

Welcome

To

Engineering Chemistry

molecule

Course Code: BSH21A04 (Sem I)

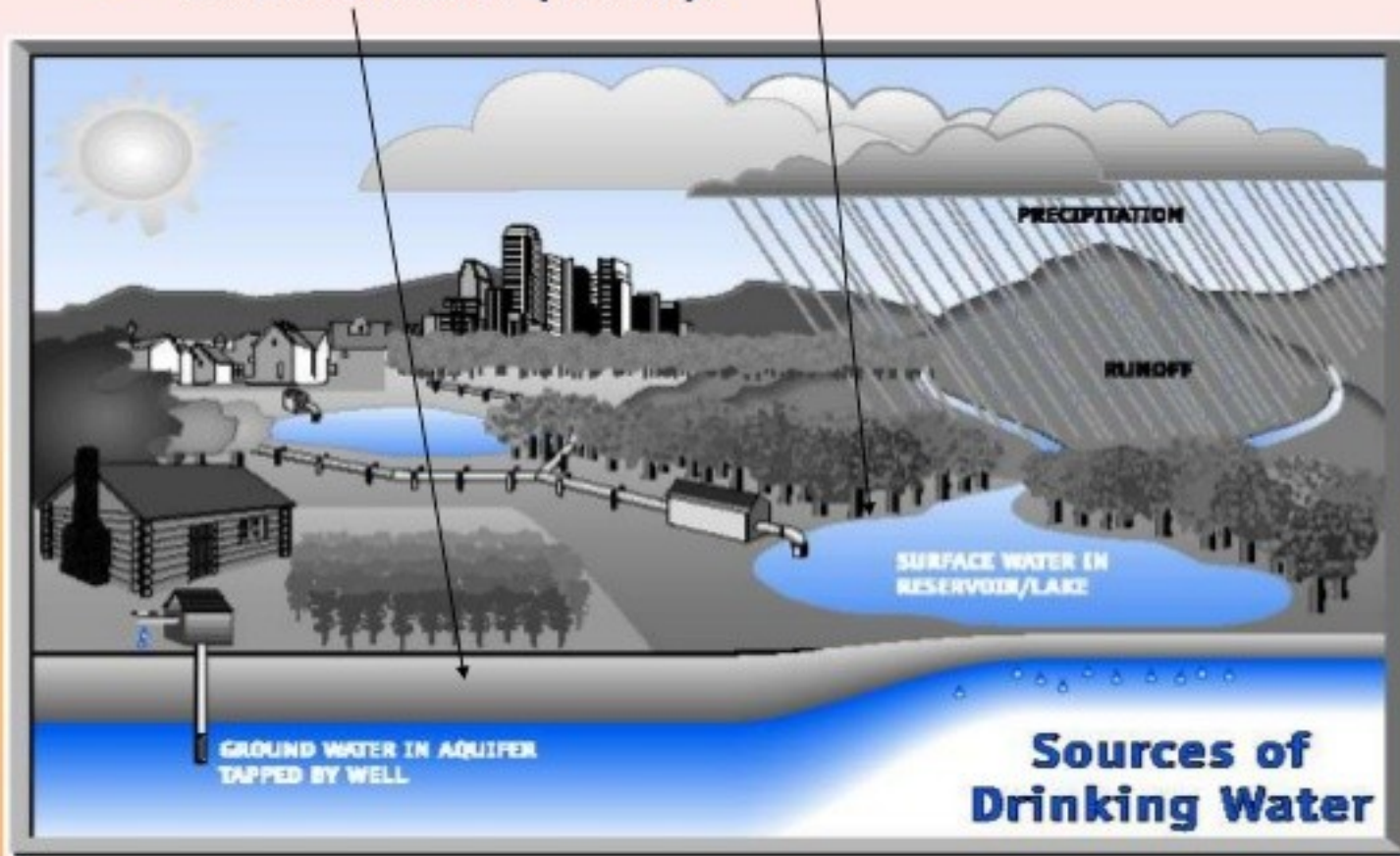
BSH22A04 (Sem II)

Unit - 1

Water Technology

WHERE DOES THE WATER COME FROM?

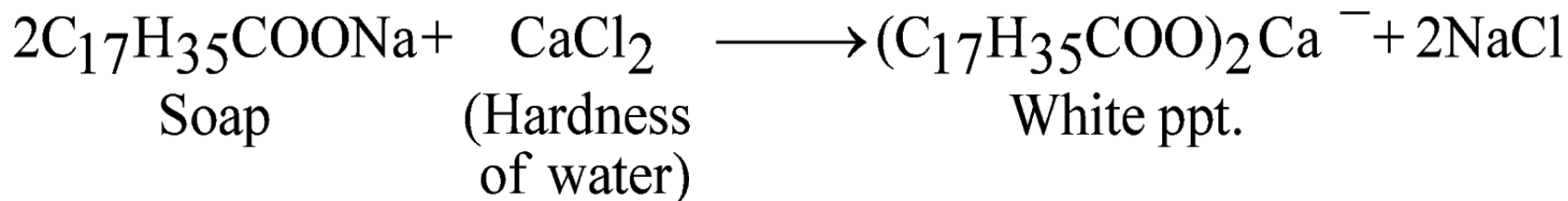
- *Surface waters (lakes, rivers, and reservoirs)*
- *Groundwater (wells).*



Hard Water

It is the water which interferes with Lather (foam) formation during washing with soap. Instead of foam, scum (curdy white ppt) is formed.

This happens due to presence of minerals in water.



Hardness of Water

Hard Water

□ Do not form lather with soap rather
Precipitate is formed

□ Contains heavier cations like Ca^{2+}
 Mg^{2+} , Fe^{2+} , Mn^{2+} , Al^{3+} ,

□ These cations make water hard

□ Such water is harmful for boiler
Machine need not to mention
their harm on human bodies

Soft Water

Forms lather with soap

Contains lighter cation like
 Li^+ , Na^+

These ions do not make
water hard

This water is safe for
industrial as well as domestic
use

Types of Hardness of Water

Permanent and Temporary Hardness

Total Hardness = Permanent hardness + Temporary Hardness

Temporary Hardness (Alkaline hardness): due to alkaline nature of water i.e. they have bicarbonates, Carbonates or hydroxides of Ca and Mg ions also called as alkaline hardness.

$\text{Ca}(\text{HCO}_3)_2$, CaCO_3 , $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{HCO}_3)_2$, MgCO_3

Mode of Removal: By boiling water



Permanent Hardness

- Also known as **non-alkaline hardness**:

Ca and Mg ions sulphates, chlorides and nitrates

MgCl_2 , MgSO_4 , CaCl_2 , CaSO_4 , CaNO_3 , MgNO_3

- Not removed by filtration but requires chemical methods for separation and making hard water soft.

Units of Hardness:

1) Parts per million = 1 part CaCO_3 equivalent hardness in 1000000 parts of water

2) Milligram per litre (mg/l) = no. of milligram equivalent hardness per liter.

1mg/l = 1 mg of CaCO_3 in 1 litre of water

we know 1000ml of water = 1000 g = 1000x1000mg of water

Therefore

1mg/litre = 1 ppm (1mg of CaCO_3 equivalent in 1000000mg of water)

CaCO₃ Equivalence of Few chemicals

$$\text{Hardness of water} = \frac{\text{weight of chemical} \times 100}{\text{mol. Wt. of chemical}}$$

$$\text{or} \quad = \frac{\text{weight of chemical} \times 50}{\text{equiv. Wt. of chemical}}$$

Remember: 1mol of CaSO₄ = 1mol CaCO₃,

1mol Mg(HCO₃)₂ = 1mol CaCO₃,

1mol MgCl₂ = 1mol CaCO₃

Calculate their CaCO_3 equiv. of following in 1 liter of water sample.

$$\text{CaSO}_4 = 20\text{mg},$$

$$\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg},$$

$$\text{MgCl}_2 = 12.5 \text{ mg}$$

Mol wt. :

$$\text{CaSO}_4 = 136,$$

$$\text{Mg}(\text{HCO}_3)_2 = 146,$$

$$\text{MgCl}_2 = 95\text{g/mol}$$

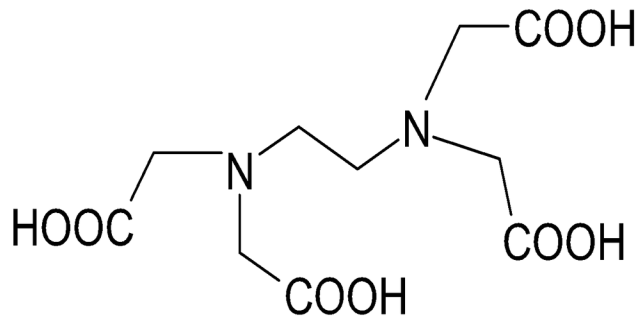
$$\text{CaCO}_3 \text{ equiv. of CaSO}_4 = \frac{20 \times 100}{136} = 14.7\text{mg/l}$$

$$\text{CaCO}_3 \text{ equiv. of Mg(HCO}_3)_2 = \frac{14.6 \times 100}{146} = 10\text{mg/l}$$

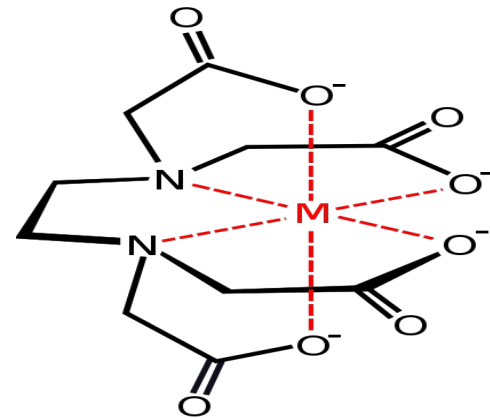
$$\text{CaCO}_3 \text{ equiv. of MgCl}_2 = \frac{12.5 \times 100}{95} = 13.6\text{mg/l}$$

Determination of Hardness by EDTA method

What is EDTA: Ethylene diamine Tetra acetic acid. It forms soluble complex with metal ion. It's a complexometric titration.



