



No. of component = 1 : H_2O

Examples:- 1. Aqueous Solution of Sugar
$C=2$

2. Aq. sol^n of Nacl : $C=2$

3. $Mn(NO_3)_2 \cdot 6H_2O \xrightleftharpoons{\Delta} Mn(NO_3)_2 \cdot 4H_2O + 2H_2O$
$\rightarrow \boxed{C=2}$

4. $CaCO_3(s) \xrightleftharpoons{\Delta} CaO(s) + CO_2(g)$
$\rightarrow \boxed{C=2}$

① $C=N$ (Total no. of chemicals) when there is no rekn.

② $C=N-R$ (No. of rek^n)

③ $C=N-R-1$ (Reaction with Ionic Species)

Eg:* Aqueous Solution of Nacl

$NaCl \rightleftharpoons Na^{\oplus} + Cl^{\ominus}$

$C = 4-1-1$
$= 2$

Eg: Aq. sol^n of Nacl and Kcl.
$P=1$

$C = 4-2-1 = 1$

$NaCl \rightleftharpoons Na^+ + Cl^{\ominus}$
$KCl \rightleftharpoons K^{\oplus} + Cl^{\ominus}$

Degree of Freedom:- Number of (Temp, press & composition) independent variables required to define a system completely.

① $H_2O(l) \rightleftharpoons H_2O(s) \rightleftharpoons H_2O(g)$

$P=3$
$C=1$
$F=0$ (Temp & press change can disturb the equilib or system)

No meaning of composition for this system. (100% H_2O).

$\therefore F=0$ (Thus invariant system).

② $H_2O(l) \rightleftharpoons H_2O(s)$
$F=1$ (mono-variant)
we can change either temp. or press. at a time so that other will adjust accordingly.

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F=2 – Bivariant

Gibb's Phase Rule:-

$$\boxed{F = C - P + 2}$$

* $H_2O(l) \rightleftharpoons H_2O(s) \rightleftharpoons H_2O(v)$
  $P=3 \quad C=1$

Now From Gibb's Phase Rule:-
$F = 1-3+2$
$= 0$ (Invariant).

* $H_2O(l) \rightleftharpoons H_2O(v)$.
  $F = C-P+2 = 1-2+2 = 1$.

$F = C-P+2$
$P=2$
$C=1$

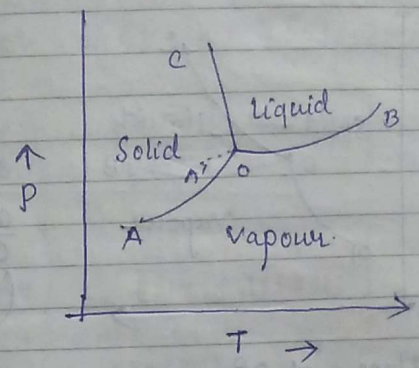
* $H_2O(l) \rightleftharpoons H_2O(v)$
  at constant pressure
  $F=0$

Phase Diagrams-

1. One component System
   H_2O, CO_2, S

2. Two Component System
   Pb-Ag, Bi-Cd

(1) Phase Diagram for H_2O



$F = C-P+2$
$= 1-1+2$ (P min).
$= 2$ (F max)

$F = C-P+2$
$= 1-3+2$ (P max)
$= 0$ (F min)

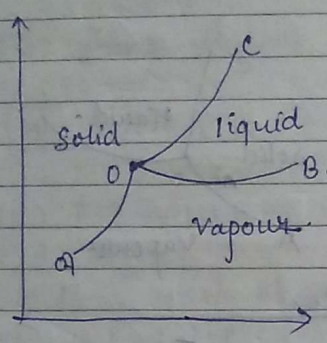
and composition does not vary so we have chosen P and T ~~curve~~ plot.

OA : solid $\rightleftharpoons$ vapour ; Sublimation Curve.
OB : liquid $\rightleftharpoons$ vapour ; Vapour pressure.
OC : solid $\rightleftharpoons$ liquid ; fusion curve.
O : Triple point.
OA' : meta stable state of $H_2O(l)$
super cooled liquid.

Slope OC : $\frac{dP}{dT} = \frac{\Delta H_{fust}}{T(V_l - V_s)} = -ve \quad (V_l < V_s)$
$V_f - V_i$

Clausius-Clapeyron equation

For CO_2:-



slope of OC

$\frac{dP}{dT} = +ve$

$(V_L > V_S)$

Slope of OB.

