

Aug, 2016

Water Technology

• Impurities :

- (1) Dissolved : Salts : Na, K, Ca, Mg salts, Gases : SO_x , NO_x , CO_2
- (2) Suspended : Organic - Animal & Vegetable Matter
Inorganic - Clay, Silica
- (3) Colloidal : Trace metals, Organic, colour dye.
- (4) MicroOrganisms : Bacteria ... etc.

Water Quality Parameters :

- (i) PH
- (ii) Water Conductivity
- (iii) Hardness
- (iv) Alkalinity
- (v) Dissolved Oxygen (DO)
- (vi) Chemical Oxygen Demand (COD)
- (vii) Biological Oxygen Demand (BOD)
- (viii) Trace metals.
- (9) Total Solids
- (10) Chlorides
- (11) Silica

P.T.O.

Hardness

- Cl^- , SO_4^{2-} of Ca^{2+} and Mg^{2+} cause permanent hardness
- HCO_3^- of Ca^{2+} , Mg^{2+} cause temporary hardness.



CaCO_3 equivalents :

1 gm mole of CaCl_2 = 1 gm mole of CaCO_3

111 g of CaCl_2 = 100 g of CaCO_3

55 g of CaCl_2 = 50 g of CaCO_3

$x \text{ g} = \frac{50}{55.5} \times x \text{ g CaCO}_3$

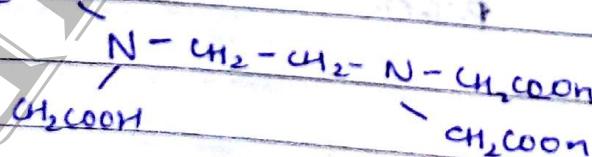
NaClO_3 equivalents = $\frac{\text{Mass of salt} \times \text{Eq. wt of } \text{CaCO}_3}{\text{Eq. wt of salt}}$

4th Aug, 16

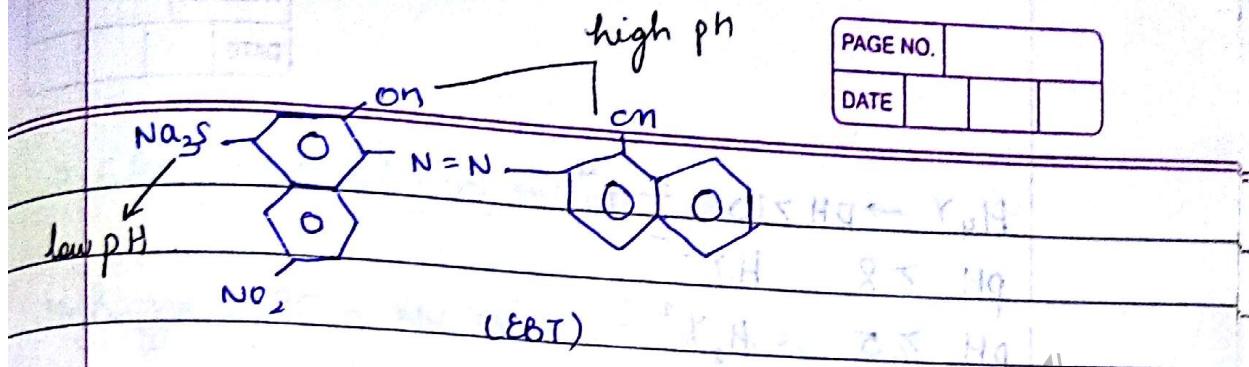
Determination of Hardness

(1) Titration Method :

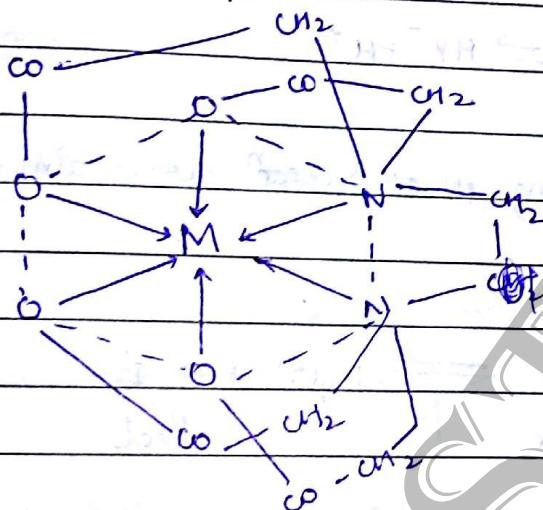
EDTA : Ethylene diamine tetraacetate



Indicator : EBT (Eriochrome Black T)

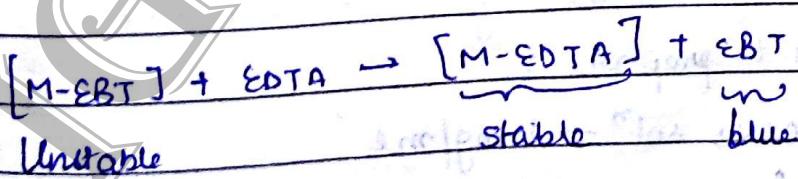
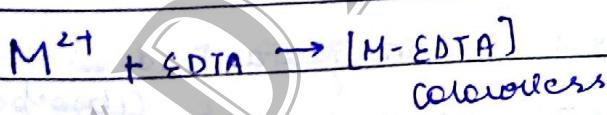
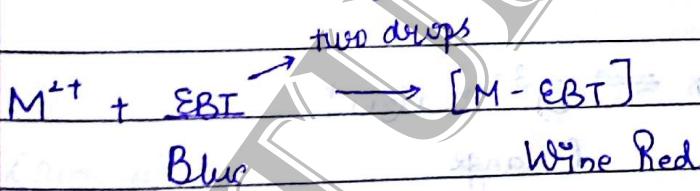


Metal EDTA complex:

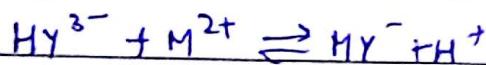
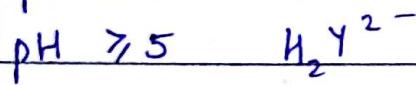
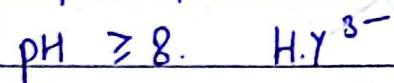
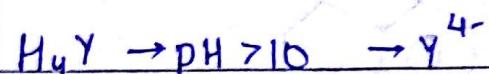


EBT solution is made in alcohol

Unionsed state of EBT is black

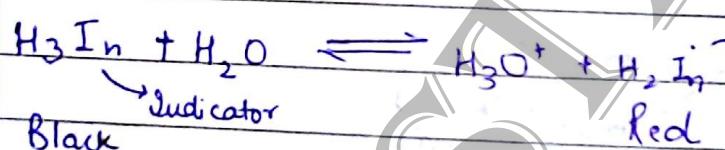


No, Colour Change: Wine Red to Blue.



for maintaining pH at 8 meacⁿ, we maintain a buffer solⁿ.

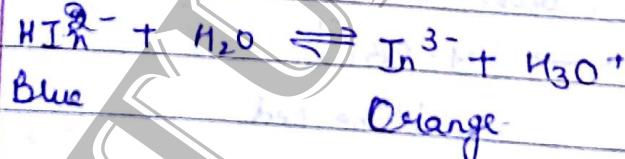
pH < 6



pH > 8



pH > 10



Note: Naon doesn't form primary standard
 $\Rightarrow \left. \begin{array}{l} \text{deliquescent} \\ \text{Absorbs water} \end{array} \right\}$

Solution to prepare :

1. Std. Naon solⁿ \rightarrow 1 mg/me
 for 100 ml \rightarrow 1 g/l

dissolve in dil HCl

(Strength: 0.01 M)

2. EDTA (0.01 M) \rightarrow 3.72 gm/l

3. EBT \rightarrow 0.5 g / 100 ml alcohol

4. Buffer : 70 g NH_4Cl + 570 ml NH_3
 $\xrightarrow{\text{DD}}$ 100 ml distilled water
 $\xrightarrow{\text{(DW)}}$

Titration

1. 10 ml std. CaCO_3 + 10 ml buffer

\downarrow
 V_1 ml EDTA
 \downarrow
+ EBT

3 concordant reading.

2. 10 ml water sample \rightarrow V_2 ml EDTA

\downarrow
Total hardness

3. 10 ml boiled & filtered water

\downarrow
Permanent hardness

Calculations

1) 10 ml of CaCO_3 = 10 mg CaCO_3 = V_1 ml EDTA.

V_1 ml EDTA \equiv 10 mg CaCO_3 .

EDTA (per ml) $= \frac{10}{V_1}$ (CaCO_3)

(2) 1 ml EDTA = $\frac{10}{V_1}$ CaCO_3 .

V_2 ml EDTA $\cdot \frac{10}{V_1}$ CaCO_3

EDTA (per ml) $= \frac{10 \times V_2}{V_1} \text{ CaCO}_3$

$$10 \text{ ml of pond water} = \frac{10 \times V_2}{V_1} \text{ mg/L CaCO}_3 \text{ (sample)}$$

$$1000 \text{ ml sample} = \frac{10 \times V_2}{V_1} \times 1000 \text{ mg/L CaCO}_3$$

$$\text{Total Hardness} = \frac{1000 \times V_2}{V_1} \text{ ppm.}$$

$$\text{Permanent} = \frac{V_3}{V_1} \times 1000 \text{ ppm.}$$

$$[1 \text{ mg/L} = \text{ppm}]$$

18/2/2016

Hardness

Temporary

(Bicarbonate)

→ simply boiling

→ CaCO_3 (insoluble)

permanent

(chlorides or sulphates)

Ques. A water sample has the following analysis:

Mg(HCO₃)₂ → 83 mg/L

Ca(HCO₃)₂ → 134

$\text{CaSO}_4 \rightarrow 124$

MgCl₂ → 84

CaCl₂ → 94

NaCl → 50.

(95)

{ 162 }

Calculate temporary & permanent hardness in degree Clark.

Ans. 1 mole of CaCO_3 = 1 mole of CaCl_2

1) 100
2) insoluble

100 g of CaCO_3 = 111 g of CaCl_2

$$x \text{ g of } \text{CaCl}_2 = \frac{100}{111} \times x \text{ g of } \text{CaCO}_3$$

Eq. of CaCO_3 : $\frac{\text{Mass of substance}}{\text{Molar Mass}} \times \text{Molar mass of } \text{CaCO}_3$

Multiplication factor

$\text{Mg}(\text{HCO}_3)_2$	83	56.84
$\text{Ca}(\text{HCO}_3)_2$	134	82.71
CaSO_4	124	91.17
MgCl_2	84	88.42
CaCl_2	94	84.68

Total temp. hardness = 139.55 mg/L

$$= 139.55 \text{ ppm}$$

$$1 \text{ ppm} = 0.07^\circ\text{C}$$

$$= 9.768^\circ\text{C}$$

Permanent hardness = 264.2 ppm

$$= 18.49^\circ\text{C}$$

Ques.) Calculate the total hardness of water sample

having following composition:

MgSO_4

2

CaSO_4

4

Fe_2O_3

0.04

MgCl_2

4

CaCO_3

20

SiO_2

0.09

°C

Ans.	MgSO ₄	4	3.33
	CaSO ₄	2	1.47
	Fe ₂ O ₃	0.04	0
	MgCl ₂	4	4.21
	CaCO ₃	20	18.81
	SiO ₂	0.09	0

Total hardness = $\frac{29.01}{2} \text{ °C}$

$$= 29.01$$

$$= 414.43 \text{ ppm}$$

Ques

1g of CaCO₃ is dissolved in dil. HCl and the solⁿ diluted to 1L, 100 ml of solⁿ required 90 ml of EDTA solⁿ. 100 ml of water sample required 40 ml of EDTA.

On the other hand, 100 ml of boiled sample consumed 20 ml of EDTA.

Calculate each type of hardness in ppm.

Ans

$$\text{EDTA per 1000 ml} = \frac{10 \times 100}{90} \text{ CaCO}_3$$

$$(1L) \quad 90$$

$$= \frac{100}{90} \text{ CaCO}_3$$

$$\text{EDTA reqd. by water sample} = \frac{10 \times 100}{90} \times 40 \text{ CaCO}_3$$

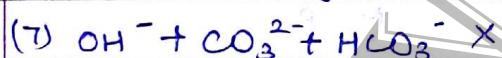
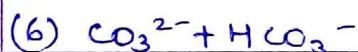
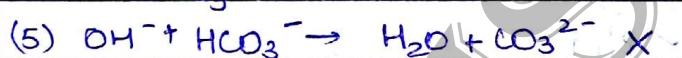
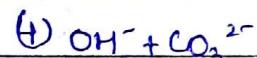
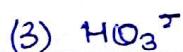
$$= 4,444.4 \text{ CaCO}_3$$

$$\text{Permanent Hardness} = \frac{20}{90} \times 1000 \text{ ppm}$$

$$\text{Temporary Hardness} = 22.22 \text{ ppm}$$

(2) Alkalinity

Caused due to OH^- , CO_3^{2-} , HCO_3^- of $\text{Na}, \text{K}, \text{Mg}, \text{Ca}$
"Capacity of water to neutralise acids"



Therefore we have only 5 possibilities.



Phenolphthalein

Methyl Orange

Phenolphthalein is weak acid.

