

WATER TECHNOLOGY

Impurities in water

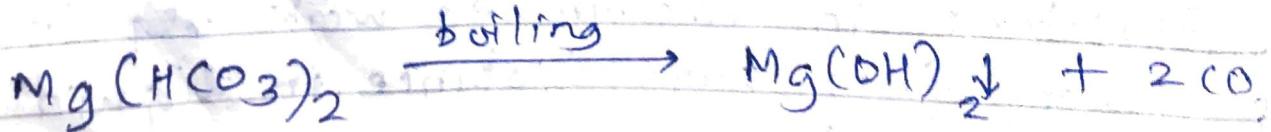
- 1) Suspended - Soil particles, organic wastes (1000A°) sand can be separated by filtration or sedimentation processes.
- 2) Colloidal - Particles at size $10-1000\text{A}^{\circ}$ separated by coagulation & filtration.
- 3) Dissolved - Inorganic salts, gases like O_2 , SO_2 , NH_3 , H_2S , CO_2 etc., organic solids like sugar, cations, anions separated by chemical treatment, warming, oxidation.
- 4) Biological - Bacteria, algae, fungi removed by sterilisation.

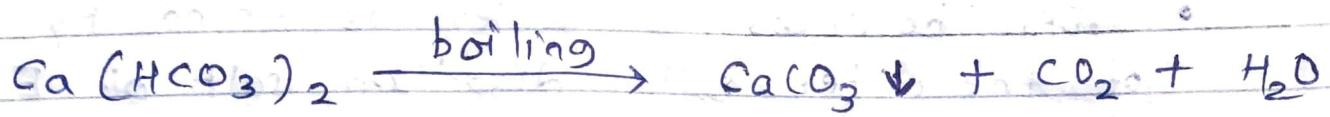
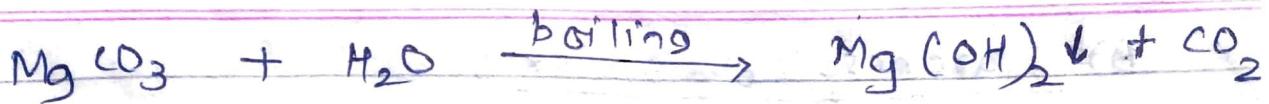
Hardness of water

- Water containing salts of Ca , Mg , Fe , Mn does not produce lather with soap, is known as hard water.
- Rain water, distilled water form ^{lather with} soap and known as soft water.

2 types of hardness

- 1) Carbonate or temporary hardness
- It is due to presence of bicarbonate & some soluble carbonate salts. e.g. $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, MgCO_3 , FeCO_3 .
- These salts can be converted to their water insoluble forms by boiling & temporary hardness gets removed.





2) Permanent or Non-carbonate Hardness

- It is due to presence of dissolved salts of heavy metals other than carbonates.
e.g., CaCl_2 , MgCl_2 , CaSO_4 , $\text{Ca(NO}_3)_2$ etc.
- These salts can be removed by chemical treatment methods, to make water soft.

$$\text{Total Hardness} = \text{Temporary hardness} + \text{Permanent Hardness}$$

Units of hardness

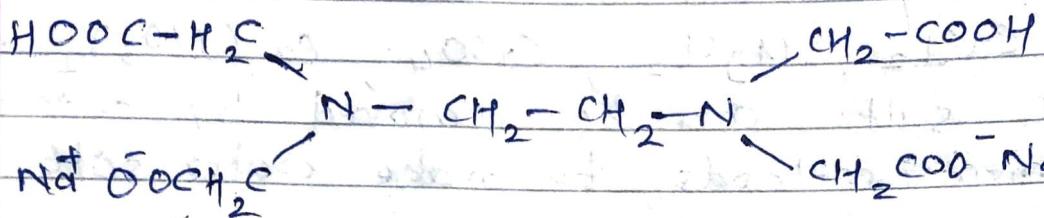
- i) mg CaCO_3 equivalent per litre
- ii) ppm of CaCO_3
- iii) ppb of CaCO_3

Chemical Analysis of Water

- In chemical analysis, we study hardness, amounts of various ions, pH, alkalinity, chloride content, micro-organisms, etc.
- After the analysis, it becomes possible to decide the kind of treatment and extent of treatment to be given to make the water suitable for a particular purpose.

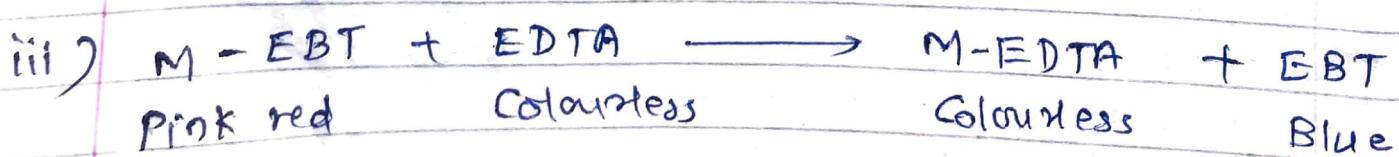
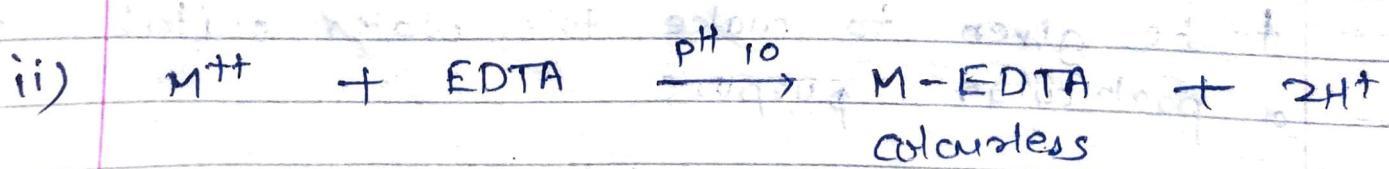
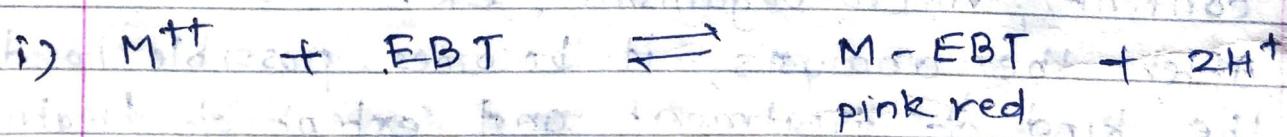
A) Hardness of water:

- Total hardness of water is found by titration of the water with disodium salt of EDTA (ethylene diamine tetraacetic acid).
- Disodium salt of EDTA (structure)



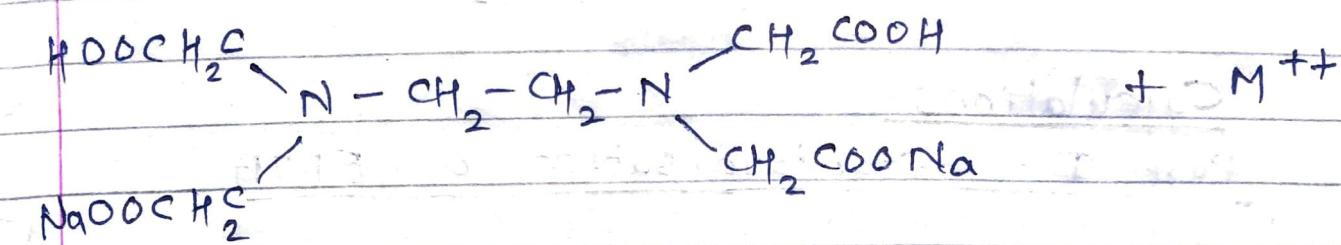
- Disodium EDTA & EDTA form complex with heavy metal ions in water (Ca^{++} , Mg^{++}).
- When suitable pH is maintained, disodium EDTA forms cyclic co-ordination complex with heavy metal ions, hence the titration is known as complexometric titration.
- During reaction, H^+ ions are formed & decrease pH of reaction mixture. Buffer soln ($\text{pH}=10$) is added in mixture.

Schematic Reactions in titration

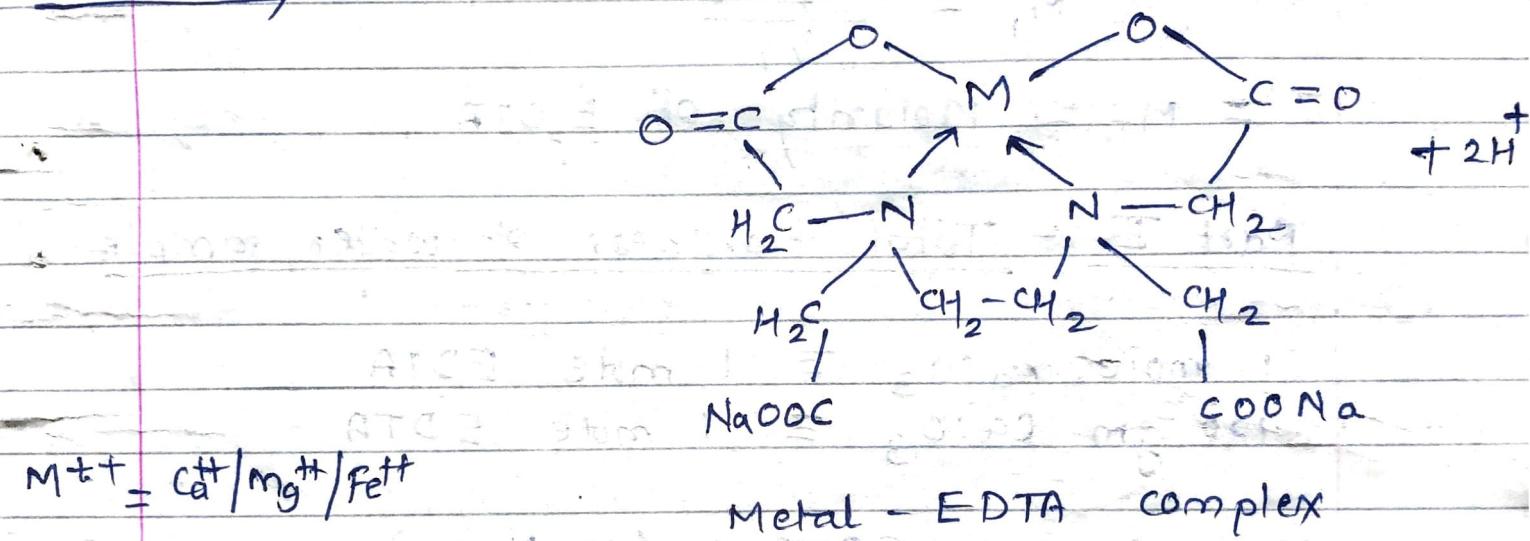


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Formation of Complex



Suitable pH



Procedure - Part I - Standardisation of EDTA

- 1) Prepare standard $\text{ZnSO}_4/\text{MgSO}_4$ soln.
- 2) Fill burette with disodium EDTA. Pipette out 25 ml std. ZnSO_4 soln in a conical flask.
- 3) Add 15 ml buffer (NH_3) soln. & 4-5 drops of EBT (Eriochrome Black T) indicator.
- 4) Titrate pink red coloured mix. against EDTA till it changes to blue. Let this reading be x ml.