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_L)} = +ve \quad (\because V_g \gg V_L)$$

$$= \frac{\Delta H_{vap}}{TV_g} \quad (V_g \gg\gg V_L)$$

$$\frac{dP}{dT} = \frac{\Delta H_{vap}(P)}{TRT} \quad (\because \text{ideal gas } PV = RT)$$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln(P_2 - P_1) = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_2}\right]$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Eg:- Vapour pressure of H_2O at 95°c is 634 mm Hg and what is the pressure at 110°c. ($\Delta H_{vap} = 40593\ J\,mol^{-1}$).

Sol:- $$\ln\left(\frac{P_2}{634}\right) = \frac{40593}{8.314}\left[\frac{1}{368} - \frac{1}{383}\right]$$

$$\ln\left(\frac{P_2}{634}\right) = \frac{40593}{8.314}\left[\frac{15}{368 \times 383}\right]$$

$$= 0.403252$$

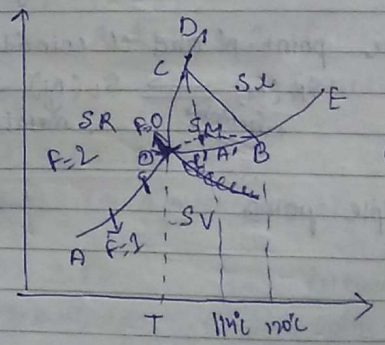
$P_2 = 1066$ mm of Hg.

Sulpher (I) Rhombic (II) Monoclinic

allotropy

Phenomenon of existance of element in diff. crystalline form.

(I) Enantiotrophy (Reversible) (II) Monotropy. (Unidirectional)



OC' - Metalstable state of SR.

OA : $S_R \rightleftharpoons S_V$: Sublimation Curve of S_R
OB : $S_M \rightleftharpoons S_V$: " " of S_M
BE : $S_L \rightleftharpoons S_V$: vapour pressure Curve.
OC : $S_R \rightleftharpoons S_M$: Transition curve.
CD : $S_M \rightleftharpoons S_L$: fusion Curve of S_M.
BA' : Meta stable state of S_L (due to cooling)
(It can have liq. form below its freezing point but if u disturb it will convert into its stable form)
(Super cooled liq.).

Transition temp = 95.6°C.

If the temp is higher than transition temp. (i.e 95.6°C) and we place rhombic sulpher at high temp. (say 100°C), then b/c sulpher will slowly changes to monoclinic, and that will be the metastable state of S_R (due to heating)

If the point A' and C' coincide. then :-
$S_R(M) \rightleftharpoons S_L(M) \rightleftharpoons S(V)$
metastable metalstable.

4 triple points.

Two Component System :-
(1) Solid-Solid (Pb-Ag, Bi-Cd)

$F = C - P + 2$
$= 2 - P + 2$
$= 4 - P$
$= 4 - 1 = 3$ (max)

So three independent variable req. to plot the diagram.
So to plot we will fix pressure (const)
At const pressure.
$F = C - P + 2 - 1$
Because 1 variable is constant,, C-P.

$F = C - P + 1$
Reduced Phase Rule

C-P+2 when C-P+2-1 then C-P+1 2 Temp & composition

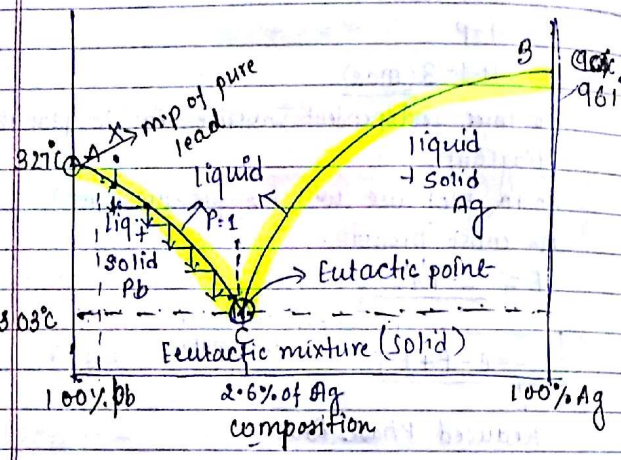
For 2 component System :-
Solid – Solid
$F = C - P + 1$
$= 2 - 1 + 1 = 2$ (need 2-axis)
Temperature & composition

Solid - Solid System :-
Pb-Ag (1) system must be Eutectic
means when you mix one solid into another the melting point of substance will dec. as compared to pure form.

100% → Pb.
90% Pb + 10% Ag
m.p dec.

(ii) Liquid obtained from solid mixture is homogeneous (miscible) : $\boxed{P=1}$

(i) and (ii) are assumptions.