EDTA



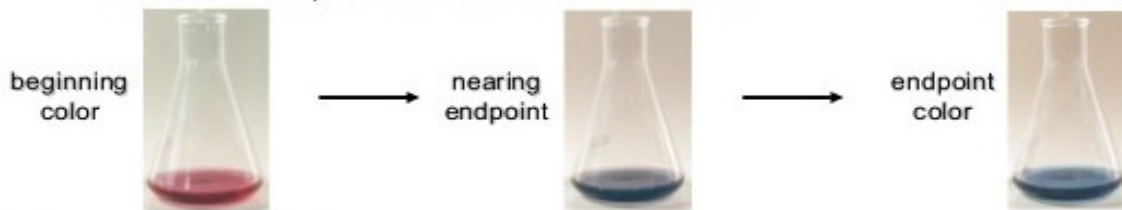
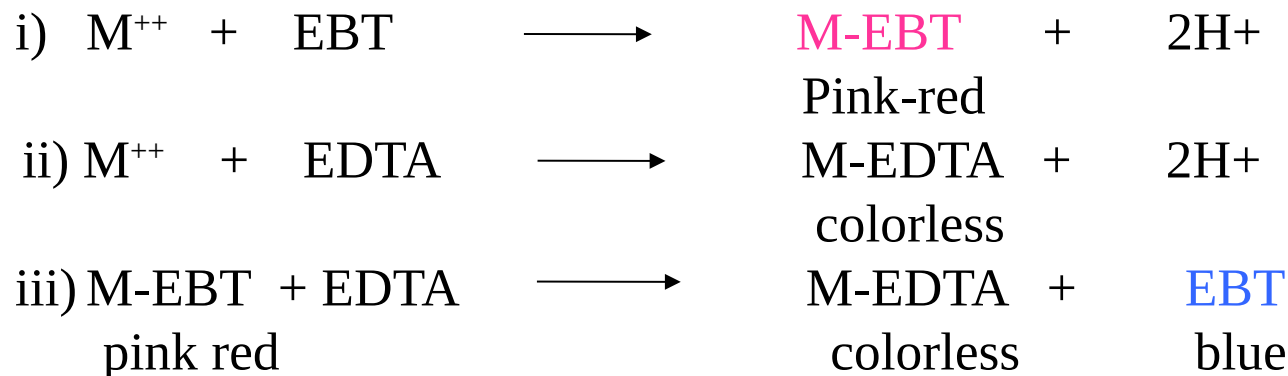
EDTA-Metal complex



Method

1. Pipette out 50 ml of given water sample in 250ml conical flask
2. Add 3-5 ml of ammonia-ammonium chloride buffer for pH 10
3. Add 1-2 dps of Eriochrome black indicator colors is wine red
4. Titrate against 0.01 M EDTA till wine red changes to blue coloration
Record volume of EDTA added in V ml and calculate hardness of water

Reactions:



Calculations:

1000ml 1 M EDTA = 1 mole of CaCO_3 = 100gm of CaCO_3

“v”ml M_2 M EDTA = $\frac{v \times M_2 \times 100}{1000}$ of CaCO_3

if V ml of hard water sample contains = $\frac{v \times M_2 \times 100}{1000}$ g of CaCO_3

then 1000ml of hard water sample contains = $\frac{v \times M_2 \times 100}{V}$ g

Total Hardness of Water sample = $\frac{v \times M_2 \times 10^5}{V}$ mg of CaCO_3 per lit

Where,

v: ml of EDTA used in titration

M2: molarity of EDTA

V: volume of hard water sample

Numerical based on EDTA titration

PROBLEM: 50 ml of water sample requires 12.2 ml of 0.02 M EDTA during the titration. 50 ml of boiled water sample requires 8.2 ml of EDTA. Calculate temporary, permanent and total hardness.

Solution: Given: Molarity of EDTA solution = $M = 0.02M$

Volume of Hard water = $V = 50 \text{ ml}$

Volume of EDTA before boiling = $v_1 = 12.2 \text{ ml}$

Volume of EDTA after boiling = $v_2 = 8.2 \text{ ml}$

a) **Total Hardness** (before boiling):
$$= \frac{v_1 \times M \times 10^5}{V} = \frac{12.2 \times 0.02 \times 10^5}{50}$$
$$= 488 \text{ ppm CaCO}_3 \text{ eq.}$$

b) **Permanent Hardness** (after boiling):
$$= \frac{v_2 \times M \times 10^5}{V} = \frac{8.2 \times 0.02 \times 10^5}{50}$$
$$= 328 \text{ ppm CaCO}_3 \text{ eq.}$$

Alkalinity of Water and its Determination

- “It means the acid-neutralizing capacity of water sample”
- Alkalinity of water is because of carbonates (CO_3^{2-}), Bicarbonates (HCO_3^-), and OH^- content and often interpreted in terms of their concentration

□ Why determination of alkalinity of water important?

For determining suitability for irrigation, industrial use, raw water or waste water monitoring.

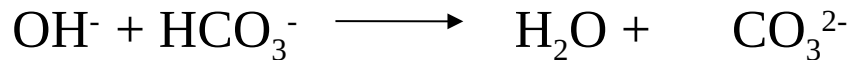
- It is important indicator of water body's ability to resist pH change due to accidental acid spill or acid ppt.

Types of Alkalinity

Five possibilities for alkaline water are:

- i) Only hydroxide (OH^-)
- ii) Only Carbonates (CO_3^{2-})
- iii) Only bicarbonate (HCO_3^-)
- iv) Hydroxide and carbonate (OH^- & CO_3^{2-})
- v) Carbonate and bicarbonate (CO_3^{2-} & HCO_3^-)

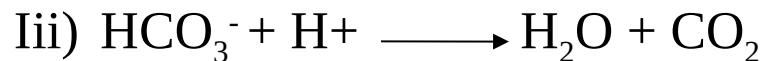
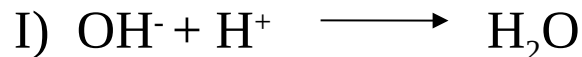
Combination of hydroxide and bicarbonate is not possible since they combine to form carbonate



Principle

Alkalinity of water can be determined by titrating it against standard acid using indicators phenolphthalein and methyl orange. Hence it is an acid neutralization titration.

Reactions:



Phenolphthalein end point: Titrating alkaline water with acid using phenolphthalein indicator will indicate completion of reaction i + ii

The end point (V1) marks the complete neutralization of OH^- and half neutralization of CO_3^{2-} (since carbonate neutralizes in two steps)

Methyl orange end point: Continuing titration with methyl orange against acid up to methyl orange end point (V2) indicate completion of reaction i+ii+iii. It indicates total neutralization.

Determination

Take 100 ml of water sample ↓ in 250 ml Conical flask

Adjust pH ↓ > 8.3

Add few dps of phenolphthalein indicator

Titrate with 0.02 N H_2SO_4 / HCl till pH endpoint
i.e. colorless solution obtained

Note V1 Volume of acid needed it is **P** (phenolphthalein alkalinity)

If pH < 8.3 add bromocresol or methyl orange indicator

Continue titration with 0.02 N H_2SO_4 or HCl till pH 4.5

V2 ml acid required to reach end point it is **M** (total alkalinity)
or methyl orange alkalinity



Phenolphthalein end point



Methyl orange end point

Calculations for total alkalinity Table

Alkalinity Relationships			
Result of P/M or P/T Alkalinity Test*	Hydrate Alkalinity (OH) Equals:	Carbonate Alkalinity (CO ₃) Equals:	Bicarbonate Alkalinity (HCO ₃) Equals:
$P = 0$	0	0	M
$P = M$	M	0	0
$P = \frac{1}{2} M$	0	M	0
$P < \frac{1}{2} M$	0	2P	M-2P
$P > \frac{1}{2} M$	2P-M	2(M-P)	0

*Note: Because the endpoints for methyl orange and total alkalinity indicator are nearly identical (pH 4.6 and pH 4.5, respectively) the industry uses both indicators interchangeably for reading total alkalinity. **Therefore, the values for M and T can be interchanged in the table above.**

Calculations

a) Phenolphthalein alkalinity (P): Alkalinity is expressed as parts per million in terms of CaCO_3

As 1000ml of 1N HCl = 50 gm of CaCO_3

$$\text{"V}_1\text{" ml of N normality Acid} = \frac{\text{V}_1 \times \text{N} \times 50}{1000} = \text{A gm of CaCO}_3$$

If V ml of alkaline water sample contains = A gm of CaCO_3

then 1000ml of alkaline water sample contains = $\text{A} \times 1000/\text{V} = \frac{\text{V}_1 \times \text{N} \times 50}{\text{V}}$ gm of CaCO_3

Therefore,

$$\mathbf{P} = \frac{\text{V}_1 \times \text{N} \times 50 \times 10^3}{\text{V}} \text{ mg of CaCO}_3 \text{ per litre}$$

b) Methyl orange alkalinity (M): Similarly if “V₂” ml of N normal acid required for methyl orange end point then methyl orange alkalinity **M** is

$$\mathbf{M} = \frac{\text{V}_2 \times \text{N} \times 50 \times 10^3}{\text{V}} \text{ mg of CaCO}_3 \text{ per litre}$$

Sample Numerical

100 ml of water required 20 ml N/50 H_2SO_4 for neutralization to phenolphthalein end point After this methyl orange indicator was added and further acid required 20 ml. Calculate alkalinity of water as CaCO_3 in ppm.