P = Phenolphthalein Alkalinity.

$$\frac{1}{50} V_1 = N \times 10$$

Acid = Sample

$$N = \frac{V_1}{500}$$

$$P = V_1 \times 50 \text{ g/L}$$

\downarrow
500 OF V

strength of Phenolphthalein alkalinity

$$P = \frac{V_1 \times 1000 \text{ ng/L}}{10}$$

$$P = 100 V_1 \text{ ppm}$$

$$M = 100 V_2 \text{ ppm}$$

	OH^-	CO_3^{2-}	HCO_3^-
1) $P = 0$	X	X	$\checkmark M$
2) $P = M$	$\checkmark P/M$	X	$\checkmark 2P + X$
3) $P = 1/2 M$	X	\checkmark	$M = 2P$
4) $P < \frac{1}{2} M$	X	$\checkmark 2P$	$\checkmark M - 2P$
5) $P > \frac{1}{2} M$	$\checkmark 2P - M$	$\checkmark 2(M - P)$	X

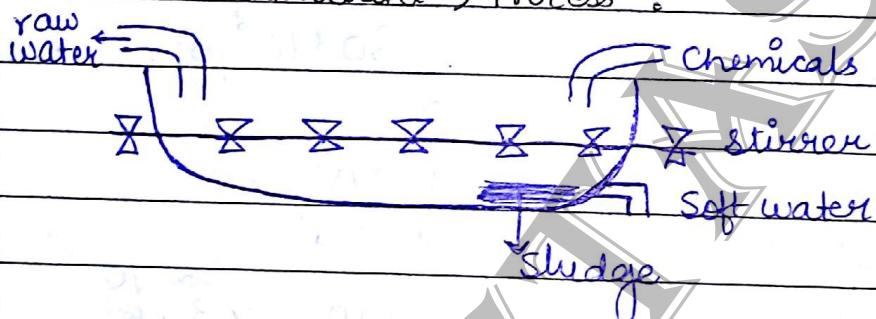
Types of Lime Soda Processes

1) Cold lime soda → Batch (Intermittent)
Process → Continuous.

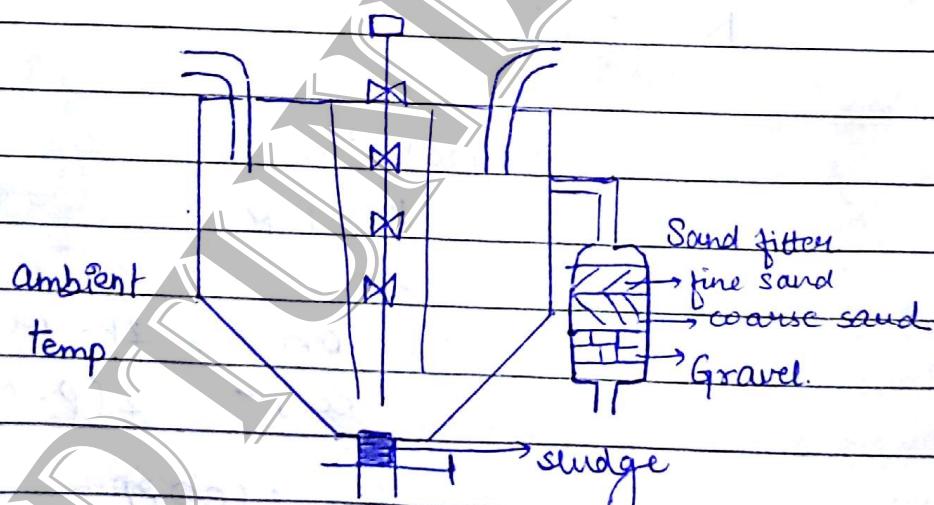
2) Hot lime soda Process : → a) Batch

→ b) Intermittent.

1)a) Batch (Intermittent) Process :



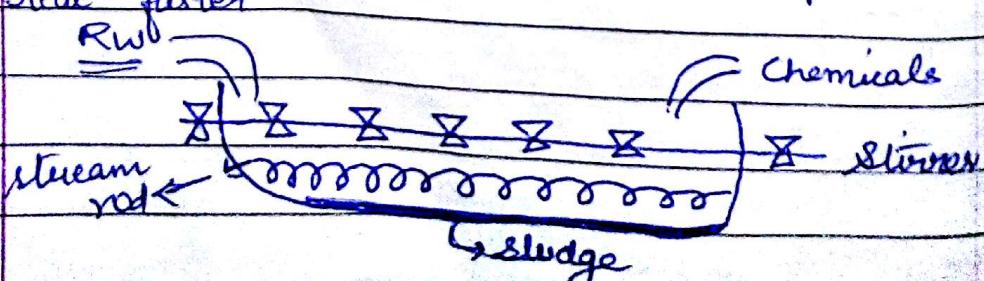
b) Continuous Process :



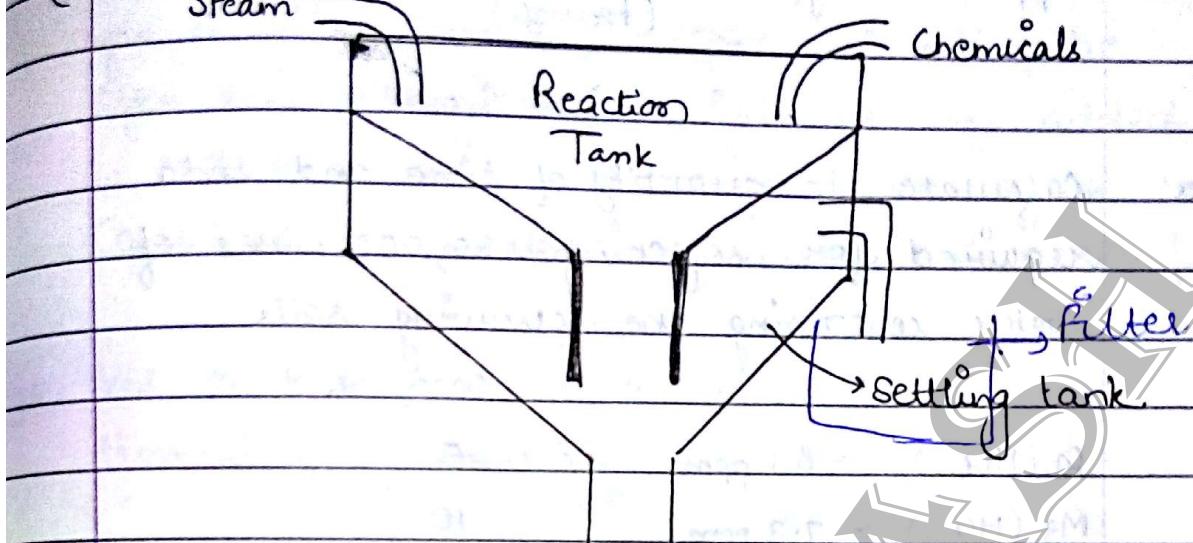
→ Coagulants needed in cold.

2)a) Hot (Batch)

Viscosity of water lowered on heating water.
Heat faster



(2) Hot (Continuous)



Within a uspan of 30 mins. soft water can be obtained
Sand filter.

Cold \rightarrow 10-15 ppm hardness remains.

Hot \rightarrow < 10 ppm hardness remains.

Disadvantages:

- 1. Lot of sludge is produced.
- 2. Not < 10 ppm hardness is removed.
- 3. Proper & skilled supervision is required.

Advantages

- 1. Prevents corrosion.
- 2. Becomes disinfectant in itself.

P.T.O.

Conversion of degree

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1 \text{ Fr} = 0.07^\circ \text{ C} \\ (\text{French}) \qquad \qquad \qquad \text{clark}$$

Ques.

Calculate the quantity of lime and soda required for softening 50,000 litres of water containing the following salts

CaCO₃ eq.

$$\text{Ca(HCO}_3\text{)}_2 = 8.1 \text{ ppm}$$

5

$$\text{Mg(HCO}_3\text{)}_2 = 7.3 \text{ ppm}$$

10

$$\text{CaO}_4 : 13.6 \text{ ppm}$$

10

$$\text{MgSO}_4 = 12 \text{ ppm}$$

2.1 10

$$\text{NaCl} \quad 4.7 \text{ ppm}$$

X

Ans

$$\text{lime reqd.} = \frac{74}{100} [5 + 2 \times 5 + 10 + 2.1] = 11.7$$

$$= 20.054 \text{ mg/L}$$

$$\text{for } 50,000 \text{ L} = 1002.7 \text{ kg/L}$$

$$= 1 \text{ kg}$$

$$\text{soda} = \frac{106}{100} [10 + 10 + 2.1]$$

$$= 1.2 \text{ kg}$$

Alkalinity

hydroxides and carbonates

(Crustic alkalinity)

Bicarbonates

(Bicarbonate Alkalinity)

Ques 100 ml of water sample reqd. 30 ml of N/50 H₂SO₄ for neutralisation to phenolphthalein end point.

After this methyl orange indicator was added to this & further acid required was again 30 ml
Calculate the alkalinity of water as Caco₃ in ppm.

Ans Vol. of water sample = 100 ml

Normality of acid = $\frac{N}{50}$

Volume of acid used = 30 ml

Normality eqⁿ:

Acid + Water

$$N_1 V_1 = N_2 V_2$$

$$\frac{N}{50} \times 30 = N_2 \times 100$$

$$N_1 = \frac{30 \cdot N}{5000}$$

Strength in terms of Caco₃:

N x gram eq.

$$= \frac{30}{5000} \times 50 \text{ g/L}$$

Strength = 0.3 g/L (Phenolphthalein end point)

$$\begin{aligned} P(\text{alkalinity}) &= 0.3 \text{ g/L} \\ &= 0.3 \times 1000 \text{ mg/L} \end{aligned}$$

$$P = 300 \text{ ppm}$$

Acid Water

$$\frac{N \times 60}{50} = N_2 \times 100$$

$$N_2 = \frac{60}{5000} N$$

$$\begin{aligned} M (\text{alkalinity}) &= 0.6 \text{ g/L} \\ &= 0.6 \times 1000 \text{ mg/L} \\ &= 600 \text{ ppm} \end{aligned}$$

$$P = \frac{M}{2}$$

CO_3^{2-} present

$$M \approx [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

$$P \approx [\text{OH}^-] + [\text{CO}_3^{2-}]$$

Alkalinity is due to the presence of
carbonate = $M = 600 \text{ ppm}$

Ques. A sample of water is alkaline both to phenolphthalein and methyl orange. 100 ml of this water sample require 20 ml of M/50 H_2SO_4 for phenolphthalein end point and another 15 ml for complete neutralisation calculate the type of alkalinity in ppm

Ans.

Acid

$$\frac{N \times 20}{50} = N_2 \times 100$$

Water

$$\frac{N \times 15}{50}$$

$$N_2 = \frac{2}{5000} N$$

$$\text{Strength} = \frac{20}{5000} \times 500 \text{ g/L}$$

$$P = 200 \text{ ppm}$$

Acid = Water

$$\frac{N}{50} \times 35 = N_3 \times 100$$

$$N_3 = \frac{35}{5000} N$$

$$\text{Strength} = 350 \text{ ppm}$$

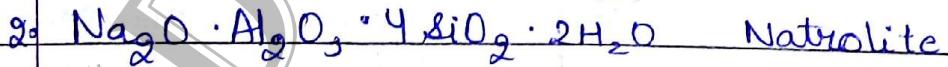
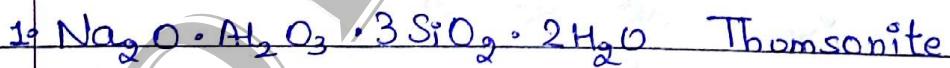
$$M = 150$$

$$2P > M$$

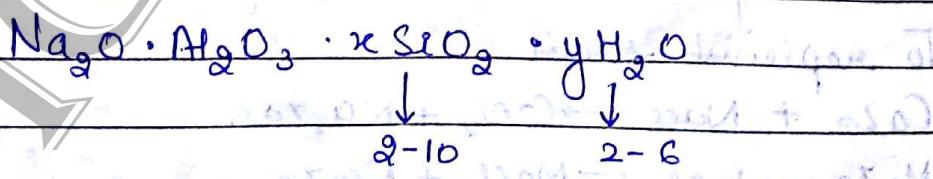
$$P > M/2$$

$$[CO_3^{2-}] = 300, [OH^-] = 50.$$

2. Base Exchange | zeolite | Permutit
 (Removal of cation) $\xrightarrow{\text{sodium aluminosilicate}}$

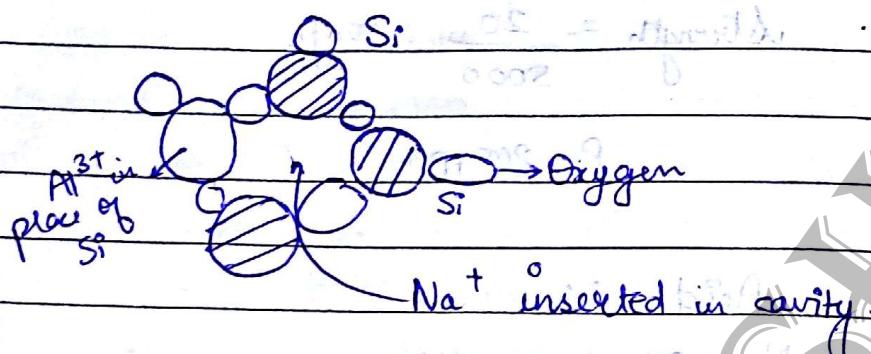


naturally available \Rightarrow Zeolite

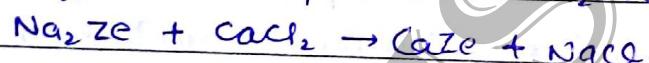
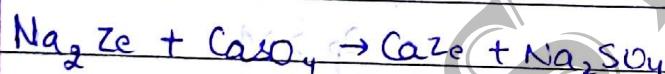
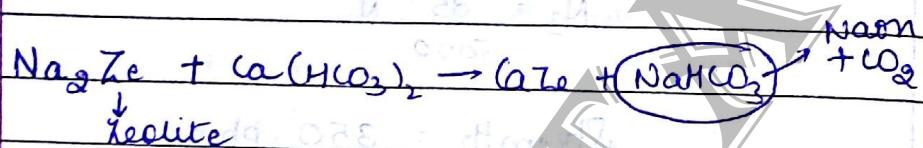


Synthetic Zeolites (Gel like) :

SiO_4 (Porous structure)



Synthetic: fluor spar, clay, sand,



hard
water

brine
soln

water

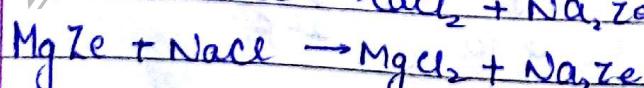
Resin

Gravel

soft water

Resin bed gets exhausted

To replenish resin



Advantages:

No sludge, Automated Process, Water of

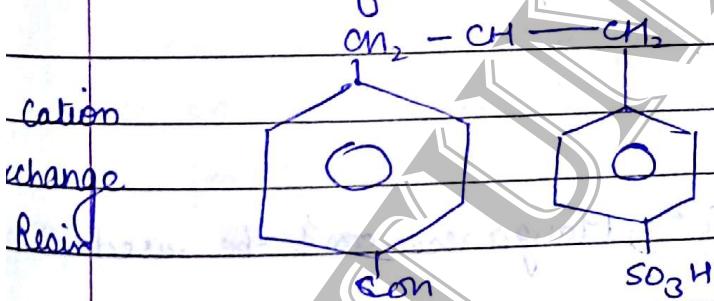
hardness 10-15 ppm is attainable, regular supply of soft water.