AC : represents melting point curve of Pb
BC : represents melting point curve of Ag.

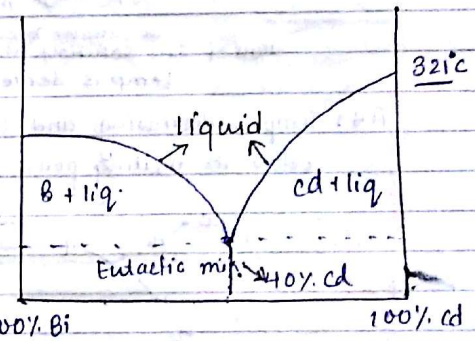
Eutactic mix :- what-ever the liq mixture gets solidify.

At E.P ⇒ F = C - P + 1
= 2 - 3 + 1 = 0
(2 solid + liq)

Pattinson's Process:-

Argeniferous lead (0.1% Ag also) and heat below the melting point the all the lead will convert into liq. & when it will cool down the lead (s) is removed
∴ thus % of Ag will ins. from 0.1% to 2.6% Ag

Bi-cd :-



Solid-liquid system :-
K-I-H_2O
(i) Solid KI (iii) Ice
(ii) KI solution (iv) Vapour
↳ at constant pressure this system is called condensed system.

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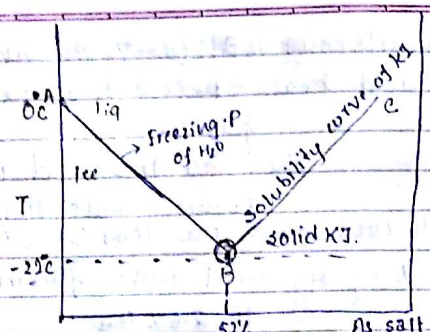
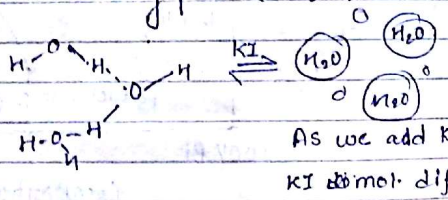
12/09/18 Jyoti Jha



% KI → As salt is added the ice melts and forms salt solution, melting of ice and formation of salt solution absorb some heat, thus temp is decreasing.

AB → Temp is decreasing and ice is melting below its melting point (why??)

ICE :-



As we add KI KI mol. diffuse into water molecule, thus stops the H-bond formation

⇒ when salt is added this (having lattice energy) so it will take some energy to ~~break~~ overcome its lattice energy so temp is dec.

At B → Saturated Solution. (Eutectic Point).
Now T↑
∴ BC → Solubility Curve of KI.

cryohydric point

Page No. Date: / /

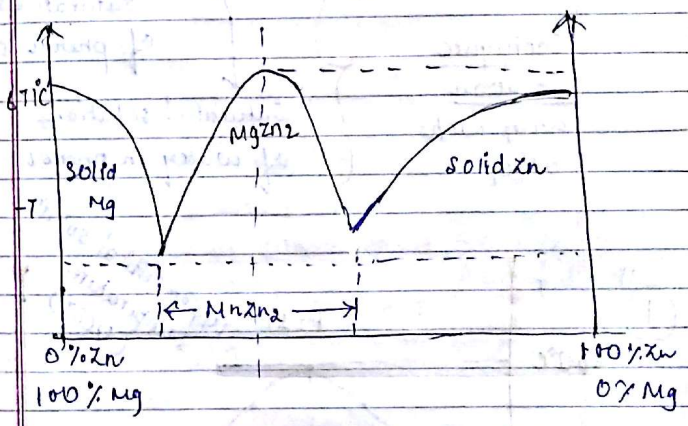
Eutectic temp

$NH_4Cl + Ice \rightarrow -16°C$

$NaCl + Ice \rightarrow -22°C$

$KCl + Ice \rightarrow -11.4°C$

Eutectic mix : 52% KI.



26 September

Partially Miscible Liquid-Liquid System

Eg :- H_2O - Phenol, when dissolved in smaller amount its gets completely miscible (P=1)
but when added in excess amount (P=2) → partially miscible.