Solution: Given: V = volume of water = 100ml, Normality of acid = N = 0.02N

V1 = 20 ml, V2 = P+M=20+20=40 ml. Hence

$$\mathbf{P} = \frac{\mathbf{V_1 \times N \times 50 \times 1000}}{\mathbf{\text{Volume of water sample}}}$$

$$\mathbf{P} = \frac{20 \times 0.02 \times 50,000}{100} = 200\text{mg equiv./lit.}$$

$$\mathbf{M} = \frac{\mathbf{V_2 \times N \times 50 \times 1000}}{\mathbf{\text{Volume of water sample}}}$$

$$\mathbf{M} = \frac{40 \times 0.02 \times 50,000}{100} = 400\text{mg equiv./lit.}$$

Since $\mathbf{P} = \frac{1}{2} \mathbf{M}$

Hence type is: $\mathbf{CO_3^{2-}}$ only

Hard water Treatment

Effects of hard water in boilers:

give rise to major problems in boilers like:

- a) Corrosion
- b) Priming and foaming
- c) Sludges and scale formation
- d) Caustic embrittlement





CORROSION

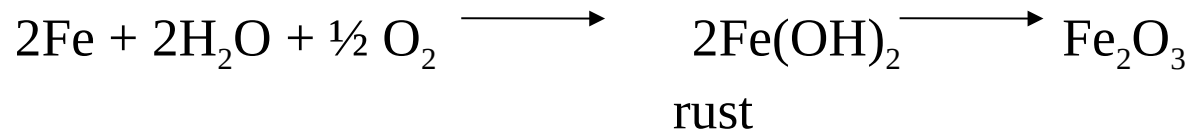


Corrosion

- ☐ Serious problem
- ☐ Reduced boiler life , Leakage of joints and valves
- ☐ Increased cost for repair and maintenance

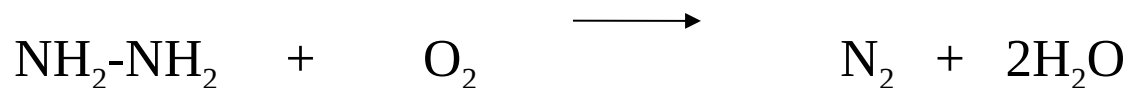
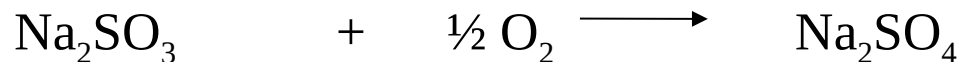
Reason:

1)Dissolved gases: Oxygen: corrodes iron of boiler by following reaction



Removal:

a) Add Na_2SO_3 (sodium sulphite) or hydrazine $\text{NH}_2.\text{NH}_2$



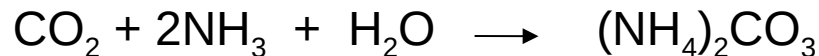
b) Mechanical deaeration

2) Carbon dioxide (CO₂):

If water containing CO₂ is fed to boiler, it forms carbonic acid H₂CO₃ which is very harmful for boiler.

Removal:

a) Add NH₃



b) Mechanical de-aeration

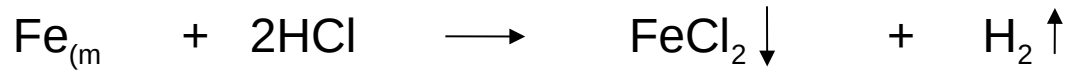
3) Hydrolysis of salts: e.g. MgCl₂, FeCl₂

Dissolved magnesium salts liberate acid on hydrolysis. The acid then reacts with iron metal of the boiler in a chain reaction producing HCl again and again. Hence even small amount of Mg-salts can cause considerable corrosion of boiler metal.



Solution to the problem of hydrolysis of salts:

- Boiler water should not have salts. They should be removed by Zeolite or ion-exchange process.
- Maintain pH 8.5-9.0 to avoid acid problems



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B) Priming and Foaming (carry over)

- ❖ Due to fast steam production, some water droplets carried along with steam makes “**Wet steam**” is called **priming**.
- ❖ Formation of continuous foam or bubbles on the surface of water is called “**Foaming**”.

Reasons for Priming:

- ☐ Very high level of boiler-feed water
- ☐ + nce of excessive foam
- ☐ High speed steam generation
- ☐ Faulty boiler design
- ☐ sudden drop in pressure

Reason for Foaming

- High conc. of dissolved salts in boiler feed water
- Presence of oil droplets and alkali
- Presence of finely dispersed suspended particles
- Violent agitation

Disadvantages:

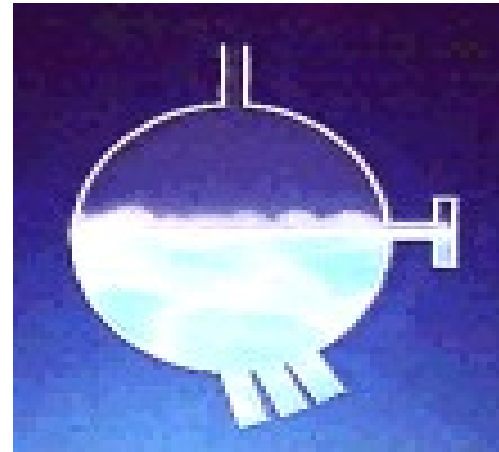
- ❖ Actual height of water cannot be found well
- ❖ Salts deposit on evaporation of water leading to reduced efficiency of machinery

Prevention of priming and foaming

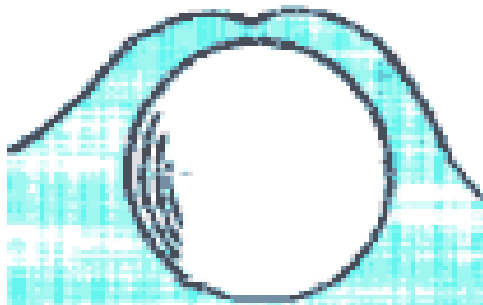
- ❖ By addition of antifoaming agents like castor oil or removing oil by adding Chemicals like sodium aluminate and blow-down operation
- ❖ Priming – preventable by use of softened water
- ❖ Pressure changes
- ❖ Use of steam purifiers