Part II :- Total hardness of water sample.

- 1) Take 50 ml water (hard) sample in a conical flask. Add 15 ml buffer & 4-5 drops EBT indicator.

2) Titrate this pink-red mix. against EDTA to get endpoint as pink red to blue. Let this reading be 'y' ml.

Calculations

Part I - Standardisation of EDTA

$$\frac{M_1 V_1}{EDTA} = \frac{M_2 V_2}{ZnSO_4}$$

$$M_1 = \frac{M_2 V_2}{V_1}$$

$Z = M_1$ = Molarity of EDTA

Part II - Total Hardness of water sample

$$1 \text{ mole } CaCO_3 = 1 \text{ mole EDTA}$$

$$100 \text{ gm } CaCO_3 = 1 \text{ mole EDTA}$$

$$1000 \text{ ml } 1 \text{ M EDTA} = (100 \times 1000) \text{ mg of } CaCO_3$$

$$y \text{ ml } Z \text{ Molar EDTA} = \frac{y \times z \times 100 \times 1000}{1000 \times 1} \text{ mg } CaCO_3$$

If V ml hard water contains $y \times z \times 100$ mg $CaCO_3$

1000 ml hard water contains

$$= \frac{y \times z \times 100 \times 1000}{V} \text{ mg } CaCO_3$$

OR

$$\text{Hardness of water} = \frac{y \times z \times 100 \times 1000}{V} \text{ ppm } CaCO_3$$

where V = volume of water sample titrated
 y = vol. of disodium EDTA (burette reading)
 x = molarity of disodium EDTA.

- To estimate Temporary & Permanent hardness

Permanent Hardness

Hardness of boiled & filtered water is found out by EPTA method.

Temporary Hardness

First total hardness is found out.

Then permanent hardness is subtracted from total hardness to get temporary hardness.

Advantages

- Colour change at end point is sharp.
- Fast, easy
- Suitable indicators available
- Accurate answer of hardness value

Alkalinity of water

- Water is alkaline due to presence of hydroxides, bicarbonates & carbonates.

Hydroxides - NH_4OH , NaOH , $\text{Ca}(\text{OH})_2$

Bicarbonates - $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Fe}(\text{HCO}_3)_2$, NaHCO_3

Carbonates - MgCO_3 , FeCO_3 , Na_2CO_3

Hydroxides & carbonates are stronger bases than bicarbonates.

Types of alkalinity

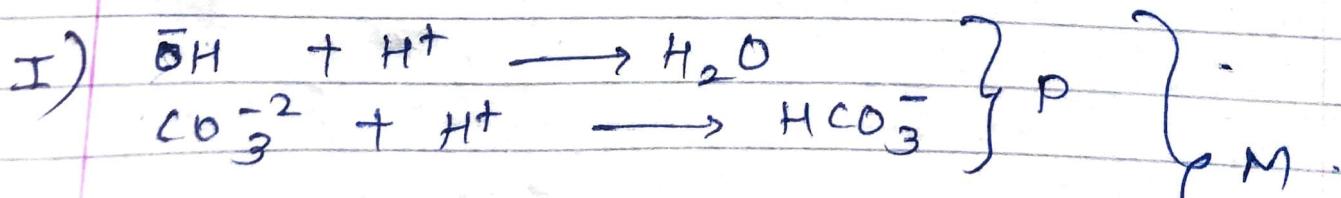
1) Phenolphthalein alkalinity

When an alkaline water titrated with a strong acid, first all OH get neutralised then all CO_3^{2-} ions are half neutralised to HCO_3^- .

At this stage, pH of reagent mix ≈ 8.2 . If completion of this stage is indicated by change in colour of phenolphthalein (Pink \rightarrow colourless endpoint)

2) Methyl orange / Total Alkalinity

On continued titration with acid all HCO_3^- get neutralised & this stage is indicated by methyl orange colour ($\text{pH}=4.5$)



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Procedure

- i) Take V_1 ml of alkaline water sample in a conical flask & add 2 drops of phenolphthalein.
- ii) Titrate this sample against standard strong acid soln ($Z\text{ N}$) from burette till pink colour changes to colourless. Let the burette be V_1 ml.
- iii) Add 4-5 drops of methyl orange indicator to the same titrating mixture and continue the titration till the yellow colour of mixture changes to orange. Note burette reading as V_2 ml.

Calculations I) phenolphthalein alkalinity

$$1000 \text{ ml } Z\text{ N HCl} \equiv 50 \text{ gm } \text{CaCO}_3$$

$$V_1 \text{ ml } Z\text{ N HCl} \equiv \frac{V_1 \times Z \times 50}{1000} \text{ gm } \text{CaCO}_3$$

i.e. $\frac{V_1 \times Z \times 50 \times 1000}{1000} = V_1 \times Z \times 50 \text{ mg } \text{CaCO}_3$

If V ml alkaline water contains $V_1 \times Z \times 50 \text{ mg } \text{CaCO}_3$
 1000 ml alkaline water contains

$$= \frac{V_1 \times Z \times 50 \times 1000}{V} \text{ mg } \text{CaCO}_3$$

OR

$$P = \text{phenolphthalein alkalinity} = \frac{V_1 \times Z \times 50 \times 1000}{V} \text{ ppm } \text{CaCO}_3$$

II) Total / Methyl orange alkalinity

Similarly, calculate for this part (as that of part I, P alkalinity).

M = Methyl orange alkalinity = total alkalinity

$$M = \frac{V_2 \times Z \times 50 \times 1000}{V} \text{ ppm CaCO}_3$$

V_1 = HCl burette reading upto Phenolphthalein end point

V_2 = HCl burette reading upto M.O. endpoint

Z = Normality of HCl

V = volume of alkaline water.

Possible combinations of alkalinites are

- i) Only \bar{OH}
- ii) Only CO_3^{2-}
- iii) Only HCO_3^-
- iv) \bar{OH} & CO_3^{2-} together
- v) CO_3^{2-} & HCO_3^- together



The amount of alkalinity due to OH^- , CO_3^{2-} , HCO_3^- types are calculated from table.

Alkalinity	Quantity of OH^-	Quantity of CO_3^{2-}	Quantity of HCO_3^-
$P = 0$	0	0	M
$P = \frac{1}{2} M$	0	$2P$	0
$P = M$	P	0	0
$P < \frac{1}{2} M$	$2P - M$	$M - 2P$	0
$P > \frac{1}{2} M$	$(2P - M)$	$2(M - P)$	0

Water Technology

Precipitation Titration - Chloride content

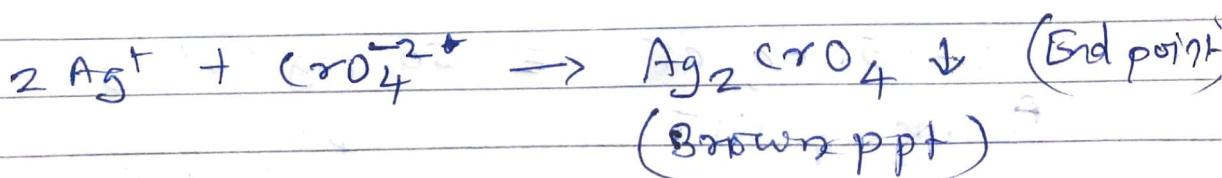
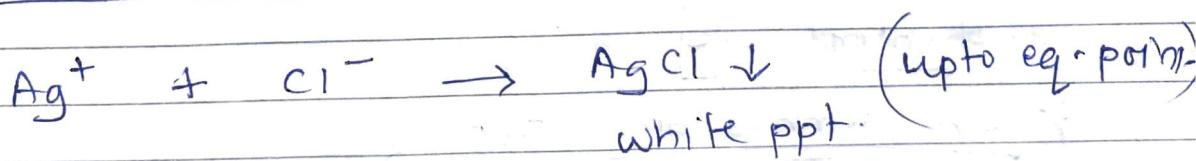
The titration during which reactants react to form water insoluble solid product, is known as Precipitation Titration.

Chloride content in water is determined by titration - precipitation titration method.

- * Highly alkaline pH leads to formation of Silver oxide (AgOH)
- * At low pH, dichromate may be formed which gives inaccurate result. Formation of CrO_4^{2-} i.e. Ag_2CrO_4 is desirable.
- * Alkaline pH of reaction mixture is required hence CaCO_3 can be added to achieve desired pH.

Chloride estimation by AgNO_3 is an Argentometric Titration.

Mohr's Method:



Procedure :

Burette : Std. AgNO_3 soln.