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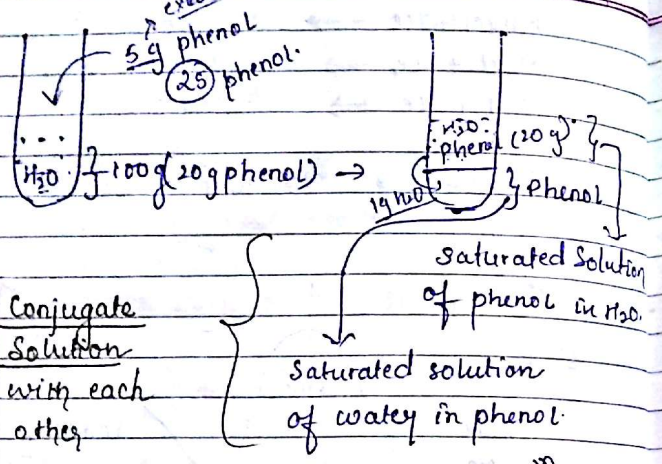
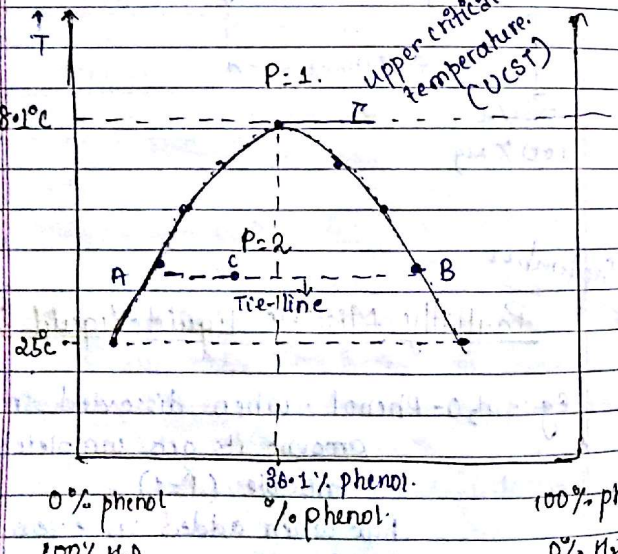


Conjugate Solution with each other

(1)



when T↑ solubility ↑

i.e T↑ % of phenol in H_2O inc.
and also % of H_2O in phenol also inc.

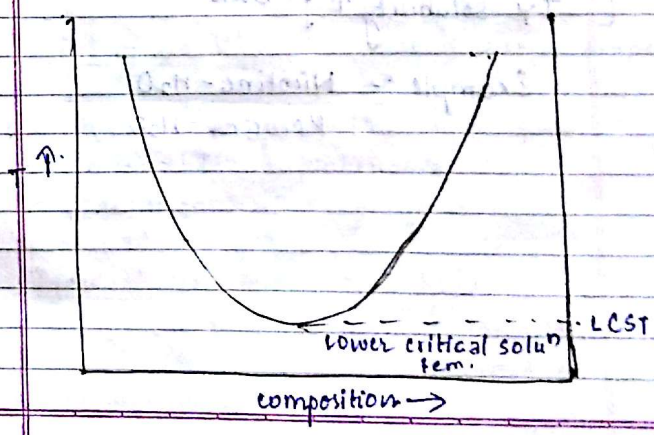
Using tie-line, ~~solution~~ calculation of composition b/w AB can be done.

Above UCST, P=1.
below UCST, P=2.

→ $\frac{\text{Mass of phase A}}{\text{mass of phase B}} = \frac{BC}{AC}$ (Lever Rule)

Examples: water-phenol
Analine-Hexane
$CH_3OH - CS_2$

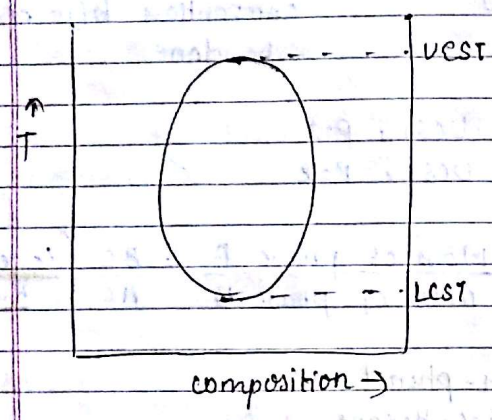
(2)



Example $Et_3N - H_2O$
$Et_2NH - H_2O$

In this case $T\uparrow$ solubility $\uparrow$

(3)



[$T\uparrow$ solubility $\uparrow$
$T\downarrow$ solubility $\uparrow$] → Both

Example :- Nicotine - H_2O
Picoline - H_2O.

2. Corrosion and its Control

Date: 3/10/16

The process of gradual deterioration of metal from its surface due to unwanted chemical reaction or electrochemical reaction.

Cause of corrosion: ore of metal (oxide, sulphide etc)
↓ Themodynamically stable.
↓ metallurgical operation + Energy.
Pure metal
(Thermodynamically unstable).
↓ Environment.
Corroded metal.