Disadvantages:

- Turbidity | Presence of Fe^{2+} , Mn^{2+} salt in water will deactivate resin
- Expensive
- Acidic / Alkaline water deteriorates resin bed.
- NaOH causes caustic embrittlement in water.
- CO_2 is corrosive

③ Demineralisation Process

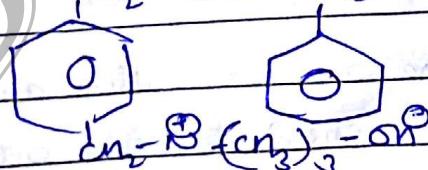
Removal of all cations and anions



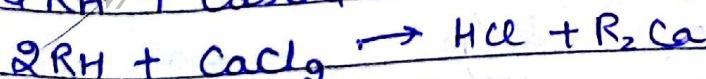
Ambertite IR 120 - Common name



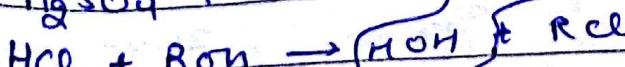
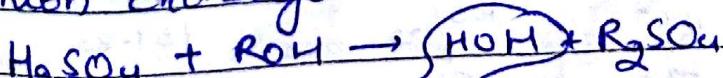
Anion resin.



Cation exchange resin

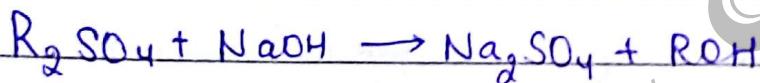
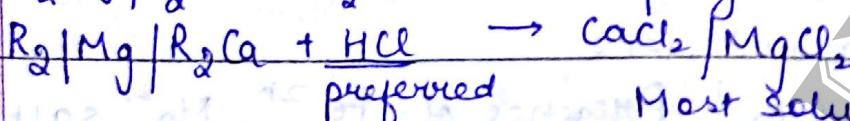
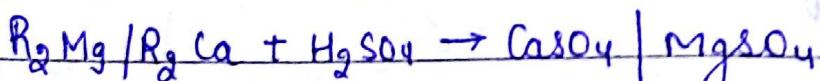


Anion Exchange Resin



Demineralised water

Regeneration of exhausted resins.



Advantages

- If carefully done, we can get 0 ppm hardness water.
- Compact process, no skilled operation needed.
- Water can be acidic/basic.

Disadvantages:

- expensive
- turbid / salts Fe^{2+} , Manganese can't be used.

Numericals :

Ques. Calculate the amount of lime and soda reqd. per litre for chemical treatment of water containing

Ca^{2+}	80	$100/40$	$CaCO_3$ eq. 19.8
Mg^{2+}	32	$100/24$	133.3
HCO_3^-	195	$100/122$	159.83
$FeSO_4 \cdot 7H_2O$	73.5	$100/278$	26.44

Ans Lime soda requirement

$$\text{Lime } \frac{\%}{100} [Mg^{2+} + HCO_3^- + FeSO_4 \cdot 7H_2O]$$

in terms of $CaCO_3$

$$= \frac{74}{100} [133.3 + 159.83 + 26.44]$$

$$= 236.46 \text{ ppm}$$

$$\text{Soda } = \frac{106}{100} [Ca^{2+}, Mg^{2+}, FeSO_4 \cdot 7H_2O - HCO_3^-]$$

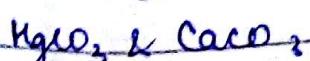
in terms of $CaCO_3$

$$= 811.04 \text{ ppm}$$

Ques calculate the amount of lime 74 %. pure and soda 92 %. pure required for softening 20,000 L of hard water containing

	(mg/L)	M	MF	equiv.
			$100/84$	<u>100</u>
$MgSO_4$	84	84		
$CaCO_3$	40	100	$100/100$	40
HCO_3^-	95	95	$100/95$	100
Cl^-	111	111	$100/111$	100
$KHCO_3$	37	148	$100/148$	25
KCl	30	No hardness		X

Note: $MgSO_4$ and $CaCO_3$ are regarded as being present in the form of their bicarbonates only their wts. have been expressed in terms of



$$= \frac{74}{100} [300 + 40 + 100 + 25] = \frac{74 \times 365}{100} \text{ mg/L}$$

Lime converts per molar mg hardness to per mg. Ca hardness.

for 20,000 L of water, lime required
 $= \frac{74 \times 365 \times 20,000}{100} \text{ mg}$

$$\text{Purity factor} = \frac{100}{74} \times \frac{74}{100} \times 365 \times 20,000 \text{ mg}$$

$$= 7350060 \text{ mg}$$

$$= 7.3 \text{ kg}$$

Soda requirement

$$\frac{100}{92} \times \frac{106}{100} \times 20,000 [\text{MgCl}_2 + \text{CaCl}_2 + \text{Mg}(\text{NO}_3)_2]$$

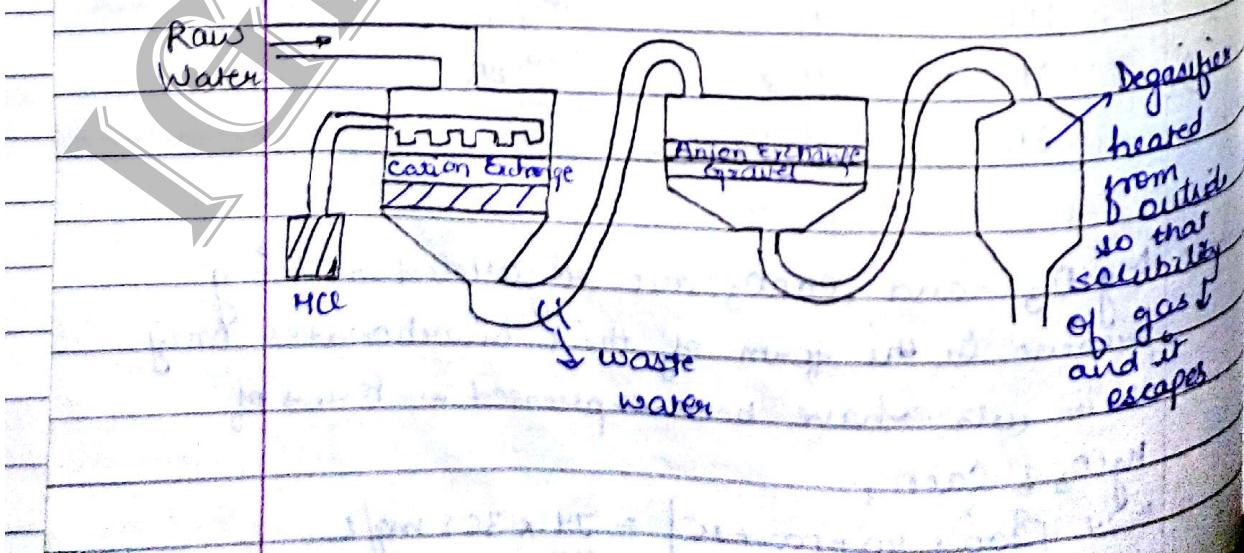
$$\Rightarrow 20,000 \times \frac{106}{92} [225] \text{ mg}$$

$$= 5184782.6 \text{ mg}$$

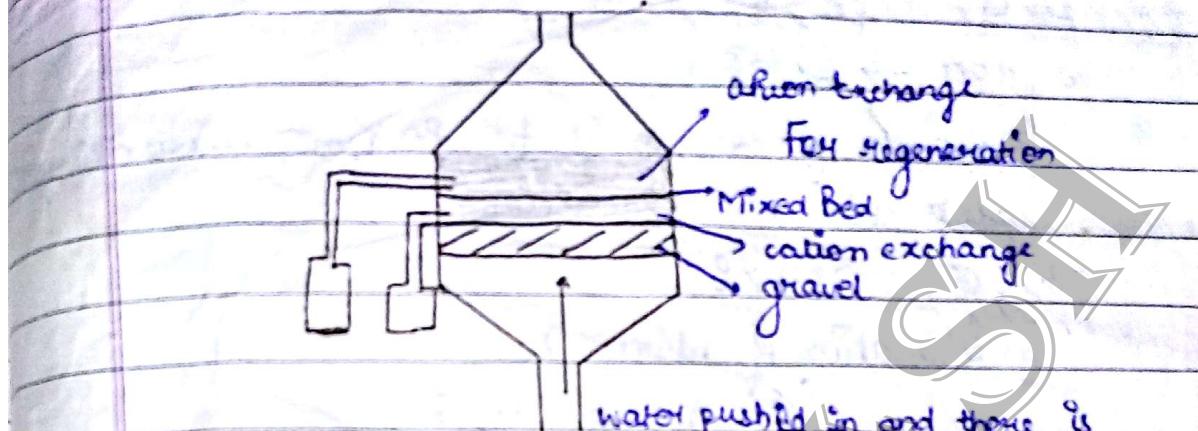
$$= 5.1 \text{ kg.}$$

③ Demineralisation Process.

(a) Conventional method



(i) Mixed Bed Method :



For making mixed bed again, air is pushed again.

Isometric Filtration



Domestic Water Supply

Raw Water \rightarrow Screening (floating Imp.) \rightarrow Sedimentation (insoluble Imp.)

\downarrow \leftarrow Disinfection \leftarrow filtration \leftarrow Coagulation + sedimentation

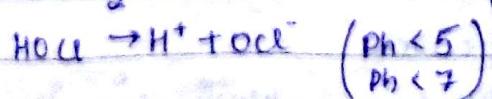
FINE SAND
CLAY SAND
GRAVEL

(Filter tank)

Rapid Gravity

Methods of Disinfection :

(i) Chlorination:



Forms of chlorine :

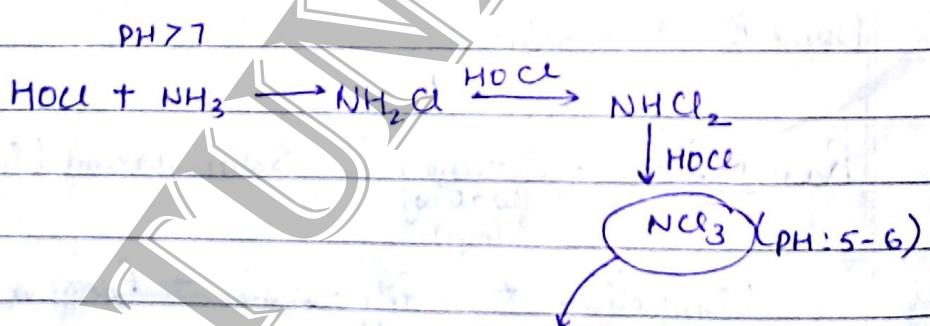
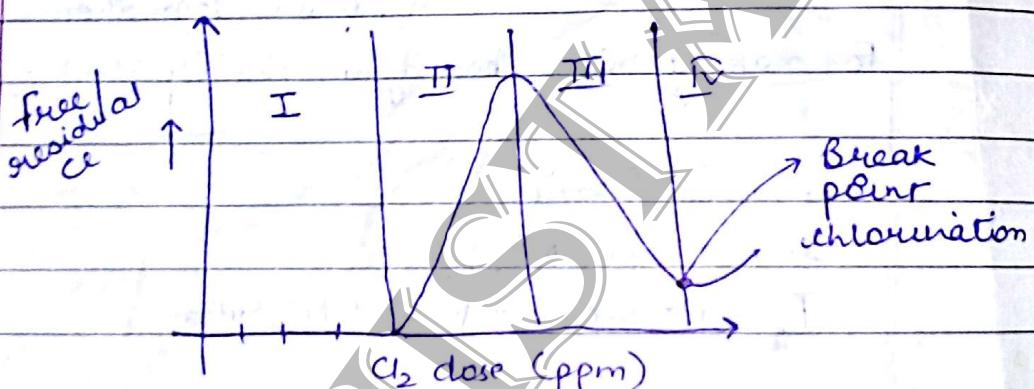
1. $\text{Cl}_2 \rightarrow \text{pH} < 5$
2. $\text{HOCl} \rightarrow \text{pH} \approx 6.5$

Most preferred as it has 80 times more disinfecting properties than other two

3. $\text{OCl}^- \rightarrow \text{pH} > 8$

(Estimation of chlorine)

(Volumetric titration.)