Pipette : chloride containing water

Indicator : K_2CrO_4 (yellow)

Endpoint : Yellow to Brown ppt

(Add CaCO_3 pinch)

Calculation : ratio of volumes straight

1 mole of AgNO_3 = 1 mole Cl^-

$$1000 \text{ ml } 1 \text{ N } \text{AgNO}_3 \equiv 35.5 \text{ gm } \text{Cl}^-$$

$y \text{ ml } \text{N } \text{AgNO}_3$ contains

$$(H_2O) \frac{y \times z \times 35.5}{1000 \times 1} \text{ gm } \text{Cl}^-$$

$$\text{chloride} = \frac{y \times z \times 35.5}{1000} \times 1000 \text{ mg } \text{Cl}^-$$

If, V ml chloride water contains

$$y \times z \times 35.5 \text{ mg } \text{Cl}^-$$

then, 1000 ml chloride water contains

y = Burette reading
 AgNO_3

$$\text{Cl}^- =$$

$$\frac{y \times z \times 35.5 \times 1000}{V} \text{ mg } \text{Cl}^-$$

z = conc. AgNO_3

V = vol. of chloride water

ppm Cl^-

* In terms of CaCO_3

$$35.5 \text{ mg } \text{Cl}^- \equiv 50 \text{ mg } \text{CaCO}_3$$

$$A \text{ mg } \text{Cl}^-$$

$$\text{mg of } \text{CaCO}_3 = \frac{50 \times A}{35.5} \text{ mg } \text{CaCO}_3$$

- chloride (content) ion conc. above 250 ppm is not acceptable

Dissolved Oxygen in Water (Redox Titration)

- 3) • Atmospheric oxygen is not readily soluble in water. Its solubility is directly proportional to its partial pressure.
- Measurement of O₂ gives idea about status of water system (Aerobic/Anaerobic). It is an indicator of water pollution. DO gives idea of about survival of aquatic life.
- DO is important factor causing corrosion of boiler material.
- DO saturation decreases with rise in temperature, salt conc., altitude and organic conc. Decrease of DO with increase in organic contaminants indicates pollution level of water bodies.
- DO level more than 3 mg/l is desirable for the existence and growth of fish and such aquatic life.

Normal river DO = 6 to 8 mg/l

- For estimation of DO content in sample, an iodide added to sample is oxidized under acidic conditions to free iodine. The amount of free iodine liberated is equivalent to the amount of DO in original water. The liberated iodine is estimated by titrating against std Na₂S₂O₃ soln using starch indicator. Amount of free iodine estimated is a measure of DO in water.

(Redox Titration)

Estimation of Dissolved Oxygen in given samples of water by Winkler's method.

Procedure: part I: Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ soln.

Burette: ~~set~~ $\text{Na}_2\text{S}_2\text{O}_3$ soln

(NK) Pipette: 0.025 N $\text{K}_2\text{Cr}_2\text{O}_7$ soln

Indicator: Starch solution.

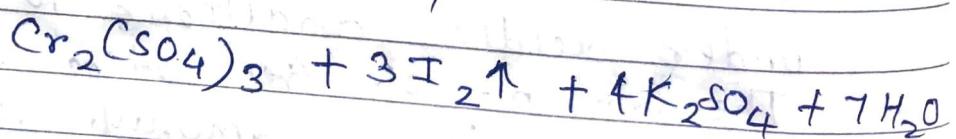
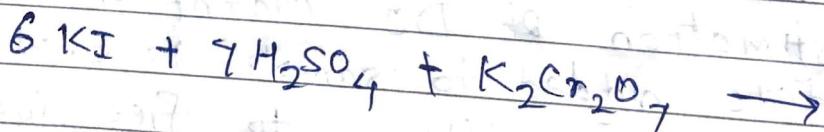
Endpoint: Blue to colourless

Take KI in conical flask. Add 100 ml distilled water (to suppress sublimation of iodine).

Add 10 ml dil. H_2SO_4 (9 ml dis. water + 1 ml conc. H_2SO_4). Add 10 ml 0.025 N $\text{K}_2\text{Cr}_2\text{O}_7$.

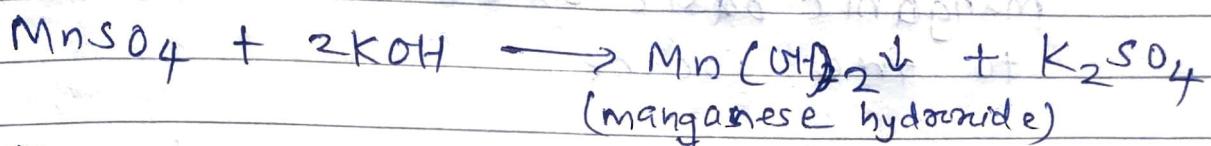
Add 100 ml drs. water (to prevent masking of starch endpoint). Wait 5 minutes to allow to release free iodine. Titrate against $\text{Na}_2\text{S}_2\text{O}_3$ till colour changes from blue to colourless. Let reading be V_1 ml. Calculate normality of $\text{Na}_2\text{S}_2\text{O}_3$ soln.

Reaction



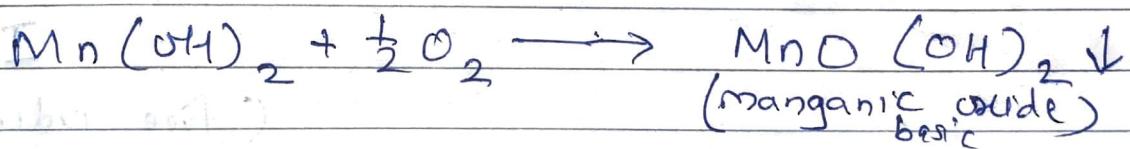
Part II : DO Fixation

Fill 300 ml BOD bottle completely with the sample. Tap bottle. Add 2 ml $MnSO_4$, add 2 ml alkali iodide azide soln using pipette. If DO is absent, a stable white ppt. of manganese hydroxide is formed.



The experiment may be stopped at this stage.

If DO is present, manganese ions are oxidised to manganic ions, a brown ppt. of manganic basic oxide is formed.



Part III : Determination of DO

Burette : Std 0.025 $Na_2S_2O_3$ soln.

Flask : Indicator soln. 2-3 drops

Indicator : Starch soln.

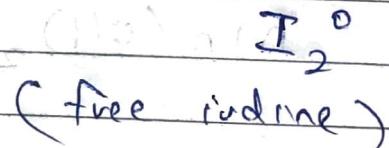
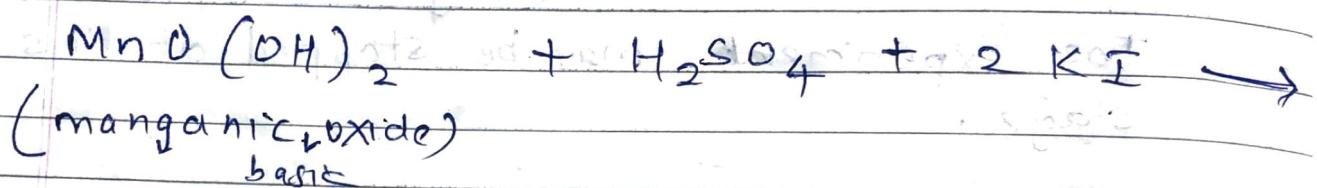
Endpoint : Blue to colourless

Ans:

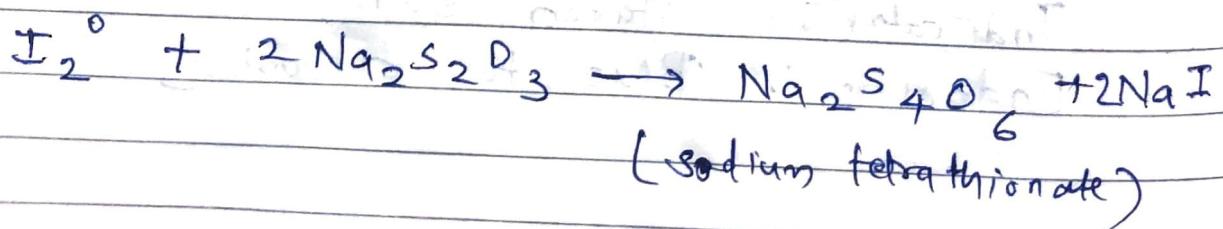
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Part III : Determination of DO

Mix contents of bottle by inverting it several times. Add 2 ml conc. H_2SO_4 . Stopper & mix by inverting. Yellow coloured free iodine solution is formed. Under acidic conditions, manganese basic oxide oxidizes free iodine to free iodine - $H_2O + \text{per cent}$.



Take above iodine soln in a flask. Titrate against std. $Na_2S_2O_3$ soln. using 1-2 ml starch indicator. Endpoint is blue to colourless (X ml).



Burette: Calculations

Part I : Standardization of $\text{Na}_2\text{S}_2\text{O}_3$



$$N_1 V_1 = N_2 V_2$$

Part III

Determination of DO

$$\text{Dissolved O}_2 = \frac{x \times N_1 \times 8}{200} \times 1000 \text{ mg/L}$$

III Effects of Hard water in steam generation

Major boiler problems are due to unsuitable water. The problems are -

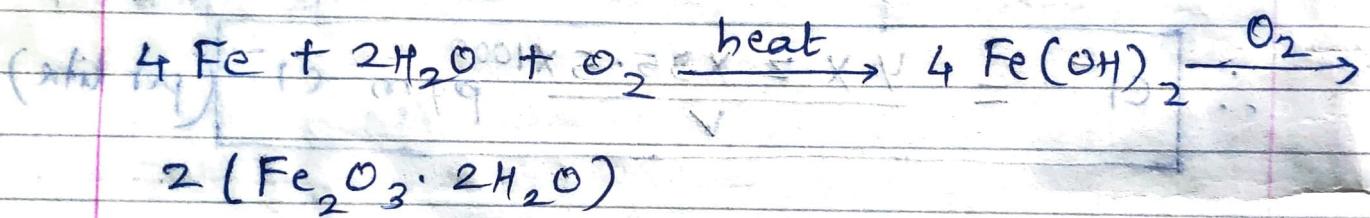
- A) Corrosion
- B) Priming & foaming
- C) Sludges and scales formation
- D) Caustic embrittlement

A) Corrosion

Boiler metal is steel.