Effect of Corrosion:
1. Loss of useful properties of metal
2. Decrease in production rate
3. Increase in maintenance.
4. Contamination of product.

Types of Corrosion: Two types
(1) chemical or dry corrosion
(2) Electrochemical or wet corrosion.

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1. CHEMICAL OR DRY CORROSION

(a) Reaction with O_2 (oxygen)

$M + O_2 \longrightarrow$ metal oxide

layer of oxide

1. If the nature of metal oxide layer formed is stable, this will rotate the inside metal and further corrosion will not happen.

2. If unstable → goes back to pure form

3. If porous → oxygen passes through these pores and continues until metal oxide is corroded

4. If volatile → It will be formed and evaporates.

(b) Reaction with Cl_2 (other gas).

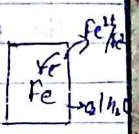
$Sn + Cl_2 \longrightarrow SnCl_2$ or $SnCl_4$
(solid) (liquid) (volatile)

If $SnCl_2$ → characteristics will be as of O_2

If $SnCl_4$ → It will evaporate till all Sn corrode

(c) Liquid - metal corrosion :- when liq. metal is flowing over solid metal, some of solid metal is dissolve in the liq. metal.

2. ELECTROCHEMICAL CORROSION



In Fe plate → one atom oxidises ($Fe \rightarrow Fe^{2+}/Fe^{3+}$) and it release some e^-s in the Fe plate. These e^-s go to the e^- acceptor (O_2 / H_2O) in environment. The overall reaction is oxidation - reduction reaction. Thus formation of a galvanic cell (cathode-anode cell). & due to this electrochemical corrosion takes place.

At Anode :- $Fe \longrightarrow Fe^{2+}/Fe^{3+} + xe^-$
corrosion

or

$M \longrightarrow M^{n+} + ne^-$

At cathode : (A) In presence of oxygen

(i) In acidic medium : $4H^+ + O_2 + 4e \rightarrow 2H_2O$

(ii) In ~~basic~~ neutral medium : $2H_2O + O_2 + 4e \rightarrow 4OH^-$

(B) In absence of oxygen :

(i) In acidic medium : $2H^+ + 2e \rightarrow H_2$

(ii) In neutral medium : $2H_2O + 2e \rightarrow H_2 + 2OH^-$

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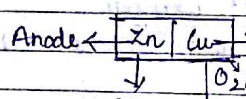
	Chemical	Electrochemical
(a)	In absence of water (Dry)	a) In presence of water (wet)
(b)	Direct reaction with chemical from environment.	b) Formation of large no. of galvanic cell.
(c)	Slow	(c) Fast.
(d)	Uniform	(d) Non-Uniform

Types of Electrochemical Corrosion:-

1) Galvanic Corrosion

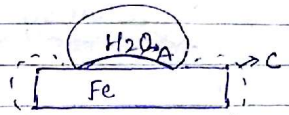
Driving force for cathode-anode formation is :- electron acceptor



$Zn^{2+} + 2e^-$ → undergoes corrosion.

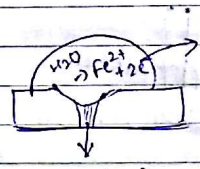
Cu plate will act as cathode but it will not reduce and nothing will happen to Cu.

2) Pitting Corrosion



If the amount of O_2 diffusing of Fe surface is known two surface can be seperated. one part is more exposed to O_2 and other is less exposed to O_2

where accessibility of O_2 is more → Cathode
" " " O_2 is less → Anode



$Fe(OH)_2$ → Fe_2O_3 / Fe_3O_4

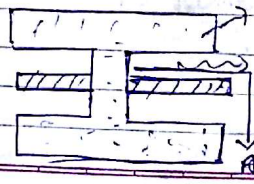
Hole formation after corrosion.

At Anode : $Fe \longrightarrow Fe^{2+} + 2e$

At Cathode : $\frac{1}{2}O_2 + H_2O + 2e \longrightarrow 2OH^{\ominus}$

$Fe^{2+} + 2OH^{\ominus} \longrightarrow Fe(OH)_2 \longrightarrow$

(3) Crevise Corrosion

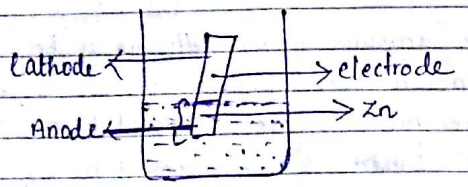


External part cathode.