Chloramine also disinfects water

II → Formation of chloramines and chloro organic compounds.

Chloramines also give t test so value is increasing.

III → Destruction of chloramines and chloro org. compounds

The break point chlorination is defined as the chlorination to such an extent that

microorganisms as well as bad tastes and odours present in the water is also destroyed

$\Rightarrow 0.2 \text{ ppm}$ added to break pt. chlorination.

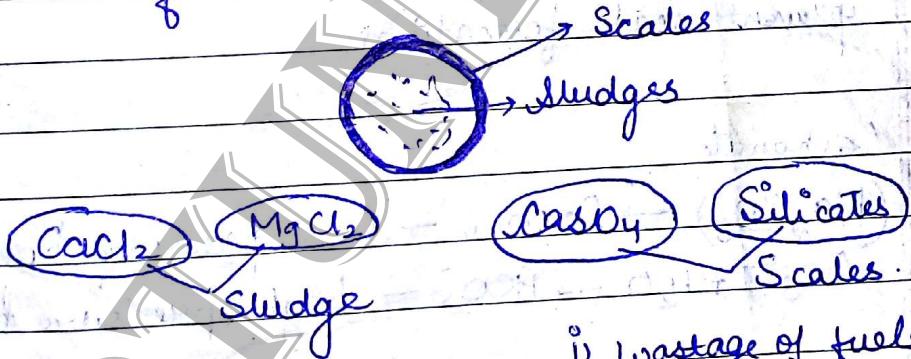
Boiler Problems

- (1) Scales & sludges
- (2) Boiler corrosion
- (3) Caustic Embarrassment
- (4) Priming & foaming

Scales and sludges:

Sludge is a non-adherent slimy ppt.

Scales are the hard coatings on the inner walls of containers.



(i) Poor conductor of heat

(ii) Checks the boiler system

i) wastage of fuel

ii) Bagging: Boiler material

loses its smoothness

and becomes distorted

causes uneven heating

iii) Danger of explosion

Removal of scales :

(i) Hammer & Chisel

(ii) By giving shock treatment (Thermal)

(iii) EDTA / dil. HCl

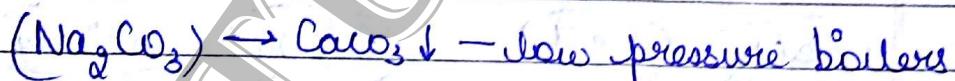
Internal treatment :

(1) Sequestration : It is the process in which an ion is prohibited to exhibit its usual properties by converting it into some other form or by forming a complex with some other compound

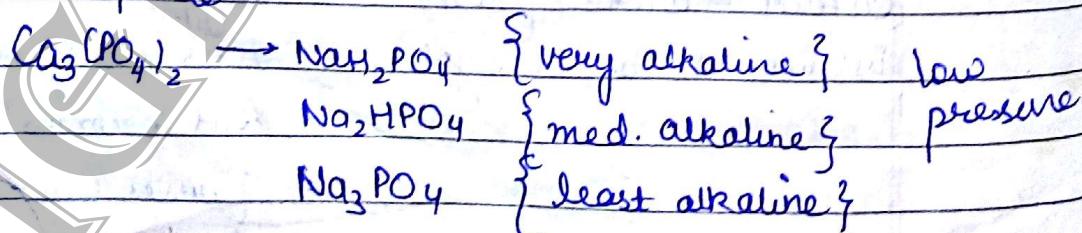
Colloidal

Kerosene, Agar-Agar gel, tannin etc. are added to water to entrap the dissolved salts to prevent scale formation.

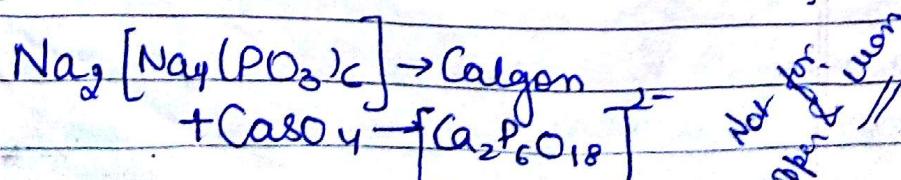
Carbonate

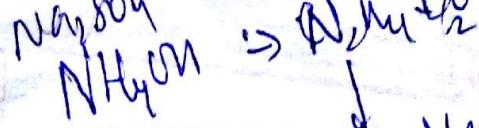


Phosphate



(4) Calgon : { Sodium hexameta Phosphate }





Date :

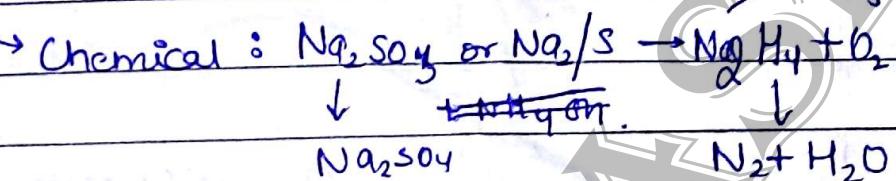
Page No.

Boiler corrosion

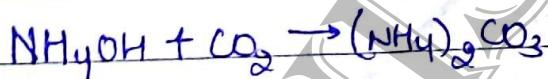
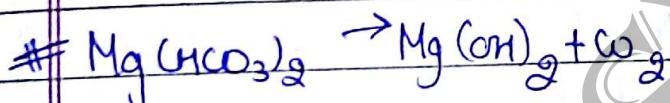
Causes : i) Dissolved Oxygen

ii) Dissolved CO_2

iii) Presence of Mineral acid

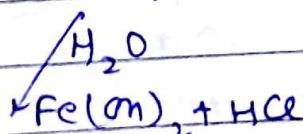
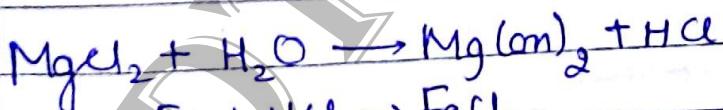


Mechanical Degasifier



Degasifier

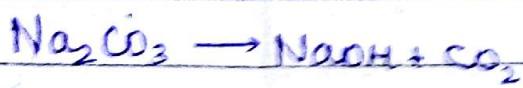
Mineral acids



Rust (Rusting Continue)

E.g. Amount of alkali is added to remove acid.

Rustic Embattlement



{ bonds / rods
beams / bars
joints

green at cracks / bonds | core
NaOH | dil NaOH Fe at surface

dissolves Na_2FeO_4 { scale formation }

Removal: By using Na_2SiF_6 or colloidal conditioning.

4. Panning & Foaming

↓ water stream limitation due to dissolved salts
water level - high
more dissolved salts
high velocity of water

Persistent bubbles on surface of water { dissolved salts come on surface & lower surface tension produces bubbles.}

Removal: 1) Steam velocity is reduced
2) Colloidal conditioning.

3) Water level of Boiler is kept low

Removal: i) Adding antifoamers
e.g. Polyamides

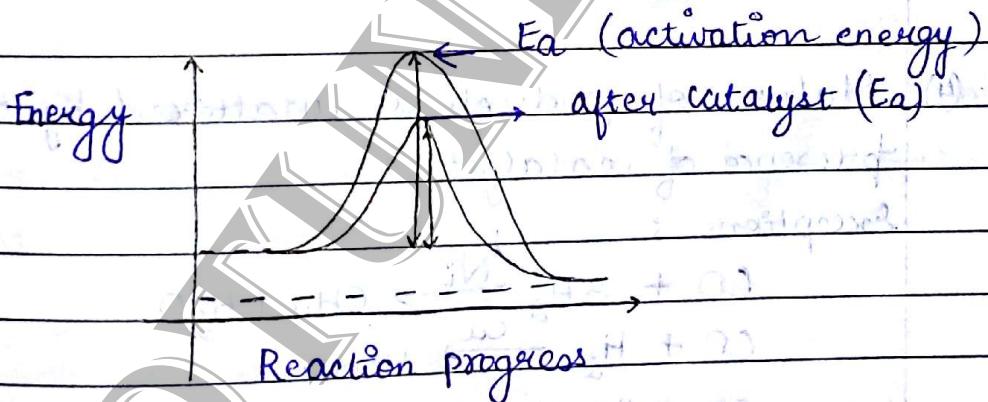
Catalysis

catalyst : A catalyst is defined as a substance which alters the rate of reaction without undergoing any change in mass & composition at the end of reaction.

catalysis : The phenomenon of altering the velocity of reaction by the presence of catalyst is called catalysis.

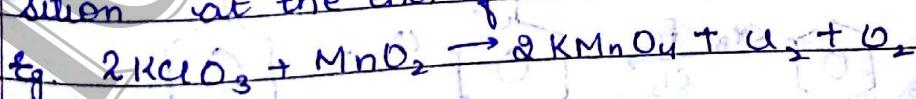
Catalyst alters the rate of reacⁿ by :

- i) By providing alternative pathway for chemical reaction.

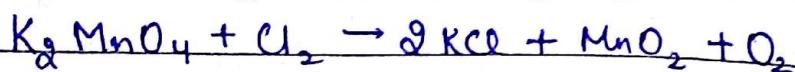


Characteristics of catalyst :

- i) Catalyst remains unchanged in mass & composition at the end of reaction



MnO_2 employed to catalyse the decomposition of KClO_3 is in the form of large crystals in the beginning of reaction but changes to fine powder in the end.

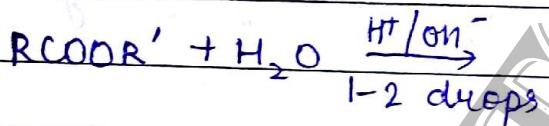


(2) Small amount of catalyst is sufficient to alter the rate of reaction.

(ion)

(1) Cu (1 g) in 10^9 l is sufficient to catalyse sodium sulphide by oxygen.

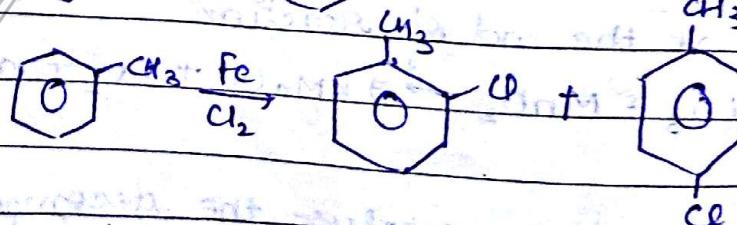
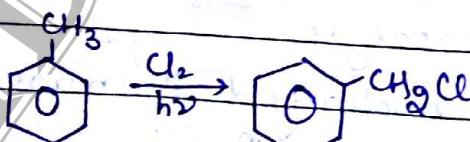
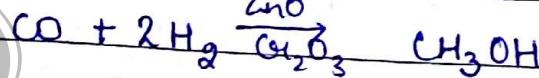
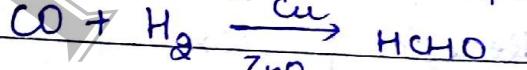
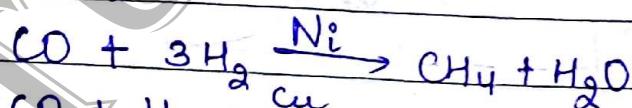
(oxidation)



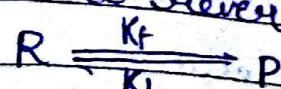
(3) Catalyst is specific in its reaction
 \Rightarrow MnO_2 may catalyse decomposition of $KClO_3$ but not $KClO_4$.

(4) Nature of products is unaltered by the presence of catalyst.

Exceptions:



(5) Catalyst doesn't alter the position of equilibrium in a reversible reaction.



(6) Catalyst doesn't initiate the reaction.

Exception : Formation of water.

(7) Optimum temperature : particular temp. at which activity of catalyst is maximum.

(8) Catalytic Promoters : Addition of small amount of foreign substances which themselves are not catalytically active increase the activity of catalyst & such substances are called promoters.

Eg. Haber's process.



(9) Catalytic Poisons : Activity of catalyst is inhibited or destroyed by minute quantity of substances called Catalytic Poisons.
(Inhibitors)

or Anticatalyst

Manufacture of H_2SO_4 (As_2O_3) (Pt)

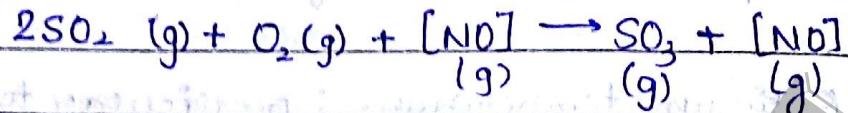
(10) High Surface Area

Types of Catalysis :

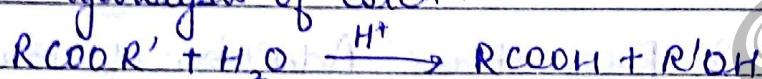
- 1) Homogeneous : same phase
- 2) Heterogeneous : different phase

Homogeneous reaction mechanism (a)

i) Gaseous Phase:

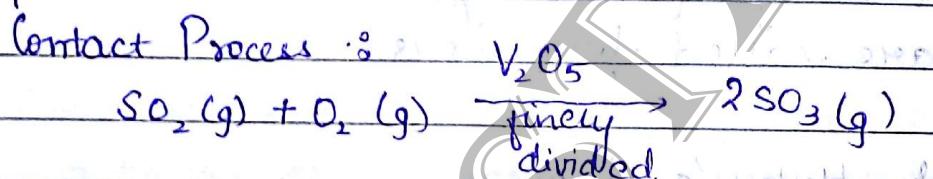


iii) liquid : Hydrolysis of ester.