Reasons for corrosion

a) Dissolved O₂



Removal of O₂ shd be there to prevent corrosion. O₂ removed -

I) By adding, Sodium sulphite (Na₂SO₃) or hydrazine (N₂H₄)



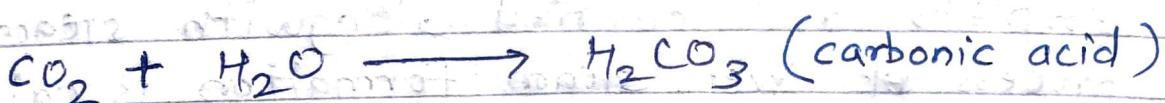
II) By using Mechanical de-aerator -

Vacuum created in tower & under pressure & heat water passed thru' tower.

ALC

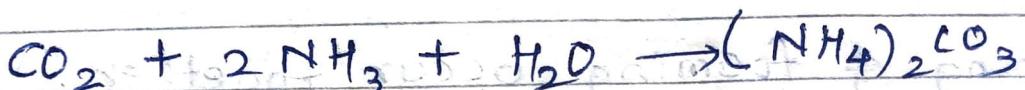
b) Dissolved CO₂

If water fed to boiler contains CO₂, it is converted to H₂CO₃ & corrodes boiler.



• Removal of CO₂ from water

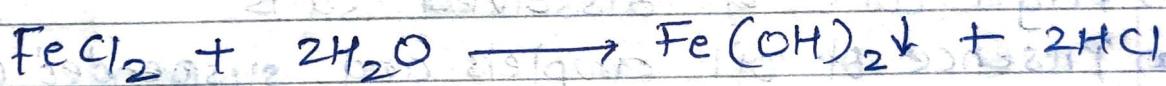
- (i) by adding NH₃



- (ii) Mechanical deaeration

c) Hydrolysis of salts

If water contains salts like MgCl₂, FeCl₂, then hydrolysis of such salts results in formation of strong acid which corrodes boiler.



To prevent corrosion due to acid, pH of boiler water shd be = 8.5 - 9.0

d) Galvanic cells

- Galvanic cell formation takes place in boiler due to different metals or impurities
- Galvanic cell corrosion can be avoided by suspending Zn plates which act as sacrificial anode in boiler. Zn acts as anodes and gets corroded & protects boiler metal from corrosion.

B) Priming and foaming

- When a boiler produces steam rapidly, water droplets are carried alongwith steam, this process or 'wet' steam formation is called as priming.
- Foaming is the formation of continuous foam or bubbles on the surface of water.

Priming & foaming occur together.

Priming Caused due to

- Very high level of boiler water
- Foam
- Faulty design of boilers
- High speed of steam generation
- Sudden drop in steam pressure

Foaming caused due to O.H.S + C.P.M

- High conc. of dissolved salts
- Presence of oil droplets and suspended materials
- Violent agitation of boiler-feed water

Disadvantages

- Height of water column can not be judged due to foaming
- Due to priming, salts in water enter in parts of machines.
- Due to priming, salts in water reduce efficiency of machine & cause corrosion.
- Foaming - wet corrosion.

Prevention

- 1) Foaming - by adding antifoaming agents like castor oil, by adding sodium aluminate, or by blow-down operation
- 2) Priming -
 - ① by using soft & filtered water
 - ② Low water level in boiler
 - ③ Using steam purifiers.

c) Sludges and scales formation

(I) Sludges

Loose, slimy mass of salts precipitated in boiler's water, is the sludge.

(a) Formation

- Formed at cooler portions of boiler & get deposited at slow flow rate areas.
- Removed by brushes, solutions, blow-down operations.

(b) Disadvantages

- Wastes heat
- Disturbs working of boiler & may choke up pipe
- Reduces water flow rate.

(c) Prevention of sludge

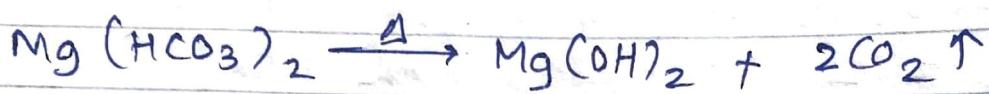
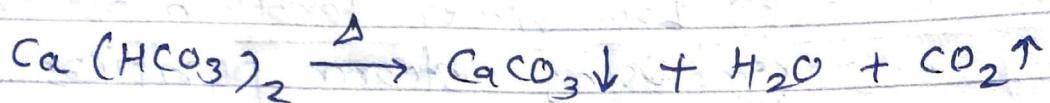
- Use of water containing low total dissolved solids
- Frequent blow down operations.

(II) Scales

Scale is the hard & strongly adhered coating to the inner surface of boiler and it is a bad conductor of heat.

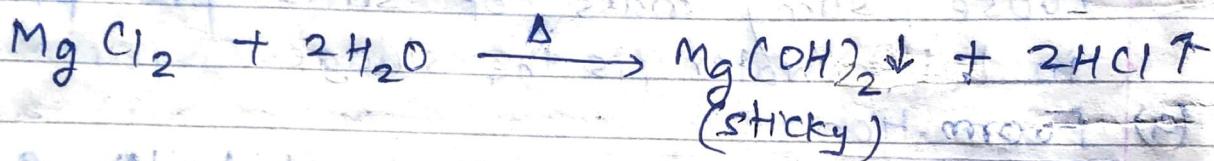
(a) Causes: scale formation

(i) Decomposition of bicarbonates



$\text{Mg}(\text{OH})_2$ & CaCO_3 are sticky & water insoluble

(ii) Hydrolysis of magnesium salts



(iii) Presence of Silica

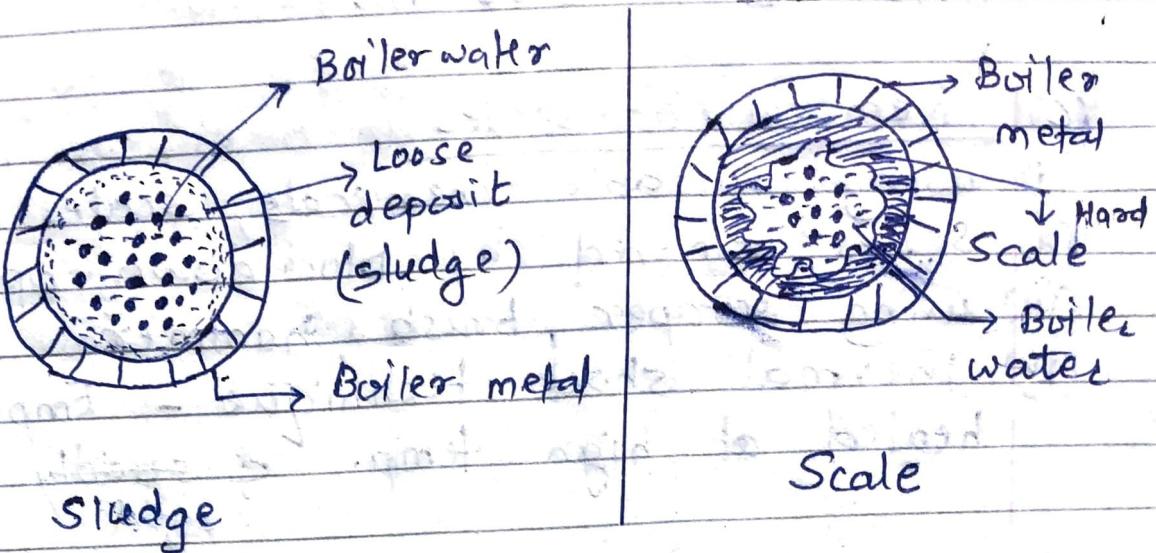
Silica in form of colloidal particles deposit as calcium silicate or magnesium silicate

(iv) Decreased solubility of CaSO_4

CaSO_4 has lesser solubility at high temperature
 $\therefore \text{CaSO}_4$ in water precipitated as hard scale material

Thus Scales are composed of CaCO_3 , $\text{Mg}(\text{OH})_2$,
 Silica, CaSO_4 as a coat.

Section of boiler tube showing sludge & scale



(B) Disadvantages of scales:

- (i) wastage of fuel: Scales are bad conductors of heat. Higher is the thickness of scale, greater is wastage of fuel. 0.25 cm scale increase fuel consumption by 2-3%.
- (ii) Over heating of boiler: Scales reduce transfer of heat from boiler to water in boiler. To keep required steam pressure, boiler shd be overheated.
- (iii) Boiler safety: Over heating of boiler makes boiler metal soft & weak. This causes distortion of boiler tube.
- (iv) Danger of explosion: When thick scale cracks due to uneven expansion, water comes suddenly in contact with overheated boiler metal. Due to this large amount of

heat is formed & high pressure is developed. Due to high pressure, softer boiler may burst with explosion.

(C) Removal of scales

- (i) using suitable chemicals, scales dissolved
- (ii) Scales removed by blow down operations
- (iii) using scraper, brush hammer
- (iv) Thermal shock technique - Empty boiler heated at high temp. & suddenly cooled.

(d) Prevention of scales

- (i) Use of softened water
- (ii) Adding sodium phosphate
- (iii) Frequent blow down operations
- (iv) Adding sodium aluminate to trap scale forming particles
- (v) Adding organic chemicals e.g. tannin forms coating on scale forming particles.

* Refer to Page No. 41 for Distinguish between Scales & Sludges

Distinguish between Sludge and Scale

Sludge	Scale
1) Sludges are loose and slimy precipitates	1) Scales are hard and adherent precipitates
2) Sludges are formed by the salts which are less soluble in cold water but soluble in hot water	2) Scales are formed by the salts which are less soluble in hot water but soluble in cold water.
3) Sludges are formed at cooler parts of the boiler.	3) Scales are formed at hot parts or regions of the boiler.
4) Sludges are formed due to increase in concentration of the salt. e.g. $MgCO_3$, $MgCl_2$, $CaCl_2$	4) Scales are formed due to decomposition of bicarbonates, hydrolysis of Mg-salts, less solubility in hot water shown by $CaSO_4$, presence of silica.
5) They can be removed by blown-down operation	5) They can be removed by EDTA treatment.
6) Sludges may lead to chocking up of pipe.	6) Scales may lead to bursting or explosion.