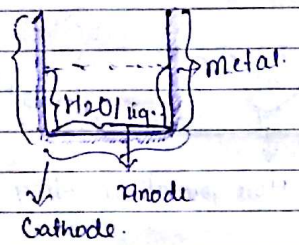
narrow gap. crevise position

Anode

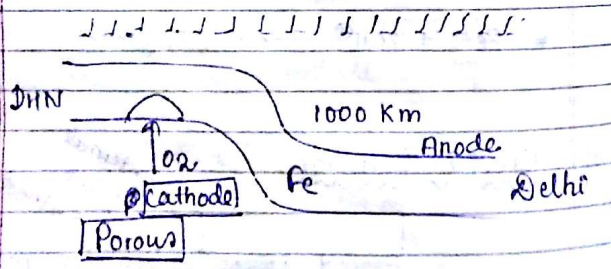
4. Concentration Cell Corrosion:



5. Water-line Corrosion



6. Soil-Corrosion



7. Microbiological Corrosion

Microbiological bacteria release some chemical that decompose the material.

Factors Influencing Corrosion:

Nature of Metal	Nature of Enviroment
1. Purity of Metal	1. Temperature
2. Nature of Oxide film	2. Humidity
3. Position in Galvanic Series.	3 Effect of PH.
4. Relative areas of Cathode and Anode	

1. 99% Zn, 1% Cu → High corrosion rate.

2. 99% Zn, 1% ZnO → Low corrosion rate

compare with 100% Zn

If area of anode > area of cathode corrosion will be ~~High~~ low.

Area		Area
low ←	Anode →	High
High ←	Cathode →	low
corrosion High		corrosion low

Because when e⁻s acceptor area will be more than more oxidation will take place and corrosion will be high.

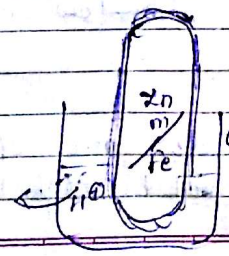
If Temperature increase → more oxidation i.e more corrosion

Humidity ↑ corrosion ↑.

PH low → corrosion ↑
High → corrosion rate lex.

Corrosion Control.

1. Corrosion Inhibitor : chemical substance when added to the corrosion medium it reduces the corrosion.



amines / Thiols.
Et_3N ⇝ lone pair will attack on metallic plate but not metal ions

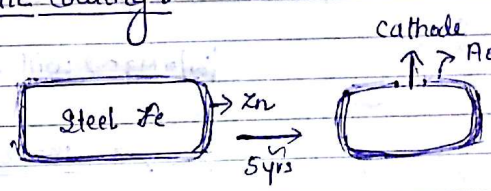
$Et_3NH^{\oplus}$ ⇝ will not not allow the electron acceptor to attack to the metal.

$\underbrace{Et_3N,\ Et_2NH,\ EtNH_2}$

which is more basic to reduce the rate of corrosion ??

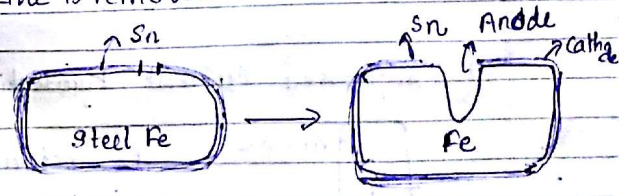
2. metallic Coating :

Anodic coating →



If some hole formation or crack forms when most of the zinc has gone. steel part will be acting as cathode & zinc coating acting as anode, but oxidation or corrosion doesnot happens to cathode thus no corrosion until all zinc is removed.

cathodic coating →



Anodic Coating is the best method to control corrosion.

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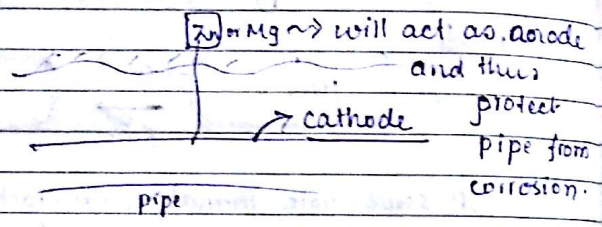
3. Inorganic Coating :

Metal is coated with metal phosphate, chromate etc.

4. Organic Coating : Painting

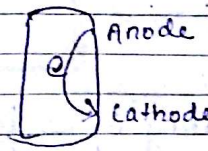
5. Electrochemical Protection

i) Sacrificial anodic protection.