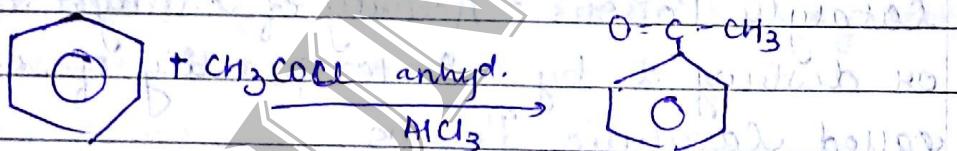


Heterogeneous reaction mechanism (b)

i) Gaseous Phase:



ii) liquid : Friedel-Craft Acylation of Benzene



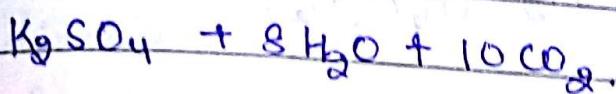
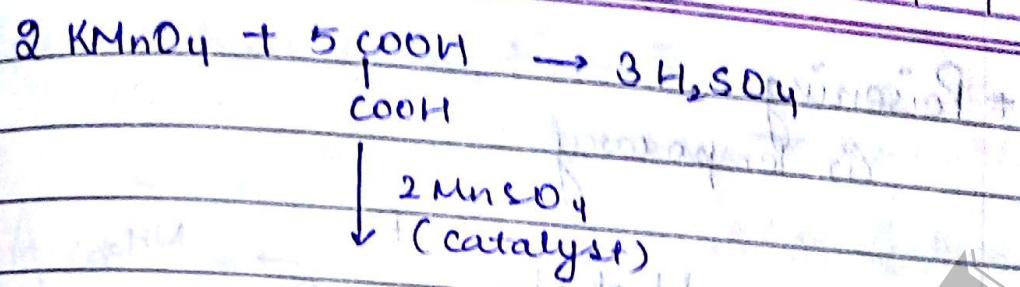
Classification :

(1) Positive : \uparrow

(2) Negative : \downarrow

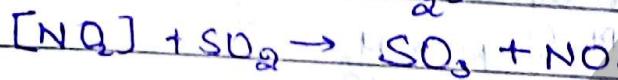
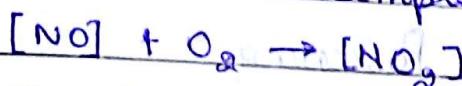
(3) Autocatalysis : \rightarrow One of the product in the reac" acts as a catalyst.

e.g. During titration of warm soln of oxalic acid by acidified KMnO_4 , the first 2 drops take appreciable time to decolourise but after some time the decolourisation takes place rapidly as Mn^{2+} ions formed during the reac" catalyse the reac".

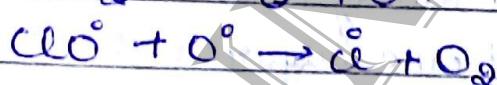


1816. Theory of Catalyst : Elemente Descusses in 1806.

(1) Intermediate complex formation theory

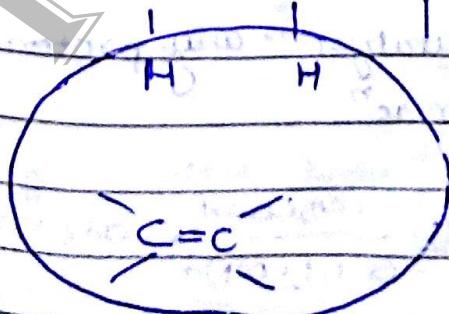
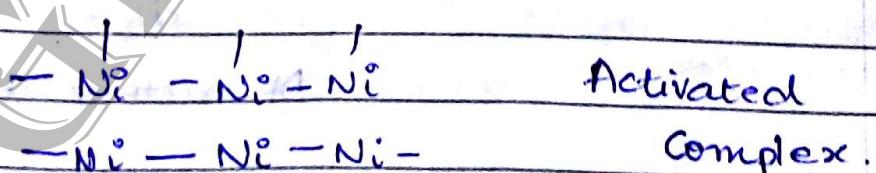
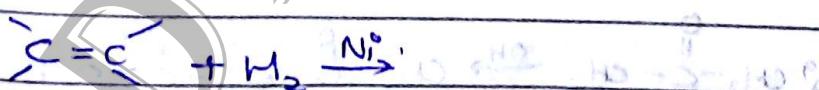


→ Depletion of Ozone



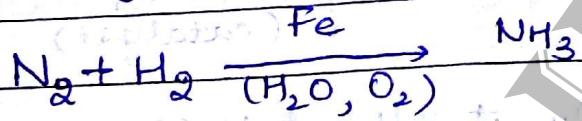
Could not explain heterogeneous catalysis

(2) Adsorption Theory

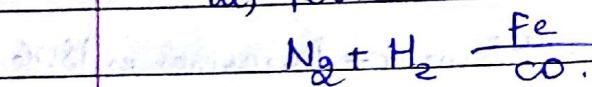


Poisoning

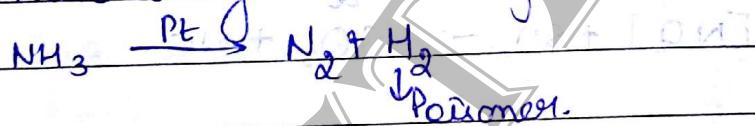
(i) Temporary



(ii) Permanent



(iii) Auto Catalytic Poisoning:



Homogeneous catalysis:

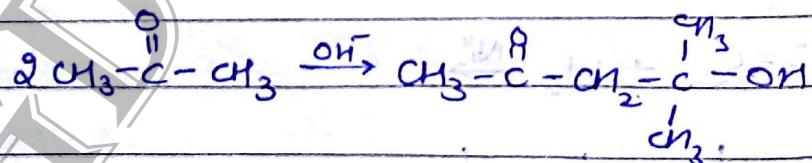
(i) Acid-Base catalysis:

i) Specific acid catalyst $\rightarrow \text{H}^+$

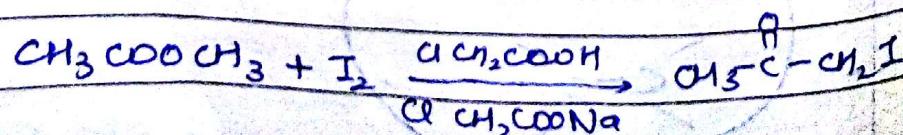
Inversion of cane sugar.

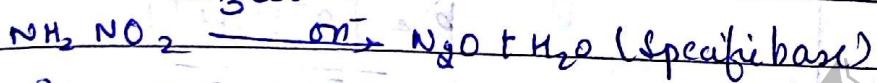
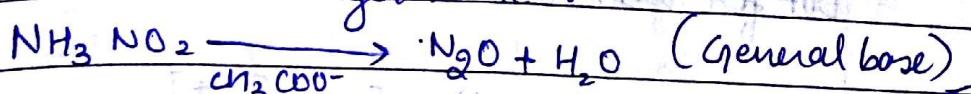


iii) Specific Base catalyst



Di-acetone alcohol

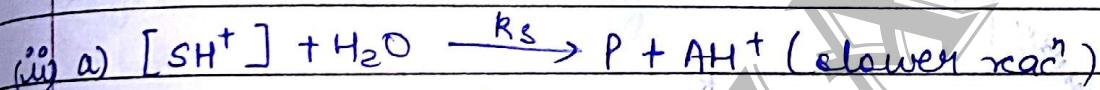
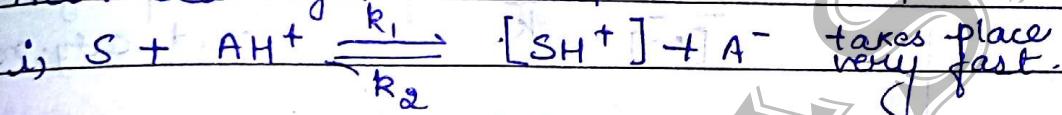
iii) General acid catalyst \rightarrow any proton donor
catalyses the reacⁿ.

iii) General base catalyst reacⁿ:

iv) Acid-Base Catalyst:

⇒ Kinetics :

(i) Acid catalyst.



$$r = k_2 [\text{SH}^+]$$

Applying steady state approximation :

$$\frac{d[\text{SH}^+]}{dt} = 0 = k_1 [S][\text{AH}^+] - k_2 [\text{SH}^+][\text{A}^-] - k_3 [\text{SH}^+]$$

$$r = k_2 [\text{SH}^+] = k_2 [\text{SH}^+][\text{A}^-] + k_3 [\text{SH}^+]$$

$$r = k_2 [\text{SH}^+] = \frac{k_3 k_1 [S][\text{AH}^+]}{k_2 [\text{A}^-] + k_3}$$

i) if $k_3 > k_2 [\text{A}^-]$

$$r = k_1 [S][\text{AH}^+] \leftarrow \begin{matrix} \text{General acid} \\ \text{catalyst reac}^n \end{matrix}$$

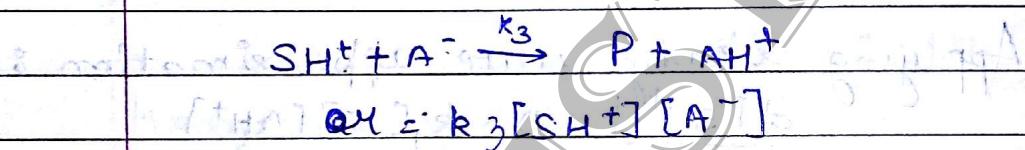
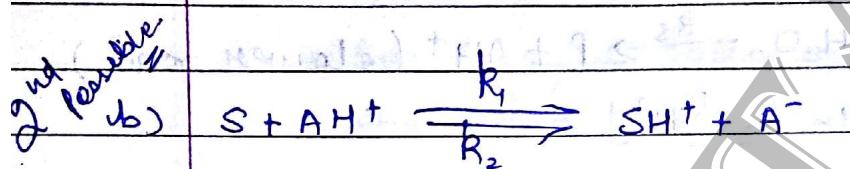
ii) if $k_2 [\text{A}^-] > k_3$

$$r = \frac{k_1 k_3 [S][\text{AH}^+]}{k_2 [\text{A}^-]}$$

But for weak acid $[AH^+] \rightleftharpoons [A^-][H^+]$

$$K = \frac{[A^-][H^+]}{[AH^+]}$$

homogeneous form $[AH^+] = [H^+]$ eqⁿ for specific acid caty. reacⁿ.



Applying Steady state approxⁿ

Rate of formⁿ:

$$\frac{d[SH^+]}{dt} = k_1 [S][AH^+] = \{k_2 [SH^+][A^-] - k_3 [SH^+][A^-]\}$$

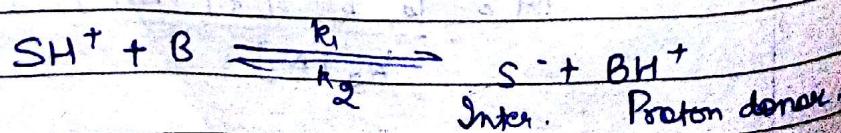
$$[SH^+][A^-] = k_1 [S][AH^+]$$

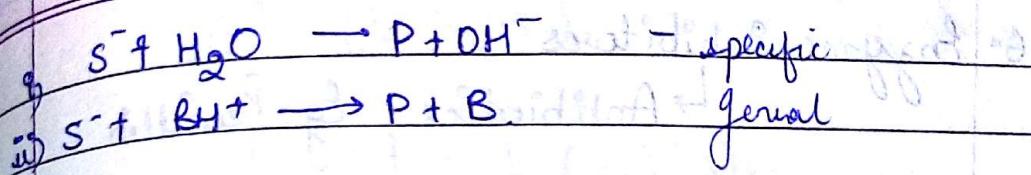
$$\rightarrow r_1 = \frac{k_1 k_3 [S][AH^+]}{k_2 + k_3}$$

General acid

$$\frac{k_2 + k_3}{k_2 + k_3}$$

q) Base catalytic reacⁿ:





Enzyme Catalysis

Characteristics of enzyme catalysis :

1. Efficient class of catalysis

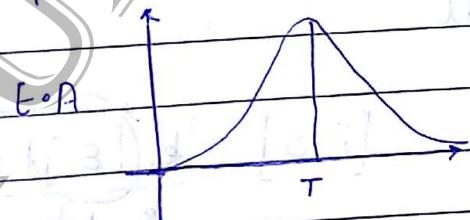
Turnover number

1 enzyme \rightarrow $100 - 10^6$ substrate molecule per unit time.