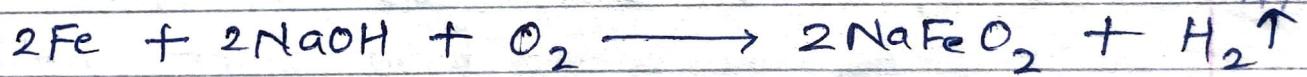
D) Caustic Embrittlement

- Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to accumulation of caustic substance.
- It is fast type of boiler corrosion caused by highly alkaline condition of water.
- When water softened by soda lime, it contains Na_2CO_3 .

After evaporation of water, Na_2CO_3 forms NaOH



- Due to NaOH , water becomes alkaline or caustic. This water creates minor cracks on inner surface of boiler.
- NaOH forms sodium ferrite with boiler metal.



This causes caustic embrittlement of boiler parts & leads to failure of boiler.

• Causes of Caustic embrittlement

- Presence of NaOH in water
- Leakages in joints
- High stress in metal

- Two types of cells forming during corrosion
- (i) Galvanic cell - stressed part acts as anode & unstressed as cathode.

- (2) Concentration cell - High conc. of NaOH in stressed part act as anode & lower conc. NaOH part as cathod.
- In both cases, anode gets corroded.

\oplus			\ominus
Iron at joints, bends	Higher conc. NaOH	Lower conc. NaOH	Iron at plain surface

- To avoid caustic embrittlement

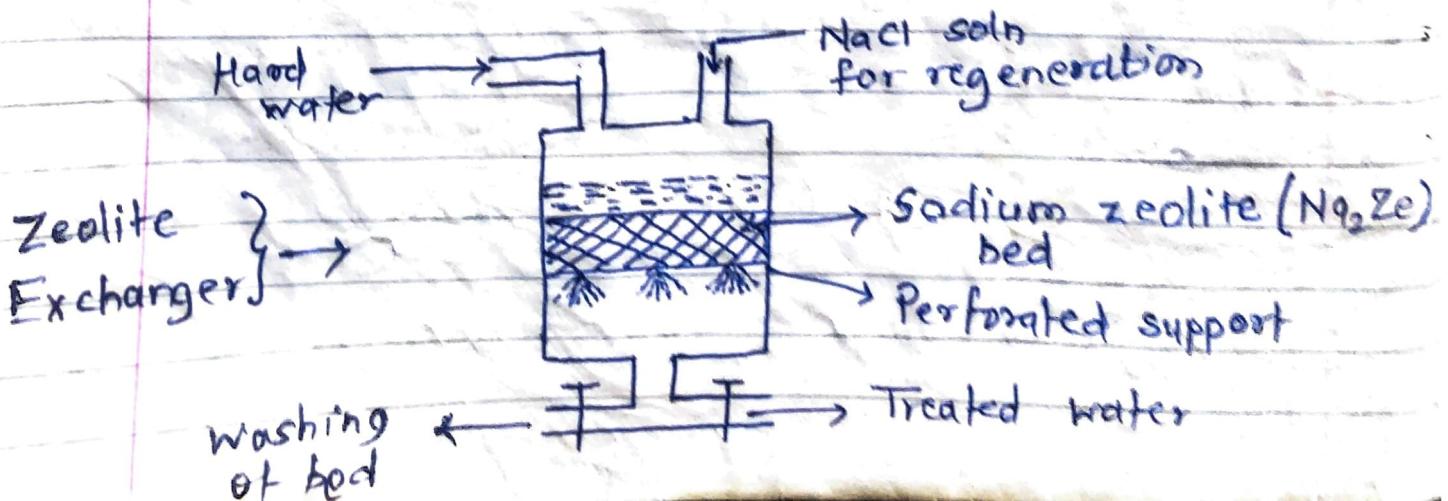
- Using sodium phosphate instead of sodium carbonate for softening water.
- Add tannin/lignin in boiler water, to block minor cracks.
- Adjust pH of water = 8-9

Softening of Water by Zeolites

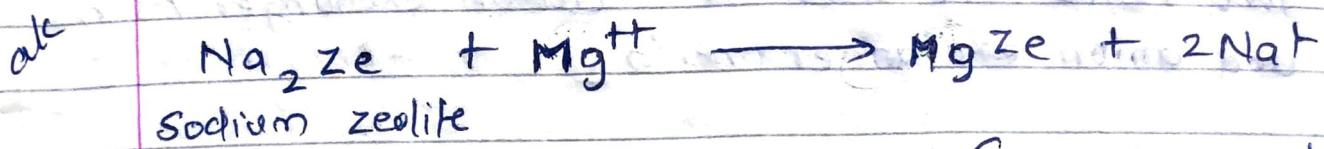
- Zeolites are complex mixture of metal silicates and metal aluminates.
- Sodium zeolites show property of exchanging heavy metal ions or organic cations in water, with their loosely held Na^+ ions.
- Zeolites are present in rocks or can be prepared by fusion of silica, soda & alumina.
- Sodium zeolites has structure like honey-combs.
- Principle - sodium zeolite has the property of capturing heavy metal ions from water and in exchange, release Na^+ . Due to removal of heavy metal ions, hard water converted into soft water, by zeolite.

Process

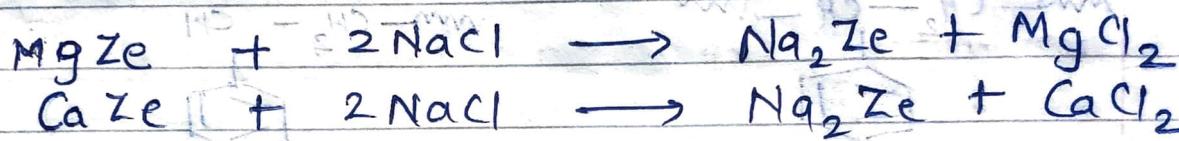
Zeolite exchanger/softener consists of cylindrical pot in which sodium zeolite is placed over a perforated plate. There is inlet at top for hard water & outlet for collecting soft water from bottom. 10% NaCl is added to regenerate exhausted zeolite bed.



- When water containing heavy metal ions or organic cations passes through zeolites, the cations from water are exchanged with Na^+ ions in zeolites.



- Regeneration: Exhausted zeolite bed is regenerated by washing it with 10% NaCl



Advantages

- Easy to operate
- Low cost operation
- Any type of hardness is treated

Limitations

- warm water can not be used
- Mn^{2+} , Fe^{2+} , get permanently captured by zeolite
- Output water contains sodium salts
- Water with colloidal impurities can not be processed as there is possibility of blocking the zeolite.

Applications

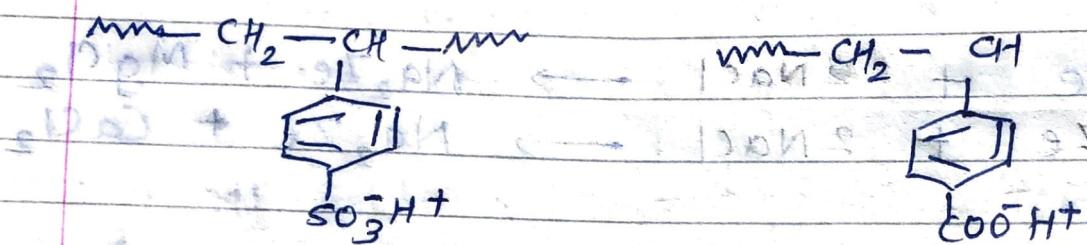
- to remove toxic metal ions & dye cations from water
- Can be used to recover valuable trace metals like Ni, Cr, Cu, Silver etc.
- applicable for small scale treatment.

Ion - Exchange (Deionisation) Process

- This method is used for obtaining pure water from ordinary water.
- Two resins are used i.e. cation exchanger resin and anion exchanger resin.

i) Cation exchanger resin

- Polymer having carboxylated /sulphonated aromatic rings attached to chain.

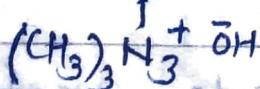
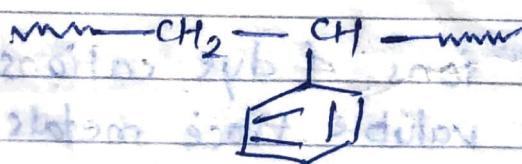


can be represented by formula H_2R .

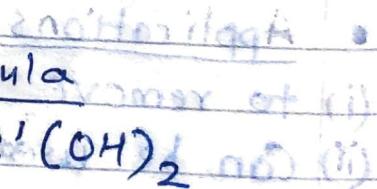
- $\text{H}^{\text{+}}$ are loosely held & can be easily exchanged with cations in water.

ii) Anion exchanger resin

- Polymer having aromatic rings with quaternary ammonium group.



Formula



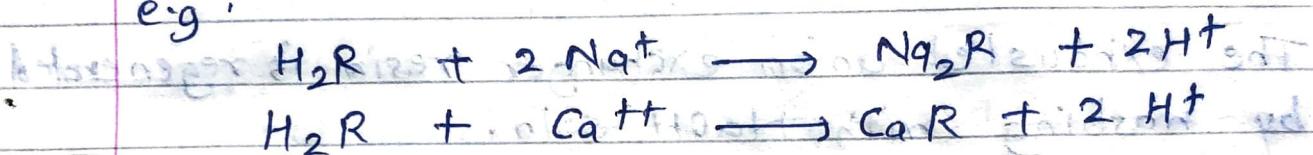
- OH^- ions are loosely held & exchangeable with all negative ions from water.