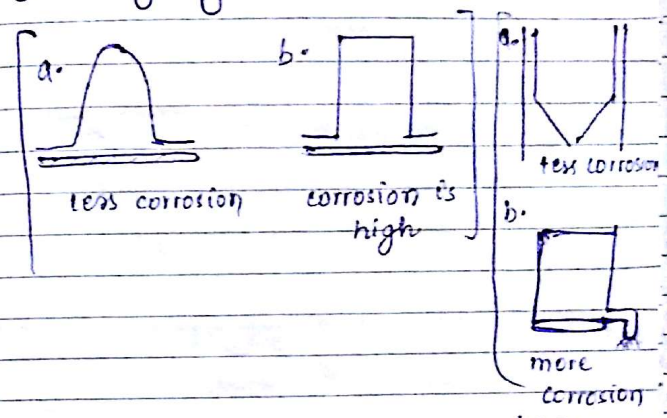
If we will not connect Zn one part of pipe will act as anode & other part of pipe will act as anode thus pipe will be corroded.

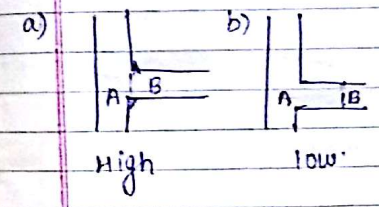
ii) Impressed Current Protection.



If electricity is passed in the opp. direction to that of the current flow in the metal than both will nullify then no current thus no corrosion.

6. By Designing





Example of crevice corrosion.
The gap is there in 1st case.

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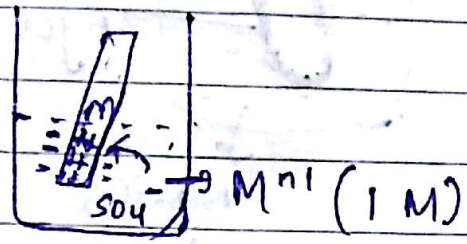
Electrochemistry

Page No.
Date: / /

1. Electrode :-



at 25°c

If you dip a pure metal in one molar concentration of corresponding solution at 25°C, you can make one electrode. Either oxidation or reduction will take place on this electrode.

Say positive charge develop on the surface of electrode then -ve charge will develop diffuse on the outer surface of electrode & the potential diff. between these two charge layer is called electrode potential.

SHE is used to measure pot. diff.

Types of Electrode:-

1. Metal - metal ion electrode

2. Metal - Metal Insoluble salt electrode.

Eg:- Ag → deposited with AgCl (layer) & dipped in $AgNO_3$ solution.

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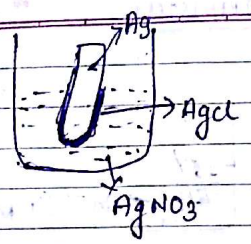
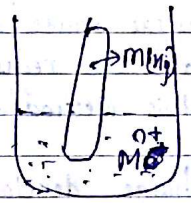


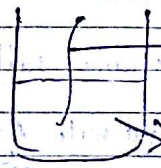
3. Metal-Amalgam Electrode



4. Gas-Ion Electrode

Eg:- Hydrogen Electrode :- Pt wire is dipped in 1molar acidic (H^+) solu^n. and hydrogen gas is passed.

5. Redox Electrode



solu^n that exist in more than 1 oxidation st.

Eg:- (Fe^{2+}/Fe^{3+} or Mn^{2+}/Mn^{3+})

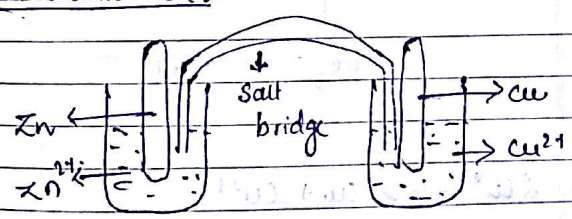
Electrochemical cell:- Two types:-

(I) Galvanic cell → converts chemical energy to Electrical energy

(II) Electrolytic cell → converts Electrical energy to chemical energy.

Battery of mobile → have both Galvanic & electrolytic cell.

Galvanic Cell:-



$\underbrace{Zn|Zn^{2+}}_{Anode} || \underbrace{Cu^{2+}|Cu}_{cathode}$

$E_{cell} = E_{cathode} - E_{anode}$.

$\Delta G = -nFE$

$\Delta G = -RT \ln K_{eq}$.

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Q. $E_{Ag^+/Ag} = 0.80\,V$ $\quad T = 25°C$
$E_{Cu^{2+}/Cu} = 0.34\,V$

Calculate Keq.