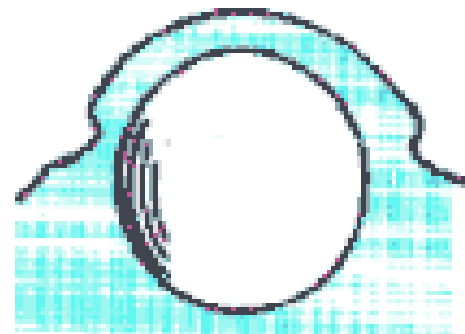
Priming



Foaming



Normal bubble

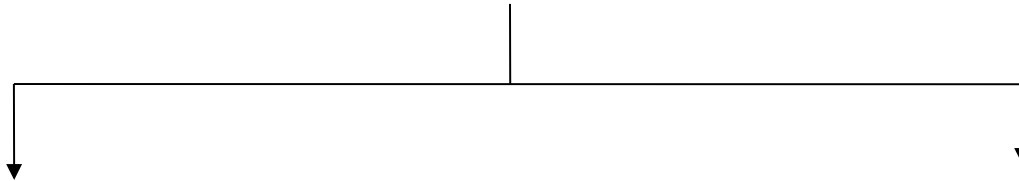


Carry-over bubble

C) Sludge and Scales Forming

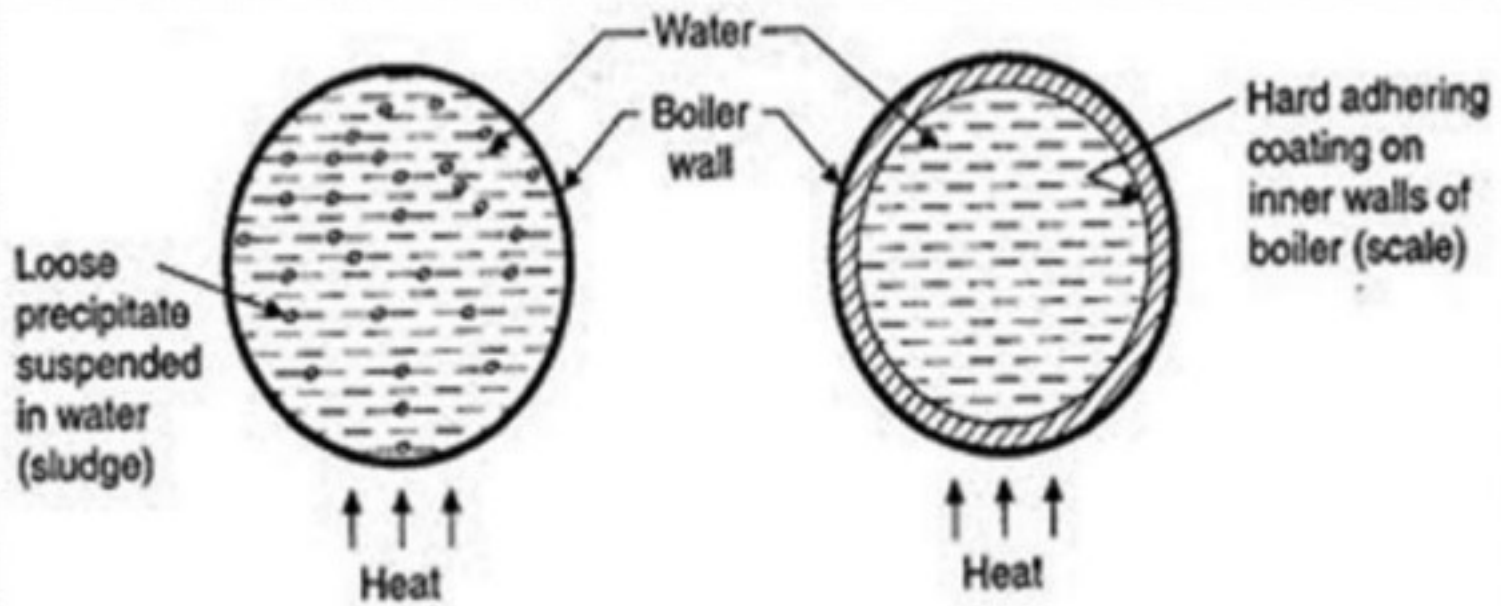


In boiler, water evaporates, concentration salts left behind increases and after saturation point get precipitated out



If ppt is loose and slimy matter it is called **sludge**

if ppt adheres strongly and form strong, bad conducting layer inner side of boiler it is called **Scale**



SLUDGE

SCALE

What is Sludge?

Loose slimy mass of salts in boiler water formed in cooler parts and loosely deposit, easy to remove by brushes, detergent solution, blow down methods

Disadvantages:

- Waste portion of heat
- reduce water flow rate
- Extensive sludge disturbs working of boiler and choke pipes

Prevention of sludges

- Use water having low dissolved solids
- Blow down technique i.e. replacing salts rich water with fresh

Scales

- It is hard and strongly attached coating in inner surface of boiler.
- It is bad conductor of electricity.
- It is main source of boiler trouble.

Reasons for scale formation

1. Decomposition of bicarbonates: At high temperature bicarbonate decomposes to form ppt as scale



2) Hydrolysis of Mg salt:



3) Silica : in form of Ca-Silicate & Mg-Silicate form colloidal particles and deposit on walls.

4) At high temperature solubility of CaSO_4 decreases and precipitate forms hard scale

Disadvantage:

- i) Wastage of Fuel – scales are bad conductor of heat therefore
More the thickness of scale = more heat loss,
0.25 cm scale consume 2-3 times more heat
- ii) Overheating of boiler
- iii) Boiler safety compromised: Due to overheating boiler metal becomes soft and fragile
- iv) Therefore there is danger of explosion due to large amount of steam formation due to uneven inner wall surface

Removal of Scale:

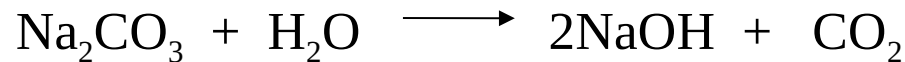
- ❖ Use of Chemicals: EDTA, sodium phosphate, calgon to loosen scales
- ❖ Wire brush
- ❖ Hammer and chisel
- ❖ Thermal shock:
- ❖ Boiler is heated → cooled suddenly → on sudden cooling boiler contract and scale cracks.

Prevention:

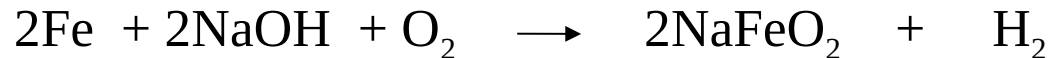
- ❖ Use of soft water,
- ❖ phosphate conditioning,
- ❖ blow down operation,
- ❖ Na-aluminate.
- ❖ Use of tannin (forms coating on inner wall of boiler)

D) Caustic Embrittlement

- ✓ Brittleness of Boiler due to accumulation of caustic substance
- ✓ It is fast corrosion of boiler due to high alkaline nature of water.
- ✓ Water evaporates and therefore Na_2CO_3 concentration increase



NaOH very corrosive attack cracks on inner surface and reacts with Fe



- ✓ Cause embrittlement of boiler parts at stressed parts like bends, joints, rivets and lead to failure of boiler.
- ✓ Cell formation Anodic part gets corroded.

Iron at joints / Higher conc. (stressed)	NaOH	// lower conc. //	NaOH	Iron at plane surface unstressed
Anode (+)				cathode (-)

Prevention of caustic embrittlement

Use Na-phosphate for water softening instead of Na_2CO_3

Add Tannin/lignin – blocks cracks

Add Na_2SO_4 to keep Na_2SO_4 : NaOH (1:1 or 2:1)

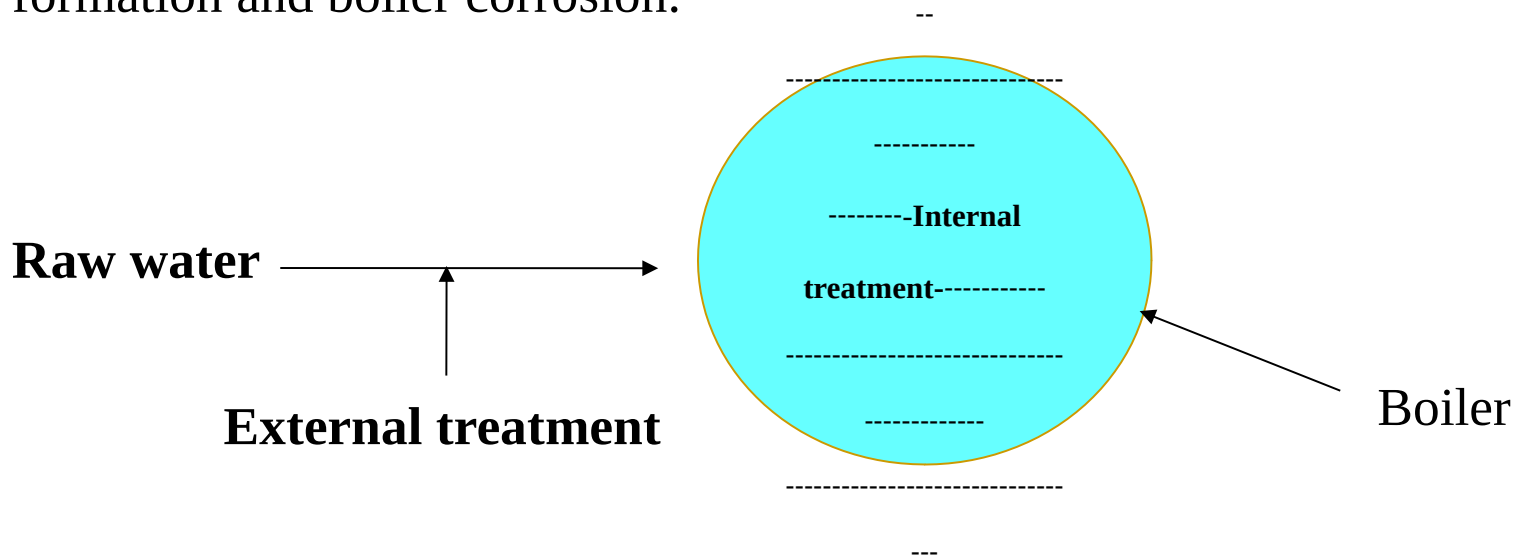
Adjust pH 8-9 carefully

Water Treatment

Raw water is converted to soft water before it is used for industrial purpose by two types of treatments:

External treatment: Here scale forming and corrosive impurities are removed from hard water before it enters the boiler.

Internal treatment: Here various substances are added to boiler feed water to remove residual, non carbonate hardness to prevent scale formation and boiler corrosion.