Principle

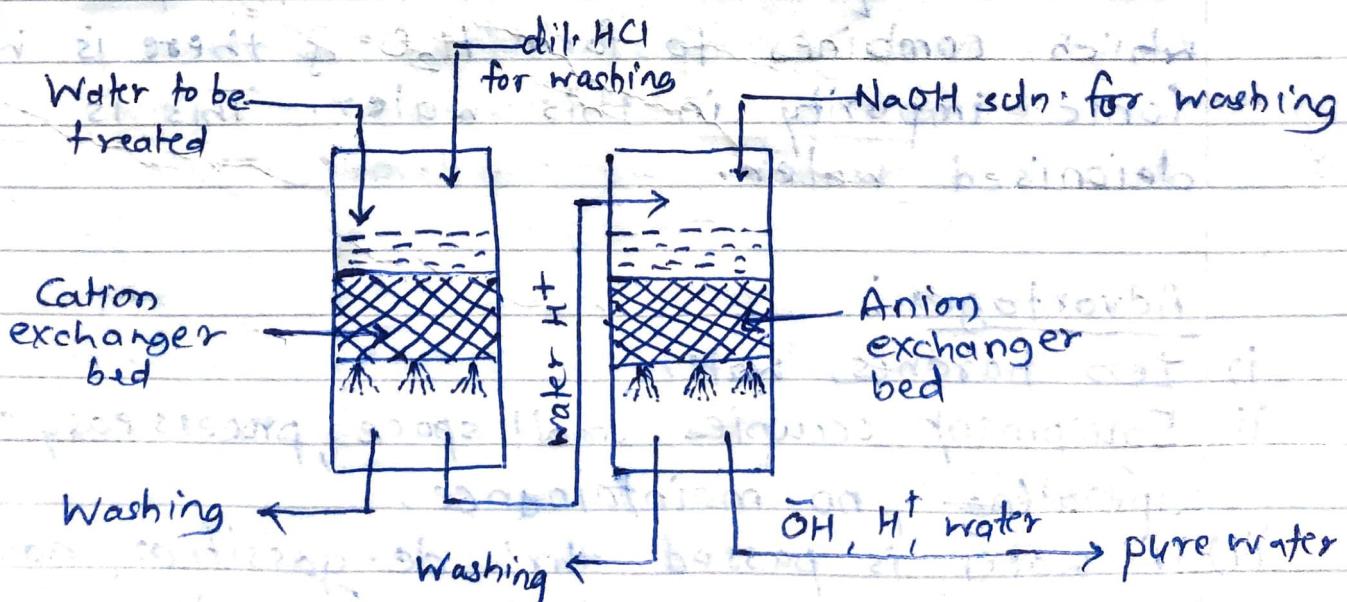
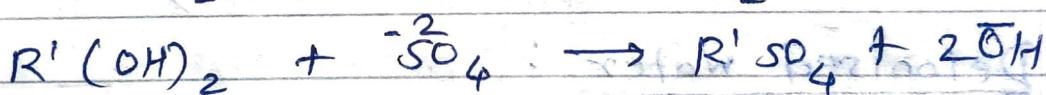
When water containing cations & anions is passed through resins, cation exchanger resin captures all cations (in exchange of H^+) and anion exchanger resin captures all anions (in exchange to OH^-), to give pure and all ions-free water.

Process

- Water enters in cation exchanger resin, where all cations are captured by resin & H^+ are released
e.g.



- Then this acidic water (with H^+) enters in anion exchanger resin where all anions are captured & OH^- are released.



Removal of hardness from water by deioniser

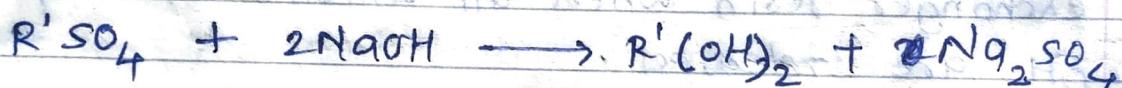
Regenerator

- The exhausted cation exchanger is regenerated by washing with HCl (dil) solution.



(regenerated resin)

- The exhausted anion exchanger resin is regenerated by washing with NaOH soln.



(regenerated resin)

Deionised water:

Water flowing out from second exchanger resin contains equivalent amounts of H^+ & OH^- ions which combines to form H_2O & there is no ionic impurity in this water. This is deionised water.

Advantages:

- Zero hardness water
- Equipment occupies small space, process easy to operate, no maintenance.
- If water is passed thr' de-gassifier, gaseous impurities are removed, to get water of 'distilled water' standard.

PHASE RULE

Gibb's Phase rule

- Phase rule is useful in study of heterogeneous equilibria
- It is possible to predict qualitatively, the effect of change in temperature, pressure & concentration on a heterogeneous equilibrium.
- The equilibrium may involve a physical or a chemical change.

Statement

The sum of number of degrees of freedom (F) and number of phases (P) is greater than number of components (C) by two, for a heterogeneous system.

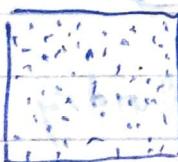
$$F = C - P + 2 \quad \text{OR} \quad F + P = C + 2$$

where F = Degrees of freedom, 2 = two additional variables operating on the system
 C = Number of components
 P = Number of phases (temp, pressure)

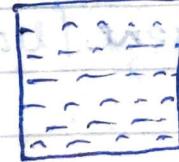
Phase (P)

A phase is physically distinct, chemically homogeneous and mechanically separable part of a heterogeneous system at equilibrium. (separated by a definite boundary).

I) Pure substance - Either solid or liquid or gas

Pure O₂

Pure Ice



Pure benzene

} One phase systems

5) The mixture of two solids

(i) Mix. of two allotropic forms of sulphur
i.e. monoclinic & rhombic sulphur.

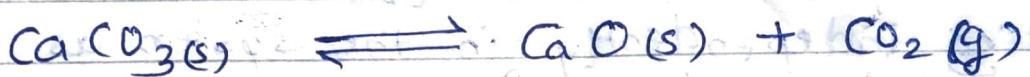
The chemical properties of these two forms are same but they are different physically.
∴ mix. constitutes two-phase system.

(ii) Two allotropic forms of carbon.

Diamond + Graphite = mixture

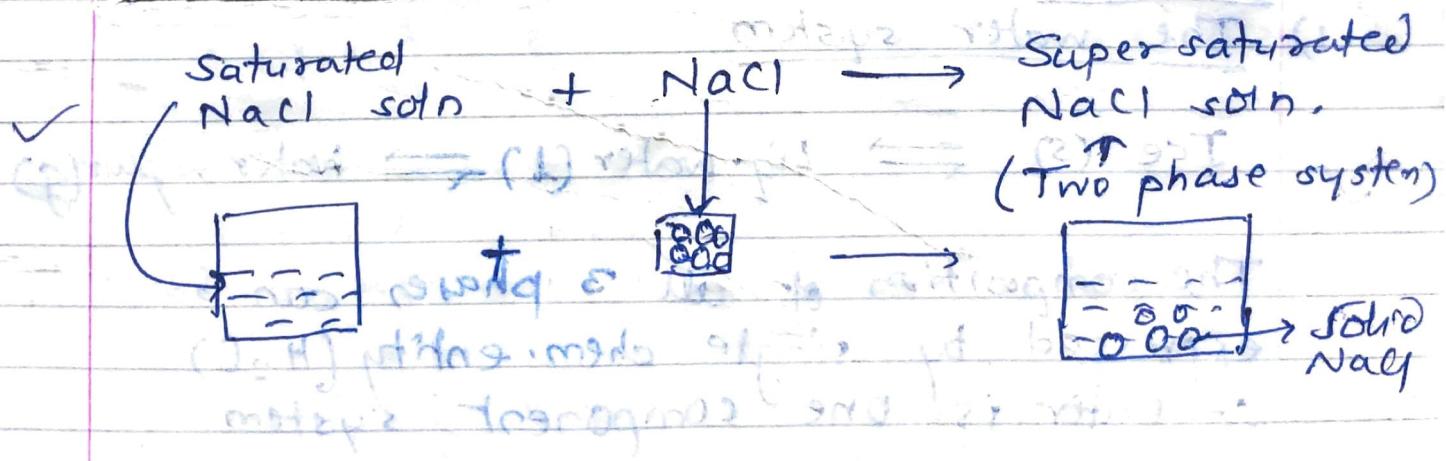
Differ in physical properties ∴ the mixture is 2-phase system.

(iii) Decomposition of CaCO_3 : Heat CaCO_3 in closed container



Two solids are physically & chemically different
∴ this is 3-phase system.

(iv) Aqueous solutions:



disagreed

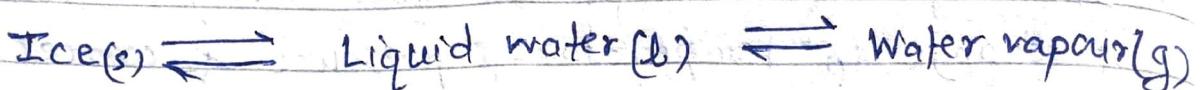
$$[\text{H}_2\text{O}] = 0.01 \text{ M}$$

$$[\text{H}^+] = 0.01 \text{ M}$$

$$[\text{OH}^-] = 10^{-13} \text{ M}$$

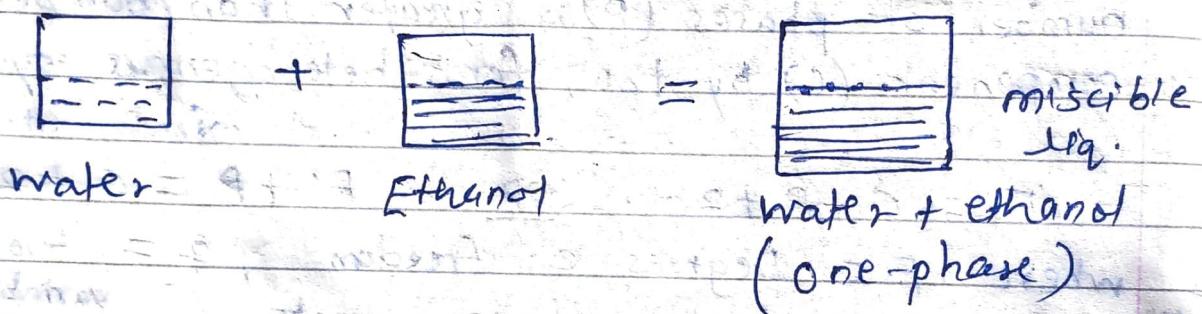
$$[\text{H}_3\text{O}^+] = 10^{-13} \text{ M}$$

- Consider water at freezing point (at 0°C)
At 0°C , the system will have all three phases present i.e. solid (ice), liquid and water vapour in equilibrium.