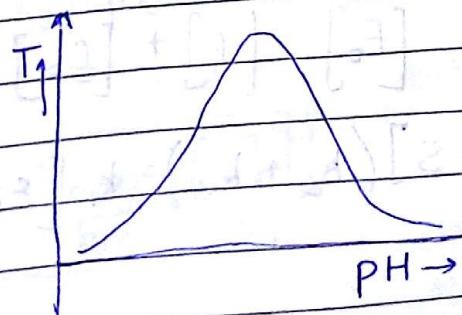
2. Selective in nature

3. Lower down the activation energy.

4. Temperature dependent



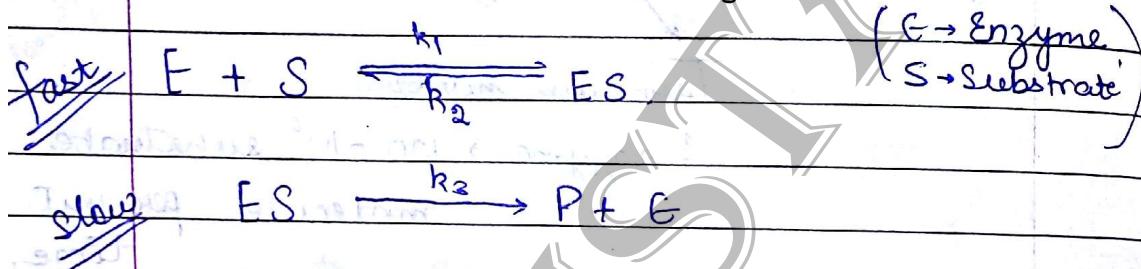
5. pH affects Enzyme Activity



6. Enzyme Inhibitors
↳ Antibiotics e.g. Penicillin

7. Co-Enzymes : e.g. Vitamins enhance the activity of enzyme in the body

Kinetics of Enzyme Catalysis.



$$r = k_3 [ES]$$

$$\frac{d[ES]}{dt} = 0 = k_1 [E] [S] - \{ k_2 [ES] + k_3 [ES] \}$$

$$[ES] = \frac{k_1 [E] [S]}{k_2 + k_3}$$

difficult to measure

Enzyme Conservation Eqⁿ

$$[E_0] = [E] + [ES]$$

$$[ES] (k_2 + k_3) = k_1 [E_0] [S] - k_1 [ES] [S]$$

$$[E] = [E_0] - [ES]$$

$$[ES] = \frac{k_1 [E_0] [S]}{k_1 [S] + k_2 + k_3}$$

$$[ES] = \frac{[E_0] [S]}{\frac{k_2 + k_3}{k_1} + [S]}$$

$$\frac{k_2 + k_3}{k_1} \rightarrow k_m$$

k_m : Michaelis constant

$$[ES] = \frac{[E_0] [S]}{k_m + [S]}$$

$$r = \frac{k_3 [E_0] [S]}{k_m + [S]} \rightarrow M-M \text{ equation}$$

(Michaelis-Menton eq.)

$$r = k_3 [ES]$$

$$E_0 = E + ES$$

$$[E_0] = [ES]$$

$$V_{max} = k_3 [E_0] = V_{max} \{ \text{Enzymology} \}$$

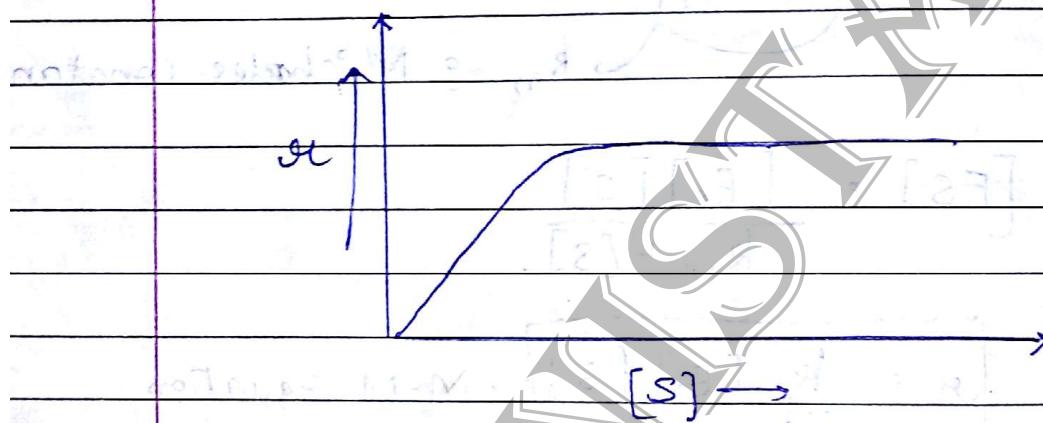
$$r = \frac{V_{max} [S]}{k_m + [S]}$$

case (i) If $k_m \gg [S]$

$$v_r = \frac{V_{max} [S]}{k_m} \text{ of } 1^{\text{st}} \text{ Order.}$$

(ii) If $[S] \gg k_m$

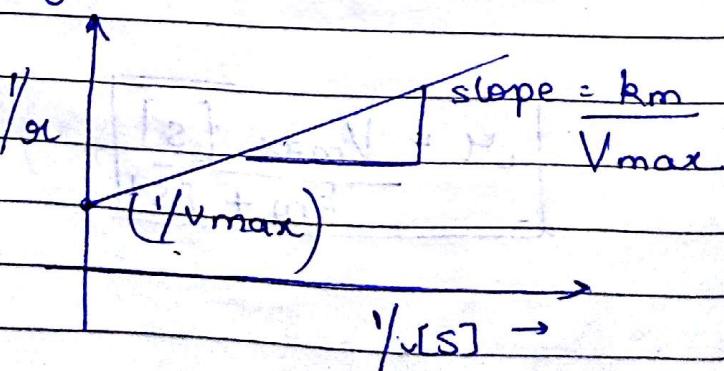
$$v_r = V_{max} \text{ of } 0 \text{ Order.}$$



Line Weavers Burk method for V_{max} & k_m

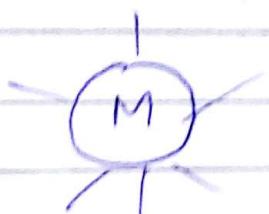
$$\frac{1}{v_r} = \frac{k_m}{V_{max} [S]} + \frac{1}{V_{max}}$$

$$y = mx + c$$

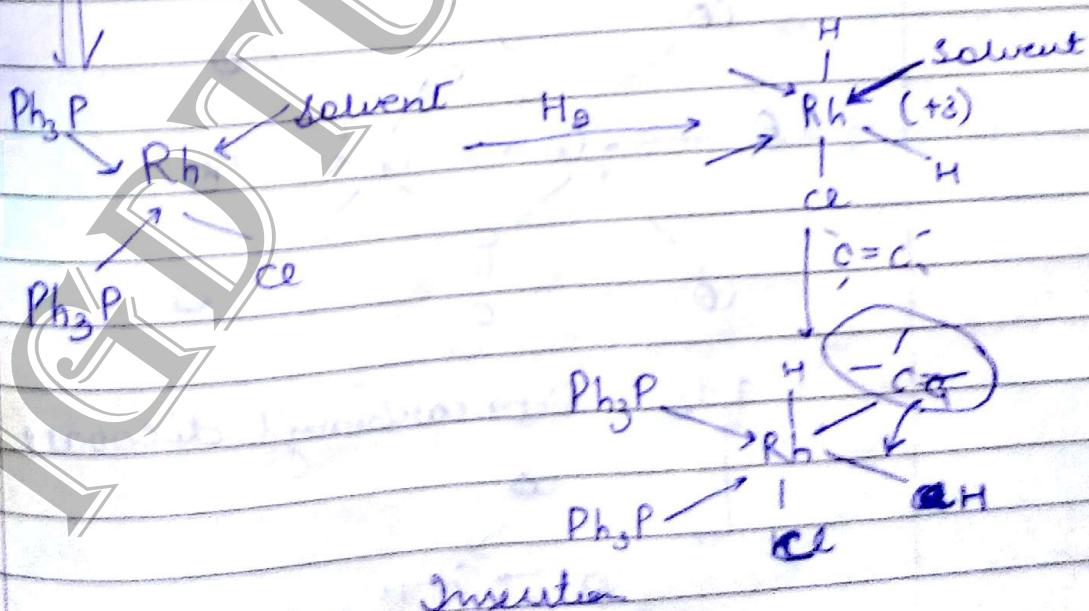
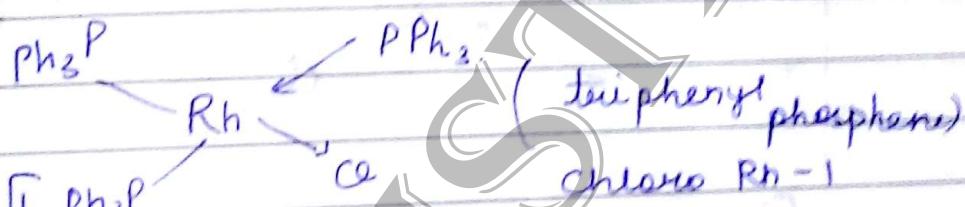


Catalysis by Metal Salts (Homogeneous)

Sympathetic : Bringing together of all the molecules in a spatial arrangement.

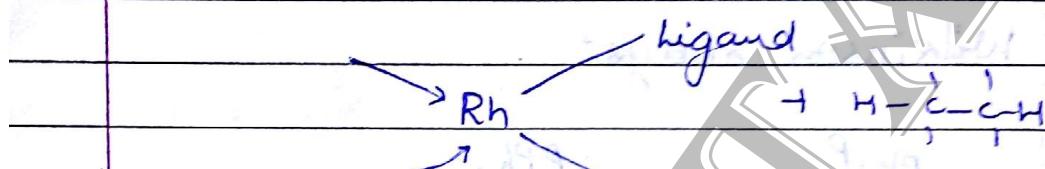
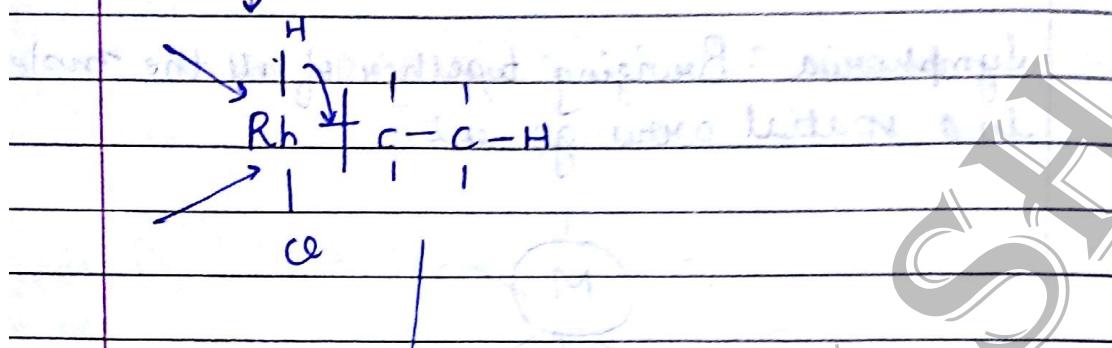


Wilkinson Catalyst



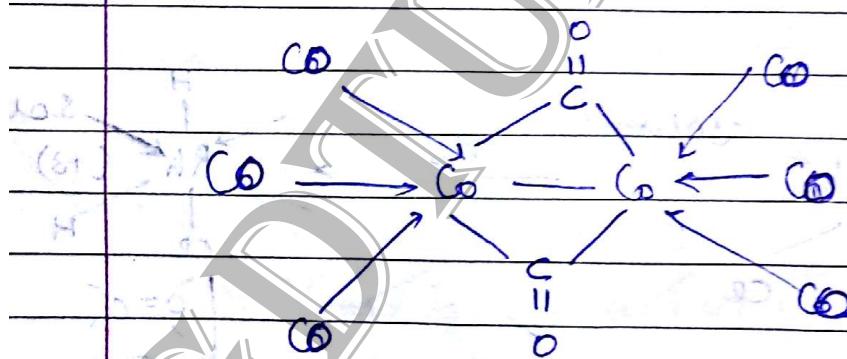
empty orbital of Rh overlaps with the cloud of $\text{C}=\text{C}$ and forms π bond

Hydrogenation of alkene by Rh catalyst

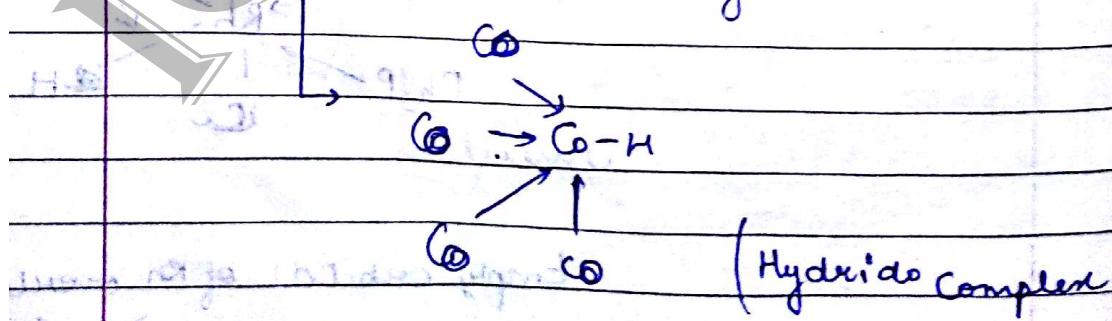


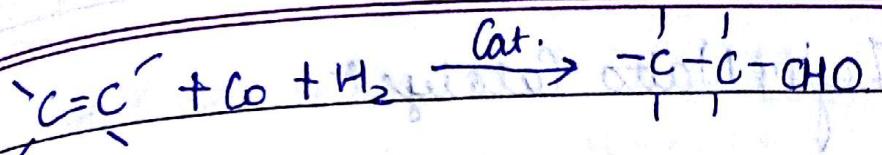
(2) Oxo process

$\text{C}=\text{C}$ to aldehyde \rightarrow alcohols



$\text{Co}(\text{CO})_2 \text{O} + \text{H}_2 \rightarrow \text{Octacarbonyl dicobalt}$





CO Solvent

$\text{Co} \leftarrow \text{H}$

CO

CO

Solvent

$\text{Co} \leftarrow \text{H}$

CO

CO

'C=C' is finally

$\text{Co} \leftarrow \text{H}$

e.g. Ziegler Natta Catalyst

empty orbital of metal overlaps with π -cloud of alkene to form π bond.

Heterogeneous Catalysis / Surface Catalysis

fast

1. Diffusion of reactant molecules on the surface of catalyst.
2. Adsorption of reactant molecules.
3. Chemical reaction - slowest
4. Desorption

fast

5. Diffusion of product molecules away from the surface.

(Langmuir - Hinshelwood Mechanism)

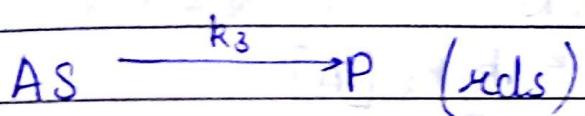
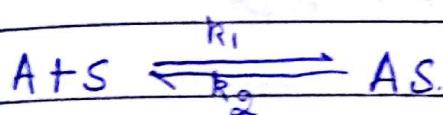
3rd step is the rate determining steps:

Assumptions :

- (1) Chemical reaction b/w the adsorbed molecules is the rds.
- (2) An equilibrium exists b/w the adsorbed & desorbed molecules.
- (3) The rate of reaction for unit surface area is proportional to θ where θ is fraction of surface covered by the reactant molecules.