EXTERNAL TREATMENT

A) Zeolite or Permutit : Cation Exchange process

Zeolite: Natural mineral , insoluble in water, mixture of metal silicates and metal aluminates. Two types of zeolites: Natural and Synthetic

$\text{Na}_x^+ [(\text{AlO}_2)_x (\text{SiO}_2)_y z\text{H}_2\text{O}]$ where, $x = 2-10$ and $y = 2-6$ or Na-Zeolite

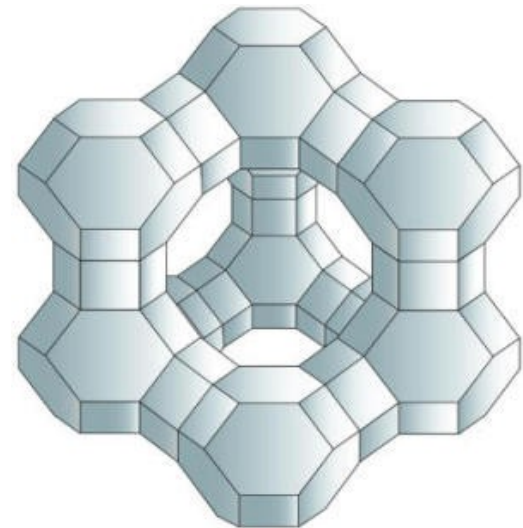
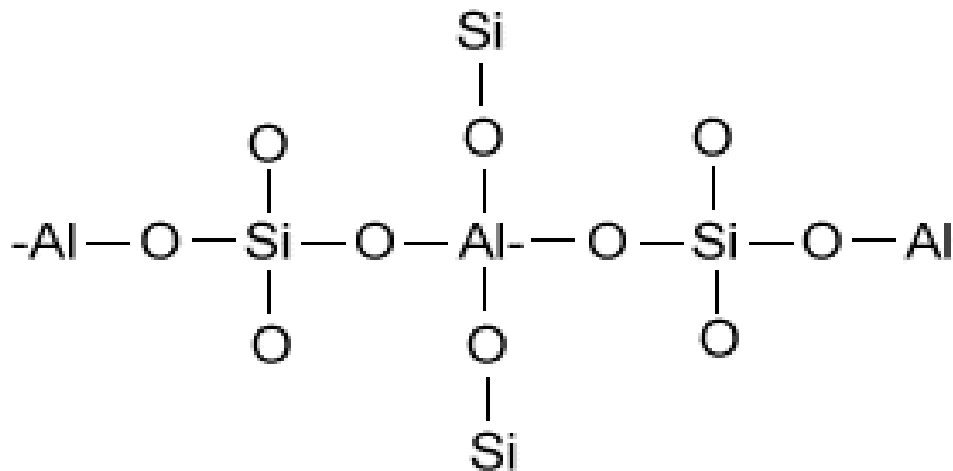
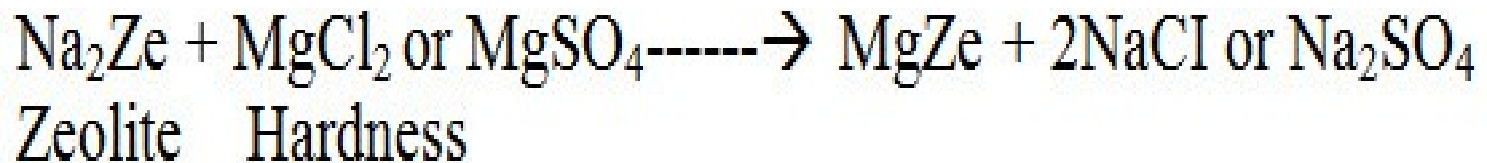
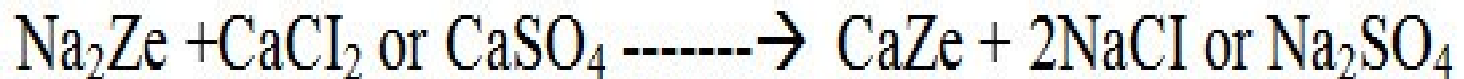
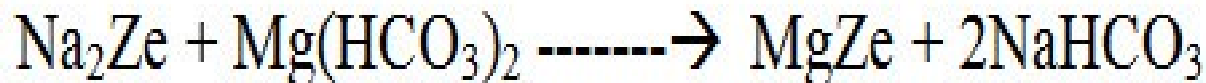
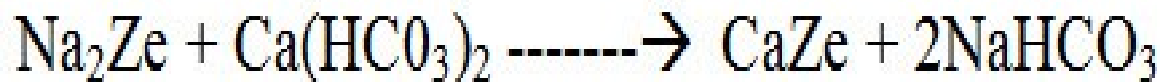


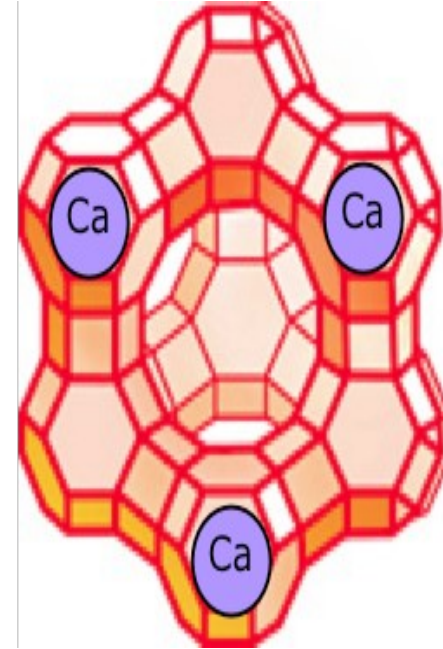
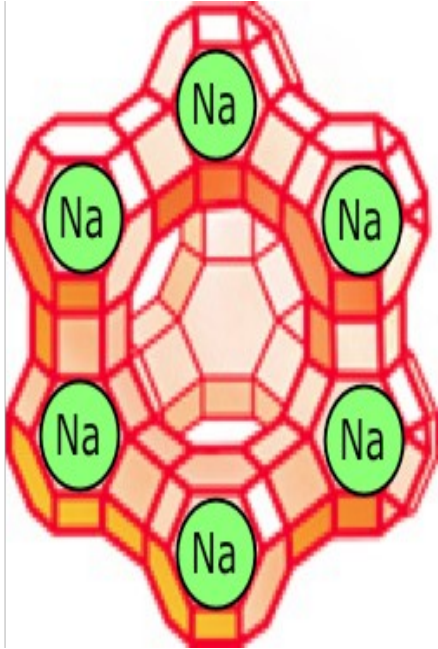
Figure 1: Basic Zeolite Structure

Principle

- Na-Zeolite has the property of exchanging ions present in them mostly loosely held Na^+ with the ions present in the solution like Ca^{2+} , Mg^{2+} etc. from Hard water.



$\text{Ca}^{2+} +$



$+ \text{Na}^+$

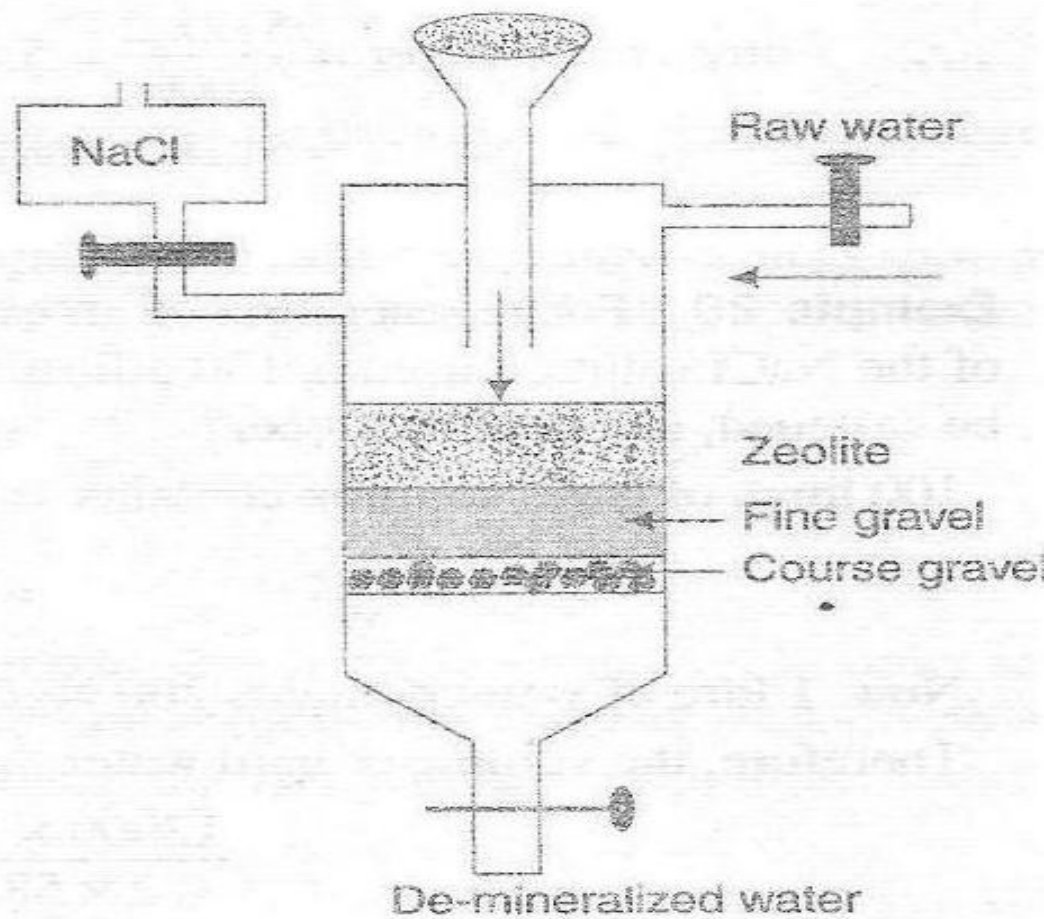


Fig. 8.11 *Zeolite method of softening*

Process

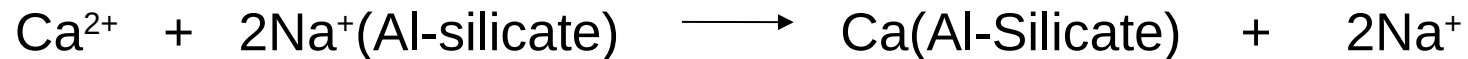
Zeolite softener consists of cylindrical column with coarse gravel
Then fine gravel and then on top of it layer of zeolite layer.