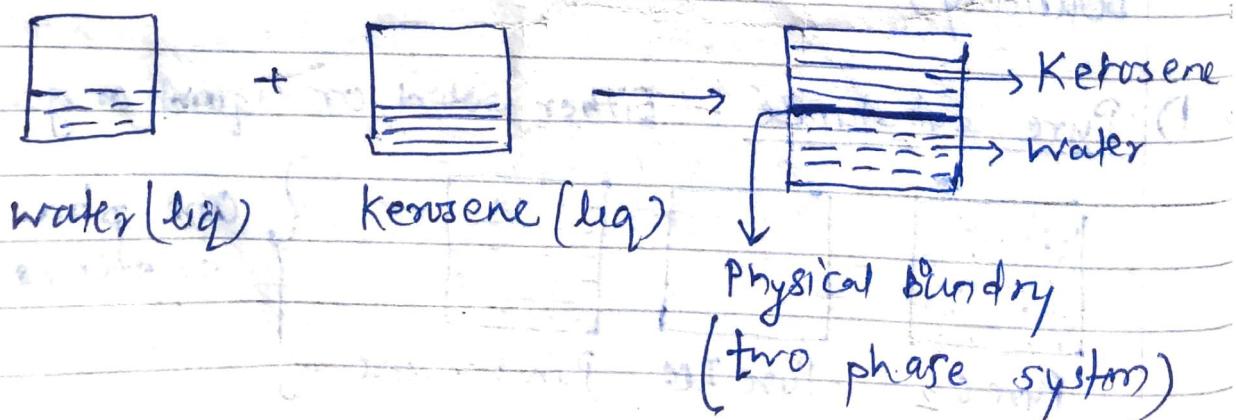
∴ this is 3-phase system.

- 2) Miscible liquids : If two completely miscible liquids obtain uniform soln, then it forms one-phase system (homogeneous system)



- 3) Mixture of gases - When two gases are mixed form a homogeneous mixture, they are one-phase systems.

- 4) Immiscible liquids : Kerosene & water are immiscible liquids



Component (C)

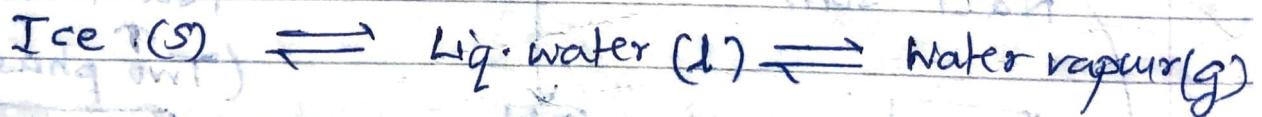
- A component is defined as the minimum no. of independent chemical species necessary to define the composition of all the phases present in the system either directly or in the form of a chemical equation.

- Rules for calculating no. of components in the system:

- On LHS, write chem. formula representing the phase composition
- on RHS, write rest of chem. constituents existing independently in the system as represented by chem. formulae
- The quantities of constituents of RHS can be made minus or zero in order to get composition of phas on LHS.

Example

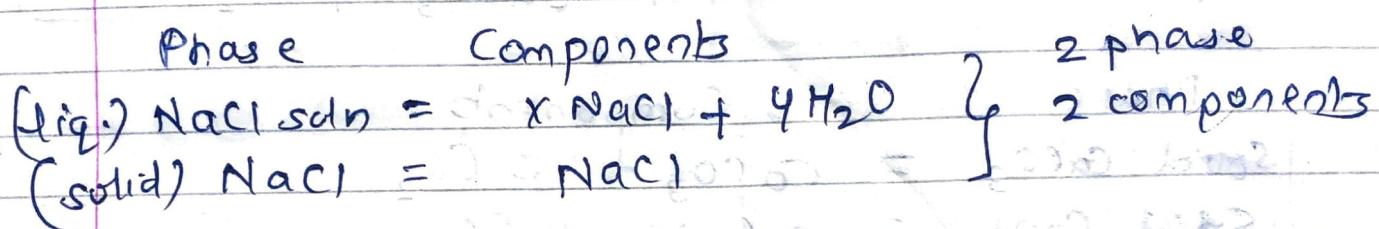
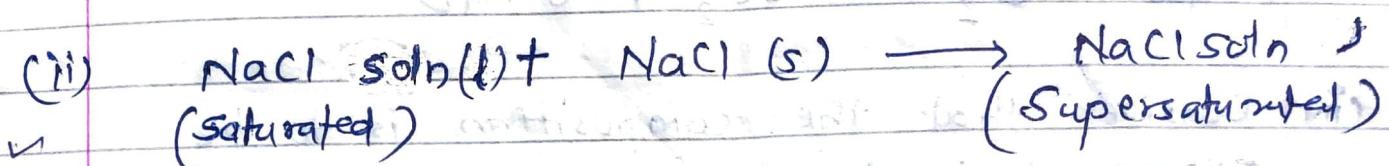
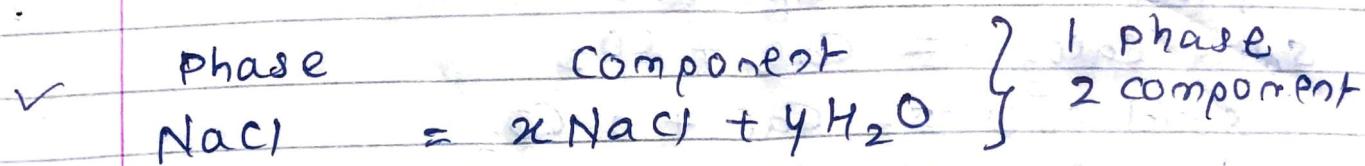
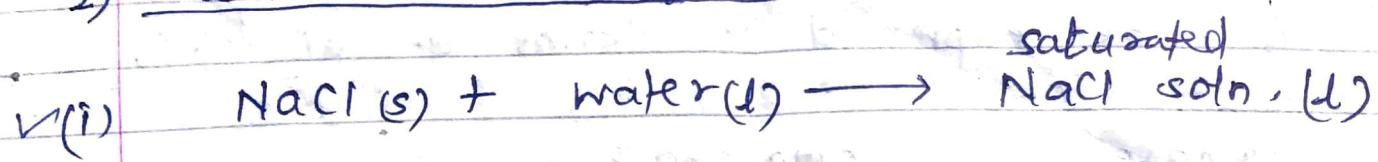
1) The water system



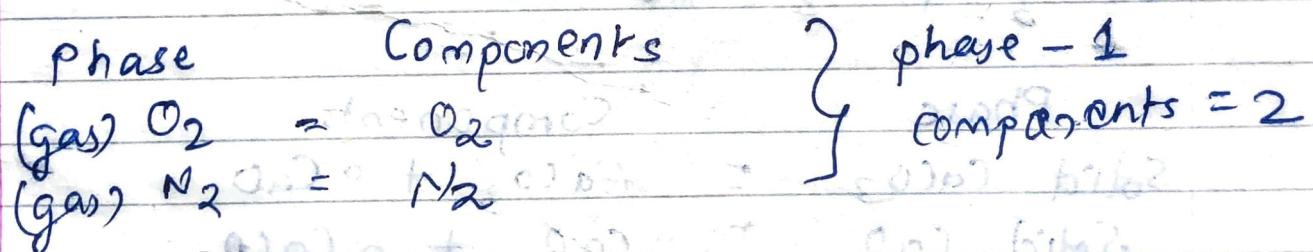
The composition of all 3 phases can be expressed by single chem. entity (H_2O)
 ∵ water is one component system

Phase	Components
(solid) Ice	= H_2O
(liquid) Water	= H_2O
(vapour) Water	= H_2O

2) Sodium chloride system



3) Mixture of gases : O_2 & N_2



4) Decomposition of CaCO_3 : When CaCO_3 is heated ~~start its to calcine in closed container.~~



Phases	Components
CaCO_3	Composition of all 3 phases can
CaO	be expressed with the help of two
CO_2	components only as \Rightarrow

(i) Consider that the composition of all phases is to be expressed in terms of CaO & CO_2

Phase	Components
Solid CaCO_3	$= \text{CaO} + \text{CO}_2$
Solid CaO	$= \text{CaO} + \text{CO}_2$
Gas CO_2	$= \text{CO}_2 + \text{CaO}$

(ii) Consider that the composition is to be expressed in terms of CaCO_3 & CO_2

Phase	Components
Solid CaCO_3	$= \text{CaCO}_3 + \text{CO}_2$
Solid CaO	$= \text{CaCO}_3 - \text{CO}_2$
Gas CO_2	$= \text{CaCO}_3 + \text{CO}_2$

(iii) Consider that the composition of all three phases is to be expressed in terms of CaCO_3 & CO_2 CaO

Phase	Components
Solid CaCO_3	$= \text{CaCO}_3 + \text{CaO}$
Solid CaO	$= \text{CaO} + \text{CaCO}_3$
Gas CO_2	$= \text{CaCO}_3 - \text{CaO}$

- To define the composition of all three phases, we need at least two phases.
 \therefore it is 3-phase, 2-component system.

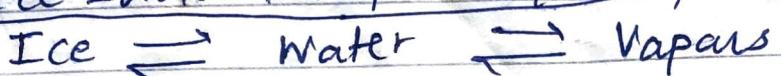
- Component of system means 'total no. of chemical entities required to describe all the phases in system.'

Degrees of freedom

It can be defined as 'the total number of factors that can be varied without altering the total no. of phases in the system at equilibrium'.

Example

(i) Ice-water-vapour system, F=0



by phase rule

No. of Phases = 3, No. of components = 0

$$F = C - P + 2 \\ = 1 - 3 + 2 = 0$$

∴ System is zero variant system

For water \rightarrow freezing temp. is fixed value

\rightarrow vapour pressure is fixed value

System has two variables temp. & pressure and both these are already fixed.

∴ No need to specify variable ∴ No degree of freedom.

(ii) Water-water vapour system, F=1



$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1$$

∴ system has one degree of freedom & it is monovariant system.