$-nFE = -RT \ln K_{eq}$

$Cu|Cu^{2+} \,||\, Ag^+|Ag$

$E_{cell} = E_c - E_a = 0.80 - 0.34 = 0.46$

Now,

$-2(96500)(0.46) = -(8.314)(298) \ln K_{eq}$

$\ln K_{eq} = 35.83$

$K_{eq} = 3.648 \times 10^{15}$

Q. $2Cu^{\oplus} \longrightarrow Cu + Cu^{2+}$

$E°_{Cu^+/Cu} = 0.52\,V$ → Cathode

$E°_{Cu^{2+}/Cu^+} = 0.16\,V$ → Anode $K_{eq} = ?$

$E_{cell} = 0.52 - 0.16\,V = 0.36\,V$

Now $-2(96500)(0.36) = -(8.314)(298) \ln K_{eq}$

$\ln K_{eq} = 14.022$

$K_{eq} = 1.2 \times 10^6$

Refrence Electrode.

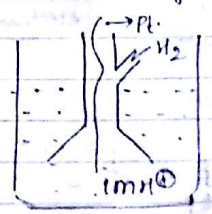
1) Primary Refrence Electrode.
ii) Secondary Refrence Electrode.

For Primary ref. electrode the potential is ~~zero~~ taken as zero

Sec. Ref electrode which is taken as reference but potential is known & not zero.

Example:- i) Hydrogen Electrode (Primary)
ii) Calomel electrode (Secondary)
iii) Ag-AgCl electrode. (")
iv) Glass-Ion electrode (")

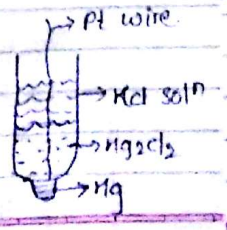
→ Construction of Hydrogen electrode:-



Read in Detail

Construction of Calomel Electrode & Glass-Ion Electrode

Calomel Electrode



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Cathode:

$$\frac{1}{2} Hg_2Cl_2(s) + e \rightleftharpoons Hg + Cl^{\ominus}$$

$$E = E^{\circ} - \frac{RT}{F} \ln a_{Cl^{\ominus}}$$

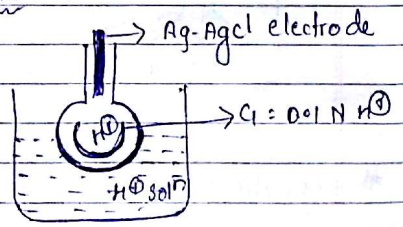
affinity of $Cl^{\ominus}$

(affinity of Hg = 1)

When the conc. or affinity of $Cl^{\ominus}$ decrease the potential inc.

[KCl]	Saturated	Calomel Electrode	
		1.0 N	0.1 N
E(volt)	0.2422	0.2810	0.3335
	Saturated Calomel electrode	Normal Calomel electrode	Decinormal Calomel electrode

Glass Electrode



To find of conc. of $H^{\oplus}$ soln we have glass electrode & inside the glass electrode we have same ion inside the bulb.

Say to measure $Na^{\oplus}$ ion conc. we should $Na^{\oplus}$ of known conc inside the bulb of Glass electrode.

A potential diff. at the boundary, Pot. will be generated.

E_b = boundary potential.

Inside bulb $H^{\oplus}$ conc = C_1
outside $H^{\oplus}$ conc = C_2

Inside boundary Potential = E_1
Outside " " = E_2

$$E_b = E_1 - E_2$$

Nernst Eqn :-

$$E_b = E_1 - E_2$$

$$= \left(E^{\circ} - \frac{RT}{nF} \ln C_1\right) - \left(E^{\circ} - \frac{RT}{nF} \ln C_2\right)$$

$$E_b = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

$E_b = 0$ (If $C_1 = C_2$) → But there exp. it is not zero & the value obtained is called assymetric potential

$$E_{G_1} = E_b + \underbrace{E_{Ag\text{-}AgCl} + E_{Assy.}}_{\text{const.}}$$

(E_{G_1} → E_{Glass})

$$= \frac{RT}{nF} \ln \frac{C_2}{C_1} + \text{constant}$$

(C_1 → ratio const)

$$= \frac{RT}{nF} \ln C_2 + K$$

(K → new const.)

Page No.
Date: | |

$$E_{Cl} = \frac{2.303 \times 8.314 \times 298}{1 \times 96500} \left(-\ln pH^{+}\right) + K$$

$$= -0.591\, pH + E^{0}_{Cl}$$

$$\boxed{E = E^{0}_{Cl} - 0.059\, pH}$$

Q Cons or working Principle of ~~Calomel~~ one of the secondary eletrode.

Electrochem:- 34 marks.

1 Q of 12 marks.
2 Q of 11 (out of three)
34

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