$\theta = \frac{\text{no. of sites occupied}}{\text{no. of sites available}}$

$w \propto \theta$



$$w = k_3 [AS]$$

$$\frac{d[AS]}{dt} = 0 \Rightarrow k_1 [A][S] = \{k_2 [AS] + k_3 [As]\}$$

$$k_1 [A][S] = (k_2 + k_3) [AS]$$

$$\frac{k_1}{k_2 + k_3} [A][S] = [AS]$$

Let C_s be the total conc. of active sites.

$$[AS] = C_s \theta$$

$$[S] = C_s (1 - \theta)$$

$$\frac{k_1}{k_2 + k_3} [A] = \frac{C_s \theta}{C_s (1 - \theta)}$$

$$\left(\frac{k_1}{k_2 + k_3} \right) [A] = \frac{\theta}{1 - \theta}$$

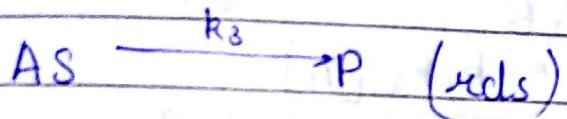
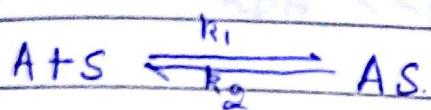
$$\frac{1 - \theta}{\theta} = \frac{k_2 + k_3}{k_1 [A]}$$

$$\frac{1 - \theta}{\theta} = \frac{k_2 + k_3}{k_1 A}$$

$$\frac{1}{\theta} = \frac{k_2 + k_3 + k_1 A}{k_1 n}$$

$\theta = \frac{\text{No. of sites occupied}}{\text{No. of sites available}}$

$w \propto \theta$



$$w = k_3 [AS]$$

$$\frac{d[AS]}{dt} = 0 \Rightarrow k_1 [A][S] - \{k_2 [A]S + k_3 [AS]\}$$

$$k_1 [A]S = (k_2 + k_3) [AS]$$

$$\frac{k_1}{k_2 + k_3} [A][S] = [AS]$$

Let C_s be the total conc. of active sites.

$$[AS] = C_s \theta$$

$$[S] = C_s (1 - \theta)$$

$$\frac{k_1}{k_2 + k_3} [A] = \frac{C_s \theta}{C_s (1 - \theta)}$$

$$\left(\frac{k_1}{k_2 + k_3} \right) [A] = \frac{\theta}{1 - \theta}$$

$$\frac{1 - \theta}{\theta} = \frac{k_2 + k_3}{k_1 [A]}$$

$$\frac{1 - \theta}{\theta} = \frac{k_2 + k_3}{k_1 A}$$

$$\frac{1}{\theta} = \frac{k_2 + k_3 + k_1 A}{k_1 A}$$

$$\theta = \frac{k_1[A]}{k_2 + k_3 + k_1[A]}$$

$$r = k_3 \theta$$

$$= \frac{k_1 k_3 [A]}{k_2 + k_3 + k_1 [A]}$$

(Gaseous reactants)

$$r = k_1 k_3 p_A$$

$$k_1 p_A + k_2 + k_3$$

i) If $k_3 \gg k_1 p_A + k_2$

$$r = k_1 p_A$$

ii) If $k_1 p_A + k_2 \gg k_3$

$$r = \frac{k_1 k_3 p_A}{k_1 p_A + k_2} \Rightarrow r = \frac{\frac{k_1}{k_2} R_3 p_A}{\frac{k_1 p_A}{k_2} + 1}$$

Divide by k_2

if p_A is very low

$$\frac{k_1}{k_2} \downarrow$$

Adsorption
Equilibrium
Constant

$$r = \frac{K k_3 p_A}{K_p A + 1}$$

iii) if p_A is very low

then $\theta \rightarrow 0$

$$K_p A \ll < 1$$

$$\eta = K k_3 p A$$

iii) If $p A$ is very large

$$\theta \rightarrow 1$$

$$\eta = \frac{K k_3 p A}{K_p A}$$

$$\eta = k_3 \quad (\text{Order} = \text{Zero})$$

for further chapters refer second notebook.

Phase Rule :-

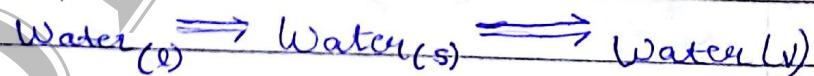
$$P = F - C + 2$$

- ① Phase : Physically distinct & mechanically separable.
- ② Component :
- ③ Degree of freedom :

Phase is a homogeneous physically distinct & mechanically separable part of a system separated from other parts of system by definite boundaries.

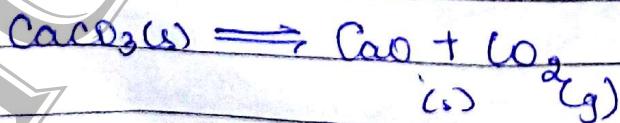
e.g. Saturated soln of NaCl has - 2 phases

Component : Number of components of a system is a smallest no. of independently variable components at eq. by means of which, the composition of each phase present can be expressed.

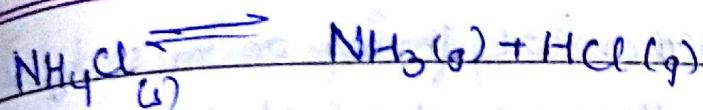


Reactive Components

$$C = S - R$$



$$C = 2$$



$\text{NH}_3(g) = \text{HCl}(g)$ (stoichiometric
1 component system component)



2 component system

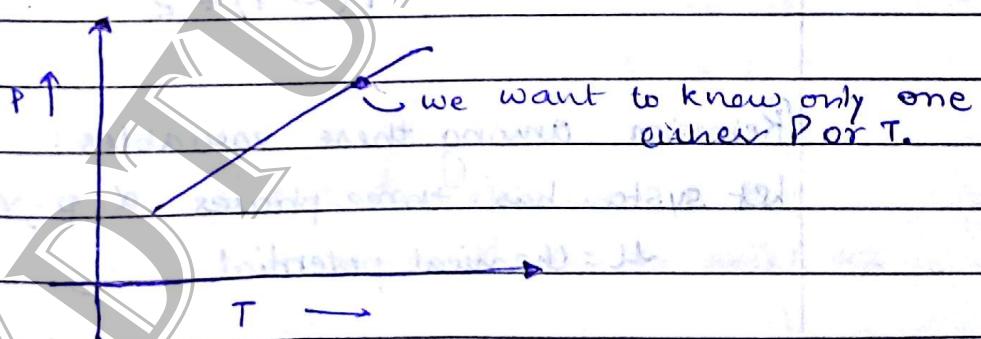
At high temp



1 component

Degrees of Freedom.

The degree of freedom of a system is defined as no. of independent variable such as temperature, pressure & composition which are specified to describe a system completely.



Triple Point : Zero degrees of freedom

Gibb's Phase Rule : $P + F = C + 2$

This rule states that if a heterogeneous system is influenced by T, P and C & not by any other action like gravity,

electrical, mechanical forces or by surface action; then the sum of no. of phases P and F : degrees of freedom is greater than no. of components C by a factor of 2.

Derivation# Gibbs Phase Rule:

(Heterogeneous)

P - Phase

C - Components

$F \Rightarrow P, T, \text{composition}$

$$P + F = C + 2$$

$$P + T = 2$$

Composition Variables

P phase - $P(C-1)$

Total no. of variables

$$= P(C-1) + 2$$

Relation among these variables:

Ict system has three phases α, β, γ

μ = chemical potential

$$\begin{aligned} \mu_\alpha &= \mu_\beta \\ \mu_\alpha &= \mu_\gamma \end{aligned}] 2 \text{ eq's}$$

Relations: $(P-1) C$

Total number of independent variables

$$F = P(C-1) + 2 - [C(P-1)]$$

$$= PC - P + 2 - PC + C$$

$$F = C - P + 2$$

One Component System :

$$F = C - P + 2$$

$$f = 1 - 1 + 2$$

$$f = 2$$

(In case of 1 phase)

In case of 2 phase

$$\Rightarrow F = 1$$

In case of 3 phase

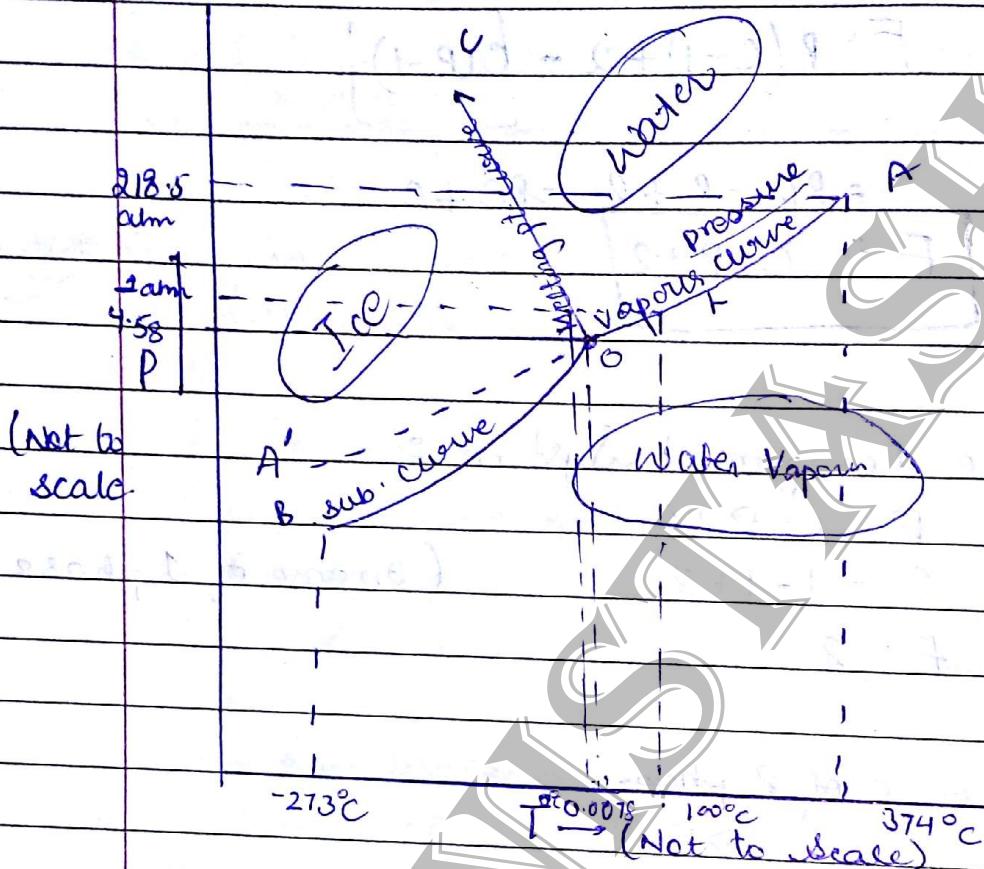
$$\Rightarrow F = 0$$

Superior system

$$f = 1 - 4 + 2 = -1 \quad \times \text{ Not Possible}$$

\Rightarrow At a time only three phases co-exist at a time.

† Water System



Areas

- 1) BOC
 - 2) AOC
 - 3) AOB
- $$\begin{aligned} & C - P + 2 = F \\ & F = 1 - 1 + 2 \\ & F = 2 \end{aligned}$$

Lines : OA : Vapour pressure curve:
Water & Water vapour phases coexist
 $\text{Water} \rightleftharpoons \text{Water Vapour}$

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$F = 1$$

Critical Temp = 374°C

Critical Pressure = 218.5 atm

Beyond Critical point, Water & Water vapour can't be differentiated

3) OC = Melting Point Curve

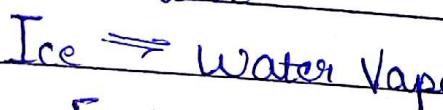


$$F = 1$$

$\uparrow P = \text{density } \uparrow$

$V \downarrow, M.P. \text{ decreases}$

3) OB : Sublimation curve:



$$F = 1$$

$$B = -273^\circ\text{C} \text{ (Lowest pr.)}$$

Points : O : Triple Point

$$F = 0$$

OA' : Super cooled Water.

(Metastable Equilibrium : Ice is not formed)

(AOA')

Temporary. Moment the dust particle comes in contact with super cooled water the water attains stable equilibrium.