At definite temp., vapour pressure has only one fixed value & vice versa. Thus if one variable is specified, other automatically gets fixed.

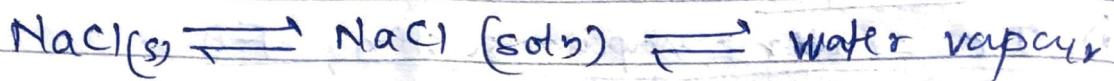
∴ water-water vapours has one degree of freedom

(iii)

Sat. NaCl soln. in eqm with solid NaCl & water vapour

$$\begin{array}{c} R \leftarrow \\ F = C - P + 2 \\ 2 - 1 + 2 \end{array}$$

component = 2



$$P = 3, C = 2$$

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 3 + 2 = 1 - 1 = 0 = 3 \end{aligned}$$

(iv) Pure gas,

$$P = 1, C = 1$$

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

(v) Mixture of gases: O_2 & N_2 std. b.p.

$$P = 1, C = 2$$

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

- * The degrees of freedom related to concentration of components are fixed

Phase Diagram

Phase diagram is a plot showing the conditions of either pressure and temperature or temperature and concentration or pressure & concentration under which two or more physical states (phases) can exist together in a state of dynamic eqm.

- Application of Phase rule to one component system

According to Phase rule

$$P + F = C + 2 \quad \text{or} \quad F = C - P + 2$$

For $C = 1$

when $P = 1$

$$F = 1 - 1 + 2 \therefore F = 2 \quad (\text{bivariant system})$$

when $P = 2$

$$F = 1 - 2 + 2 \therefore F = 1 \quad (\text{uni/Monovariant sys})$$

when $P = 3$

$$F = 1 - 3 + 2 \therefore F = 0 \quad (\text{Invant system})$$

for one component system, maximum # no. of degrees of freedom i.e., $F = 2$

such system can be completely represented by a two-dimensional diagram.

∴ Temp. & pressure are convenient variables (degrees of freedom) to describe eqm conditions of one component system.

- Phase Diagram for one component system

The equilibrium conditions in a one component system may be conveniently represented with the help of phase diagram, taking into consideration temperature & pressure.

These phase diagrams are known as pressure-temperature (p-t) diagrams.

Important parts of phase diagram are

- I) Area II) Boundary line/curve III) Point

I) Area : It represents bivariant system. Because to define system completely at any point in the area both temperature & pressure shd be fixed.

II) Boundary line or curve : Lines or curves represent monovariant system. Because equilibrium condition at any point on the line could be completely defined by either fixing temperature or pressure as the other variable gets fixed automatically.

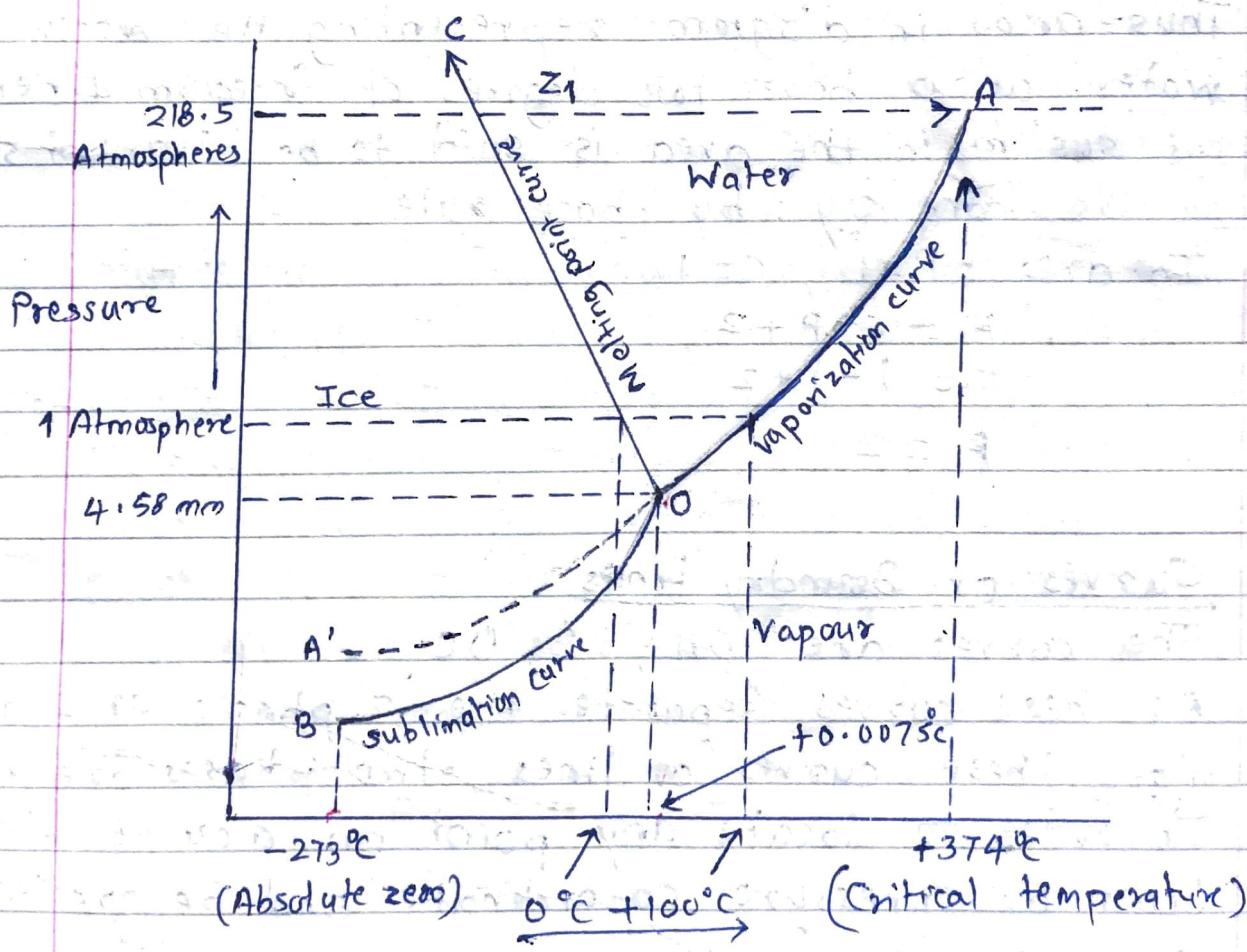
III) Point : Point in diagram, where the three lines meet, usually 3 phases are in contact with each other, represent an irvariant system. Because it is completely defined by itself.

• The Water System

For water system, component = H_2O (only one)

3 phases = ice, water, vapour

The actual no. of phases existing in the equilibrium at a particular instance depends upon the conditions of temperature & pressure. At different conditions of temperature & pressure, phase diagram for water system is as follows:



Water System

The phase diagram consists of

I) Areas: 3 areas i.e. AOB, AOC & BOC.

These areas represent conditions of temp. & pressure under which only one set of the 3 phases i.e. ice water, water vapour exist & is stable.

Area AOB : water vapour exist

AOC : water

BOC : Ice

In order to define the system completely at any point in the area, it is essential to specify both temp. and pressure co-ordinates to locate the point.

Thus areas in diagram, representing ice, water & water vapour have two degrees of freedom & hence, the system in the area is said to be bivariant system.

i.e. we can say, by phase rule

$$\text{In area, } P=1, C=1$$

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

II) Curves or Boundary Lines

The curves are OA, OB, OC.

As these curves separate the 2 phases or 2 areas along these curves or lines, two phases are in eqm.

In order to locate any point on a curve either temp. or pressure co-ordinates shd be specified because for fixed value of one co-ordinate, the second is automatically fixed. Thus, any point on boundary lines has one degree of freedom or system is uni or monovariant along the boundary line.

This also follows phase rule as $P=2$, $C=1$

$$\therefore F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

i) Curve OA : It divides liquid region from the vapour region. Thus along curve OA, water & water vapour co-exist. \therefore This curve is called as vaporization curve.

ii) Curve OB: Along OB, ice & water vapour co-exist and are at eqm. Curve OB is called as sublimation curve.

iii) Curve OC : It divides solid ice region from the liquid water region. Along OC, ice & water co-exist. Curve OC is called as melting point or fusion curve or freezing point curve.

III) Point

The curves OA, OB & OC meet in point 'O'.

This point 'O' is called the triple point. At this point, ice, water & water-vapour can co-exist and are at equilibrium. Only one set of condition is possible for 3 phases to exist. The triple point 'O' corresponds to a temperature 0.0075°C & a pressure 4.5 mm. At this point, system has zero degree of freedom which can be justified as

At point 'O', $P=3 \neq C=1$

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

\therefore System at triple point is non-reactant/invariant.

Water System

Number of components = 1

No.	Name of the system as represented in the phase diagram	Phases in eqm	Degrees of freedom $F = C - P + 2$
I	A Area	One	
	a) BOC	Ice	$F = 1 - 1 + 2$
	b) AOC below	Water	$\therefore F = 2$
	c) BOA	Water vapour	Binariant system
II	Curves	Two	
	a) OA (Vaporization)	Water & water vap.	$F = 1 - 2 + 2$
	b) OB (Sublimation)	Ice & water vapour	$\therefore F = 1$
	c) OC (Fusion or melting point)	Ice & water	Monovariant system
III	Point O (Triple point)	Three	$F = 1 - 3 + 2$
		Ice, water, water vapour	$\therefore F = 0$ (zero)
			Invariant system

Ques. If we draw invariant in 2D graph axis

$$1+2+3=6 \quad \text{LHS}$$

$$2+3-1=4$$

$$5+2-1=6$$

$$3=3$$

General feature of binary system is

Applications of Phase Rule

- applicable to physical and chemical eqm
- predicts the behaviour of a system under different sets of variables.
- applicable to macroscopic systems.

Limitations of Phase Rule

- Fails for slow equilibrium systems
- All phases must be present simultaneously under given sets of conditions like temp. & pressure.
- does not give information if solid-liquid phases are present in finely divided state, otherwise deviations occur.
- Care is required in deciding no. of phases existing in eqm since ~~is~~ no. of phases are required than their amounts.