A slow stream of hard water passed through the material



Ca^{2+} , Mg^{2+} present in hard water are exchanged with Na^+ ions in Zeolite



Regeneration:

Over a period of time Na_2Ze
converted to



$\text{Ca-Ze} + \text{Mg-Ze}$



Therefore zeolite softener gets exhausted and needs to be
regenerated for further Use

This is done by passing brine solution (NaCl) on Zeolite layer



Advantages :

- ✓ Easy to operate
- ✓ Low cost operating system
- ✓ Small space is required

Limitations:

- Warm water cannot be used
- Mn^{2+} , Fe^{2+} permanently captured by Zeolite so no regeneration
- Soft water has equivalent quantities of Na^+
- Colloidal hard water cannot be used it may clog/block zeolite structure.

Applications:

- ✓ Extensive use
- ✓ Remove toxic metal ion and dye cations from polluted water.
- ✓ Recover trace metal like Cu, Ag, Au etc.
- ✓ Simple, convenient but applicable to small scale use.

Sample – Numerical

An exhausted zeolite bed is regenerated by passing 4.8 litres of NaCl solution Having concentration 100g/NaCl/litre. The bed gets exhausted by treatment of 1200 litres of a water sample. Calculate hardness of water sample.

Step I : Find out amount of NaCl (In mg) in total 4.8 lit. of brine

100g of NaCl present in 1 litre of water
Therefore ? g of NaCl present in 4.8 lit
 $= 4.8 \times 100 = 480\text{g of NaCl} = 4.8 \times 10^5 \text{mg of NaCl}$

Step II: Find out CaCO_3 equivalent in mg of NaCl

Molwt. Of NaCl: 58.5 g/mol

$$\begin{aligned} &= \frac{\text{mg of chemical} \times 50}{\text{equiv. Wt. of chemical}} = \frac{4.8 \times 10^5 \times 50}{58.5} \\ &= 4.1 \times 10^5 \text{ mg CaCO}_3 \text{ eqvi.} \end{aligned}$$

Step III: Hardness of water

$\text{CaCO}_3 \text{ equiv..} = \text{liters of Hard water} \times \text{hardness of water}$

$$\text{Hardness of water} = 4.1 \times 10^5 / 1200 = 341.9 \text{ ppm of CaCO}_3$$

b) Ion Exchange Method (Use of Resin)

This process removes all cations and anions water and such water is called **demineralized** or **deionized water**.

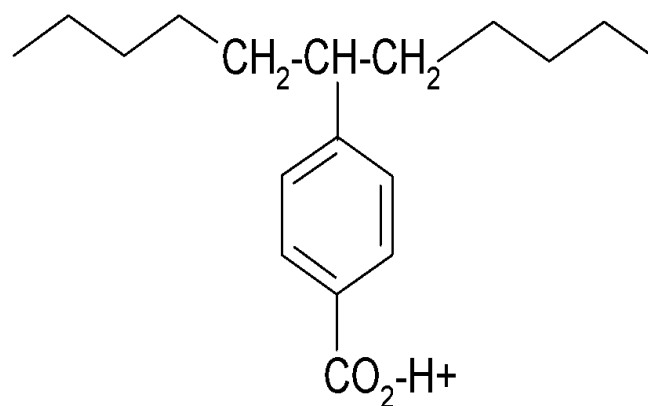
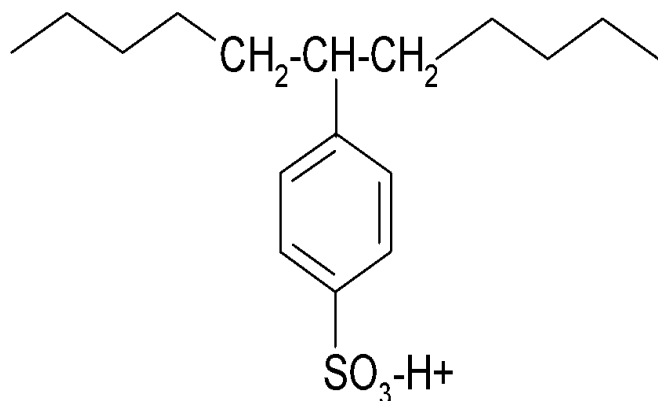
Resins are insoluble, crosslinked, long chain organic polymer with Micro porous structure and with “**functional groups**” attached to the Main Chain Which are responsible for the **ion-exchanging property**.



It has two main units -

Cation Exchange Resin & Anion exchange Resin

i) **Cation Exchange resin:** It is an polymer having Carboxylated or sulphonated aromatic rings on the polymer chain.

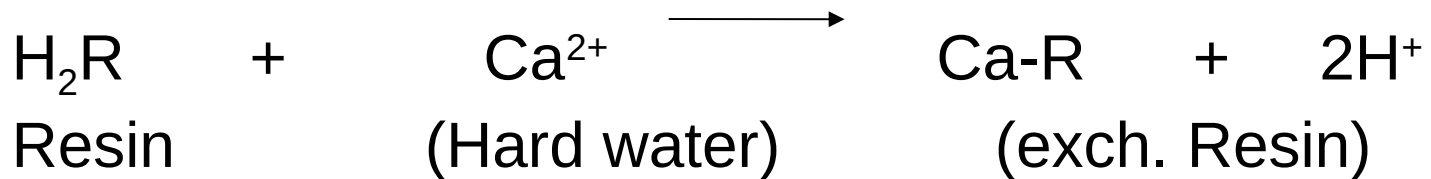
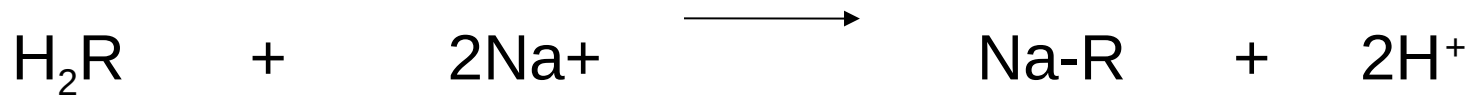


These acidic groups have **loosely held H^+ ions** which get displaced/exchanged with M^{n+} from hard water.

Amberlite IR 120, Dowex 50 are some commercial examples

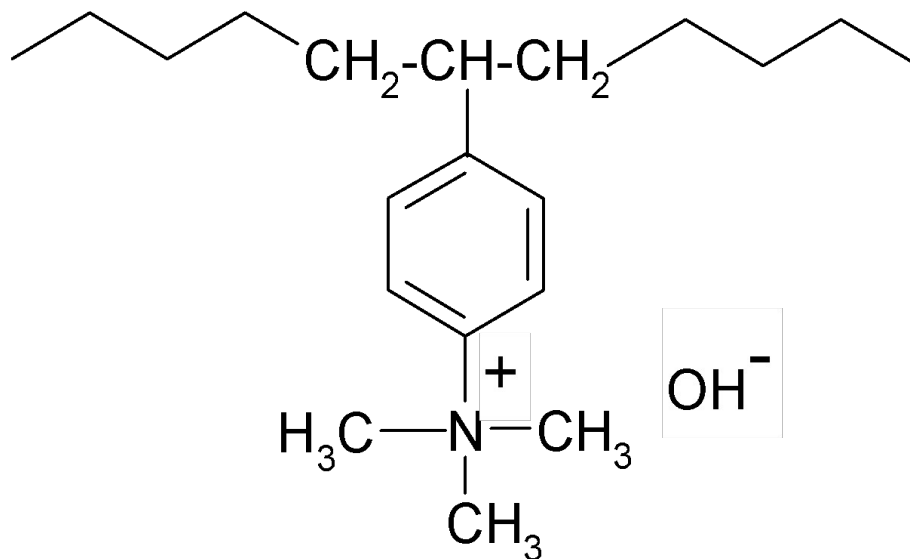
Gen. formula for Cation exchange resin is **H₂R**

Reactions:



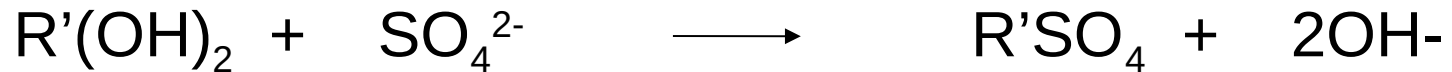
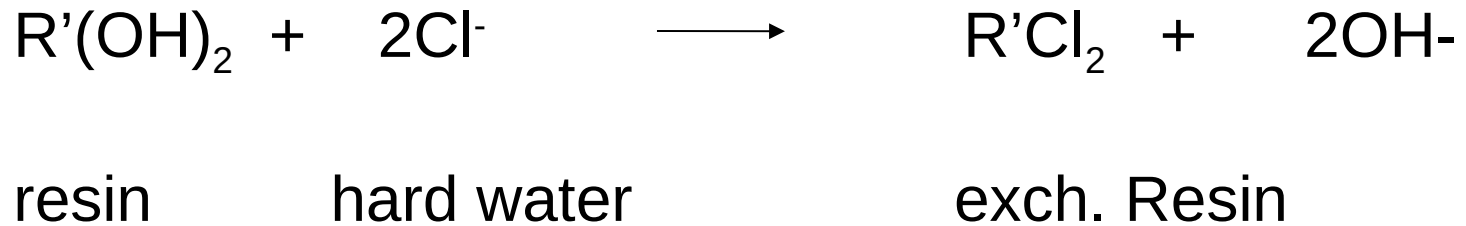
ii) Anion Exchange Resin:

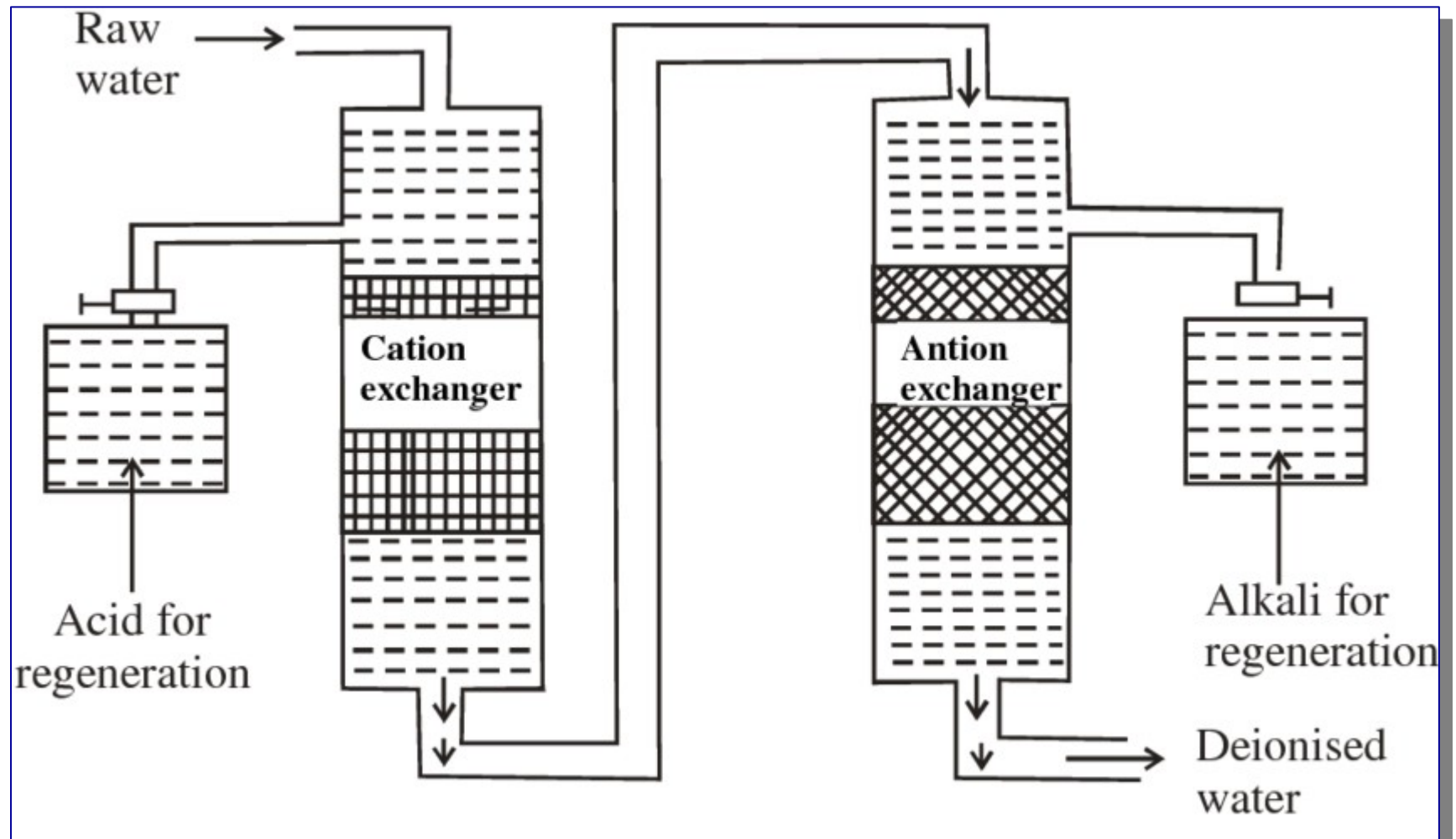
It is an polymer having aromatic rings containing quaternary ammonium group with loosely held OH^- anion.



Amberlite 400, Dowex 3 are some examples of this resin.

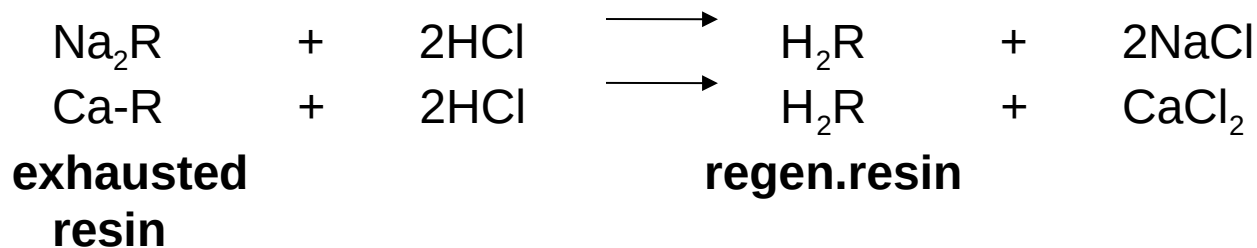
Reaction at Anion E.R.



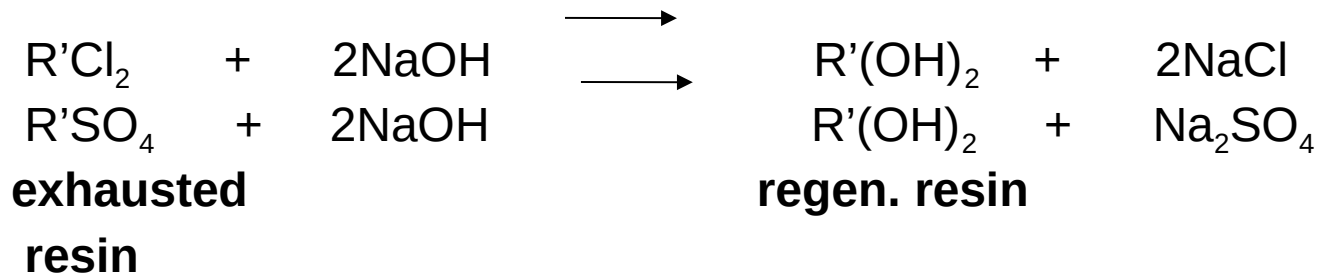


Regeneration

For Cation exchanger: By washing with **dil. HCl** solution



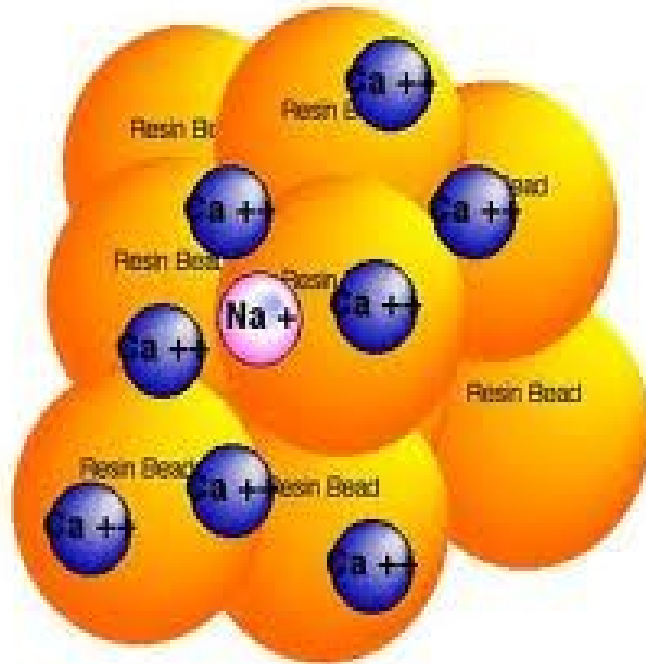
For Anion exchanger: By washing with **NaOH** solution



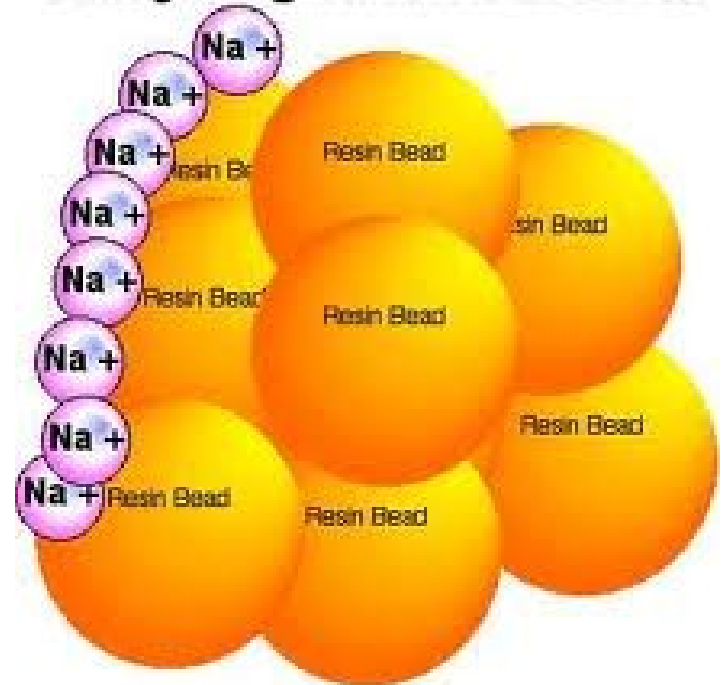
❖ Hard water after passing through cation and anion exchange resin contains only H^+ and OH^- which react to form H_2O so no ions in soft water.