Two-Component System:

$$F = C - P + 2$$

$$F = 4 - P$$

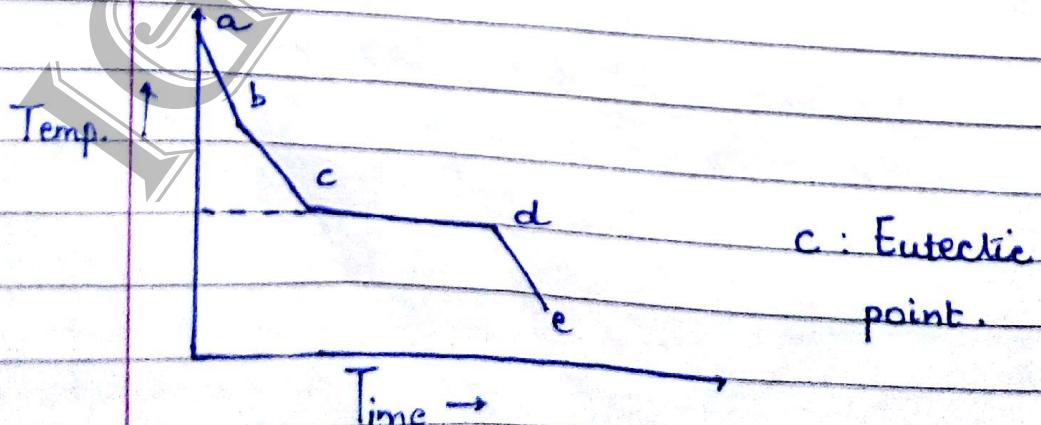
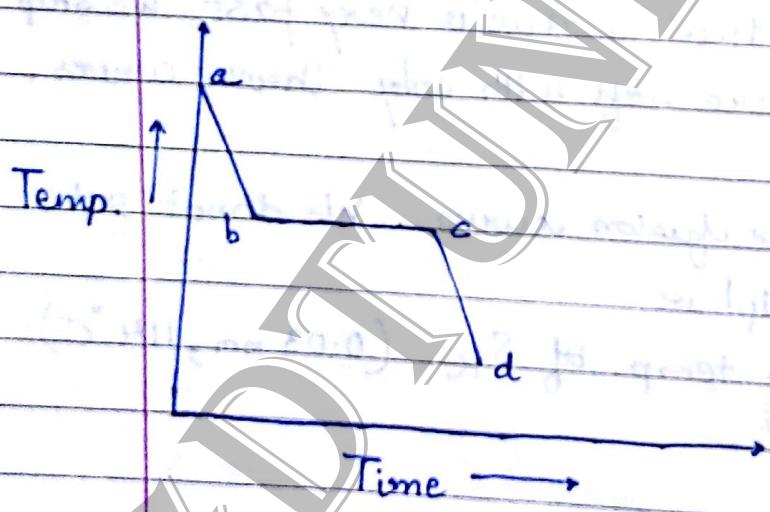
Pressure is fixed at 1 atmosphere.

$$\begin{aligned} F' &= C - P + 2 - 1 \\ &= C - P + 1 \end{aligned}$$

Condensed Phase Rule.

And the system is called Condensed System.

Thermal Analysis



A binary system consisting of two substances which are miscible in all proportions.

: Solid solution of two or more substances having lowest freezing point of all possible systems.

Minimum freezing point attainable corresponding to Eutectic mixture is known as Eutectic point. This Eutectic mixture has

In this way it resembles a compound but is not a

Components are not in stoichiometric proportion.

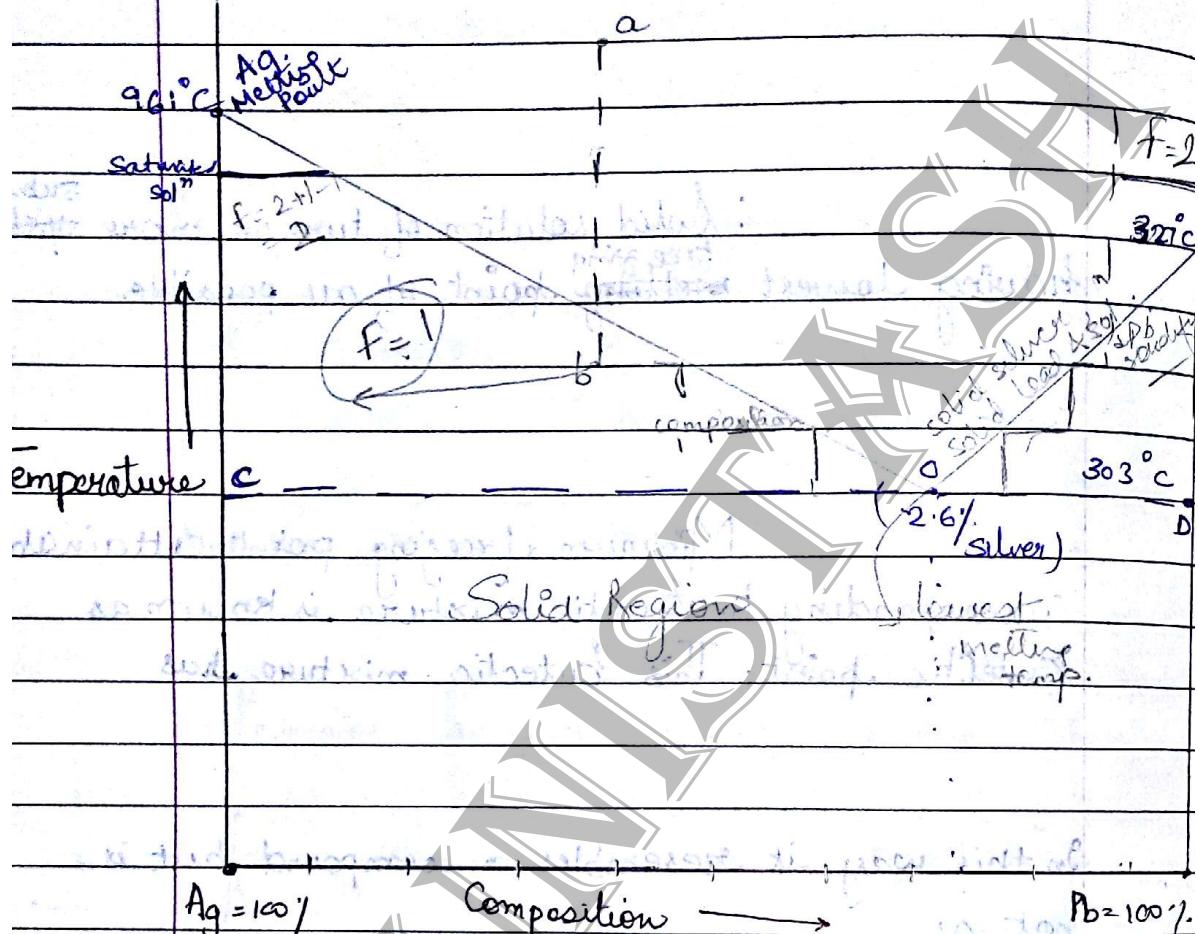
Example: Bismuth - 50%
Lead - 25%
Tin - 12.5%
Cd - 12.5%

Safety Plugs

(+70°C)

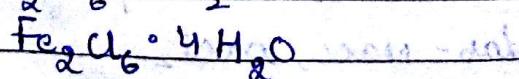
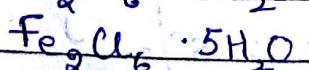
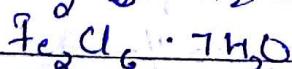
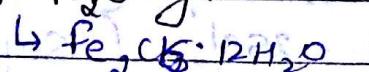
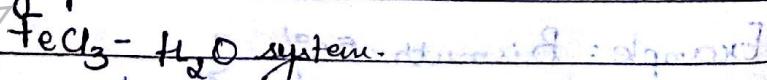
Ice cream, Pressure Cooker.
23% NaCl

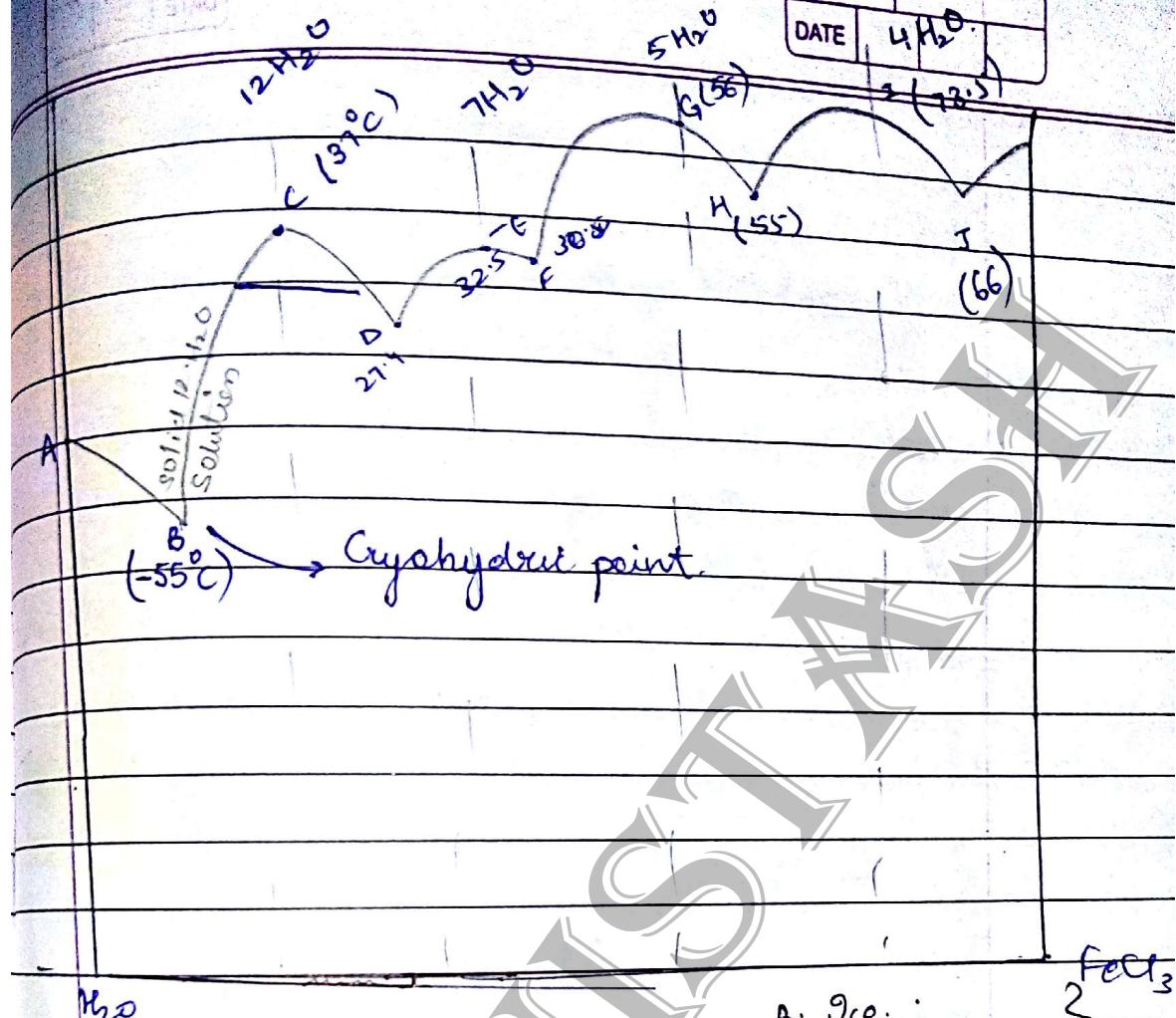
(I) Ag-Pb



Application : Pattinson's Process

(2) Formation of stable Compounds with Congruent Melting point.





B. Ice · Dodecahydrate
solid sol^m

AB : Ice & Sol^m.
BC : Solid Dodecahydrate &
Sol^m.

C : Congruent Melting point of Fe₂Cl₆ · 12 H₂O
· 12 H₂O

cB : Solubility curve

D : Solid 12 H₂O, solid 7 H₂O, solution

E : Congruent Melting Point of Fe₂Cl₆ · 7 H₂O

EP : Solubility Curve of Fe₂Cl₆ · 7 H₂O

F : Solid crystal of FeCl₆
Pentahydrate, sol^m.

Two solubilities at same temp : Retereoffee
solubility

Characteristic of a system producing solid
compsnr.

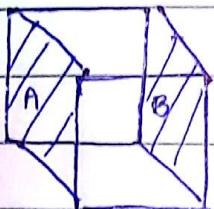
Gaseous State

Principle of kinetic molecular theory of gases:

1. Negligible volume.
2. Random motion.
3. No attractive forces.
4. Collision are elastic \rightarrow transferring from one particle to another.

5. K.E $\propto T$

for one molecule:



N = no. of molecule.

m = mass

c = velocity

$$c^2 = u^2 + v^2 + w^2$$

(x) (y) (z)

$$\begin{aligned}\text{Total change in momentum} &= mu - (-mu) \\ &= mu + mu \\ &= 2mu\end{aligned}$$

Total rate of change of momentum per unit time

$$\frac{\Delta p}{\Delta t} = \frac{2mu}{\ell/u} = \frac{2mu^2}{\ell}$$

$$\frac{\Delta p}{\Delta t} = \frac{2mu^2}{\ell} + \frac{2mv^2}{\ell} + \frac{2mw^2}{\ell}$$

$$\frac{\Delta p}{\Delta t} = \frac{2m}{\ell} (u^2 + v^2 + w^2)$$

$$\frac{\Delta p}{\Delta t} = \frac{2mc^2}{\ell}$$

\Rightarrow for n molecule:

$$\bar{c}^2 = \frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2}{3}$$

$$N\bar{c}^2 = \sum n_i c_i^2$$

$$\frac{\Delta p}{\Delta t} = \frac{2m N\bar{c}^2}{l}$$

$$N\bar{c}^2 = \frac{\Delta p \times l}{2m}$$

P.S.: Small attached page.

Graham's law:

$$PV = \frac{1}{3} m N \bar{c}^2$$

$$\bar{c} = \sqrt{\frac{3PV}{mN}}$$

$$\bar{c} = \sqrt{\frac{3P}{d}}$$

$$\bar{c} \propto r \quad r = \text{rate of diffusion}$$

$$r \propto \sqrt{\frac{l}{d}}$$

Dalton's law of partial pressure:

$$P_1 = \frac{1}{3} \frac{m_1 N_1 \bar{c}_1^2}{V}$$

$$P_2 = \frac{1}{3} \frac{m_2 N_2 \bar{c}_2^2}{V}$$