□ Therefore Ion-exchange method is also called **Deionization method**

Resin which is nearly saturated with Calcium ions



Fully Regenerated Resin



Advantages of Ion-exchange Resin:

- ✓ This method gives **zero hardness** and no ionic impurities.
- ✓ O_2 , CO_2 etc. gases also can be removed by passing through de gasifier
- ✓ Small space required
- ✓ Easy to operate.

Limitations:

- ☐ High expense
- ☐ Only for small scale purification of Hard water

BOD and COD of Waste Water



Wastewater – types, characteristics & regulation

- a) Domestic:** wastewater by residential, shop houses, offices, schools etc. and normally generated from toilets, sinks and bathrooms.
- b) Industrial:** wastewater generated by industries. Quantity and quality depends on the type of industry
- c) Storm water:** rainwater, may contain pollutants



Why treat wastewater?

- Untreated wastewater harmful to health
- Breeding sites for insects, pests and micro organisms
- Can cause environmental pollution and affect ecosystem
- Normally, wastewater has high organic content. The organic content are measured by Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) and the value is about 100 to 400 mg/While the BOD test measures biochemically decomposable or degradable organic matter, the other two measure total organics.



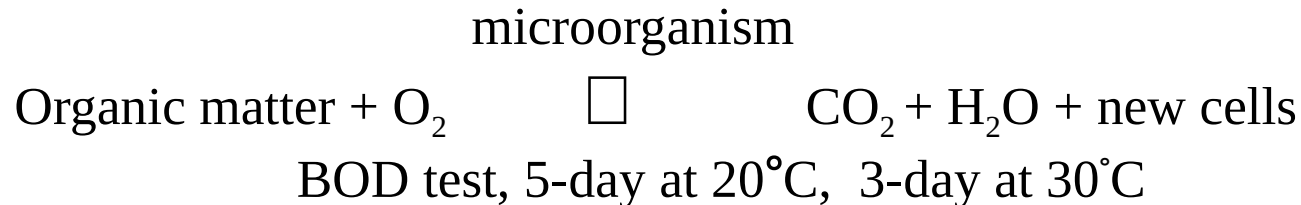
Dissolved oxygen

- The DO level in a surface water body is an important indicator of its 'health'.
- Presence of DO in water is necessary for maintaining favorable conditions for growth and reproduction of a normal population of fish and other aquatic life.
- The absence of a low level of DO in surface waters indicates pollution by organic matter.
- Under such conditions organic matter is decomposed by anaerobic bacteria resulting in production of obnoxious end-products, such as mercaptans, hydrogen sulphide, ammonia, etc .

Biochemical Oxygen Demand (BOD)

The quantity of oxygen utilized by a mixed population of microorganisms to biologically degrade the organic matter in the wastewater under aerobic condition.

- BOD is the most important parameter in water pollution control
- It is used as a measure of organic pollution as a basis for estimating the oxygen needed for biological processes, and as an indicator of process performance.



Biochemical Oxygen Demand (BOD)

Procedure:

1. A water sample containing degradable organic matter is placed in a BOD bottle.
2. If needed, add dilution water (known quantity). Dilution water is prepared by adding phosphate buffer (pH 7.2), magnesium sulphate, calcium chloride and ferric chloride into distilled water. Aerate the dilution water to saturate it with oxygen before use.
3. Measure DO in the bottle after 15 minutes (DO_i)
4. Closed the bottle and placed it in incubator for 5 days, at temperature 20°C
5. After 5 days, measure DO in the bottle (DO_t).



Calculation of BOD

Where

BOD_t = biochemical oxygen demand, mg/L

DO_i = initial DO of the diluted wastewater sample about 15 min. after preparation, mg/L

DO_t = final DO of the diluted wastewater sample after incubation for five days, mg/L

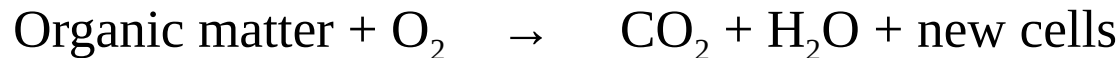
P = dilution factor =

Need for Dilution:

- For a valid BOD test, the final DO should not be less than 1 mg/L. BOD test is invalid if DO_t value near zero.
- Dilution can decrease organic strength of the sample. By using dilution factor, the actual value can be obtained.
- Dilution of wastes: - By direct pipetting into 300 mL BOD bottle

BOD Analysis

- In aerobic processes (O_2 is present), heterotrophic bacteria oxidize about 1/3 of the colloidal and dissolved organic matter to stable end products ($CO_2 + H_2O$) and convert the remaining 2/3 into new microbial cells that can be removed from the wastewater by settling.
- The overall biological conversion proceeds sequentially, with oxidation of carbonaceous material as the first step (known as carbonaceous oxygen demand):



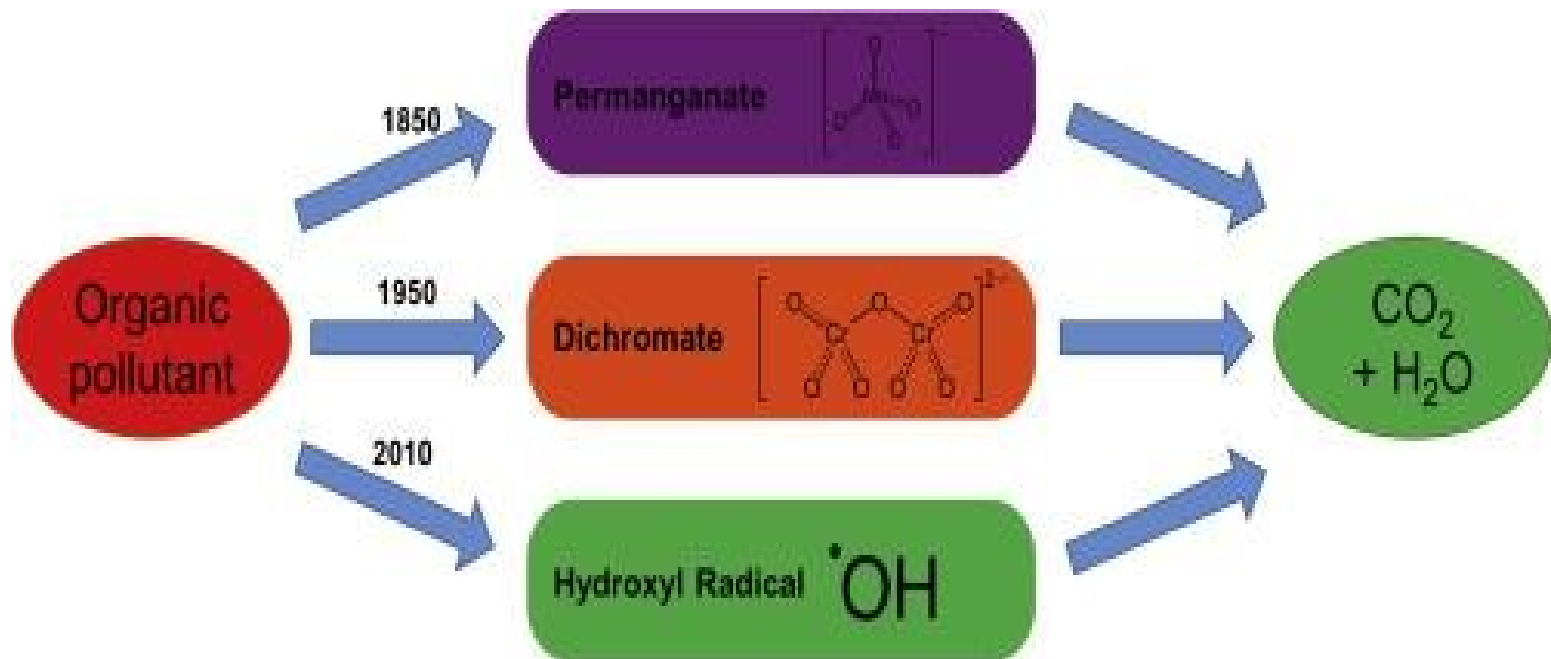
- Under continuing aerobic conditions, autotrophic bacteria then convert the nitrogen in organic compounds to nitrates (known as nitrification oxygen demand).



Chemical Oxygen Demand

The quantity of oxygen needed to chemically oxidize the organic compound in sample, converted to carbon dioxide and water.

Commonly used to define the strength of industrial waste waters.



Procedure

1. Add measured quantities of potassium dichromate, sulphuric acid reagent containing silver sulphate, and a measured volume of sample into a flask.

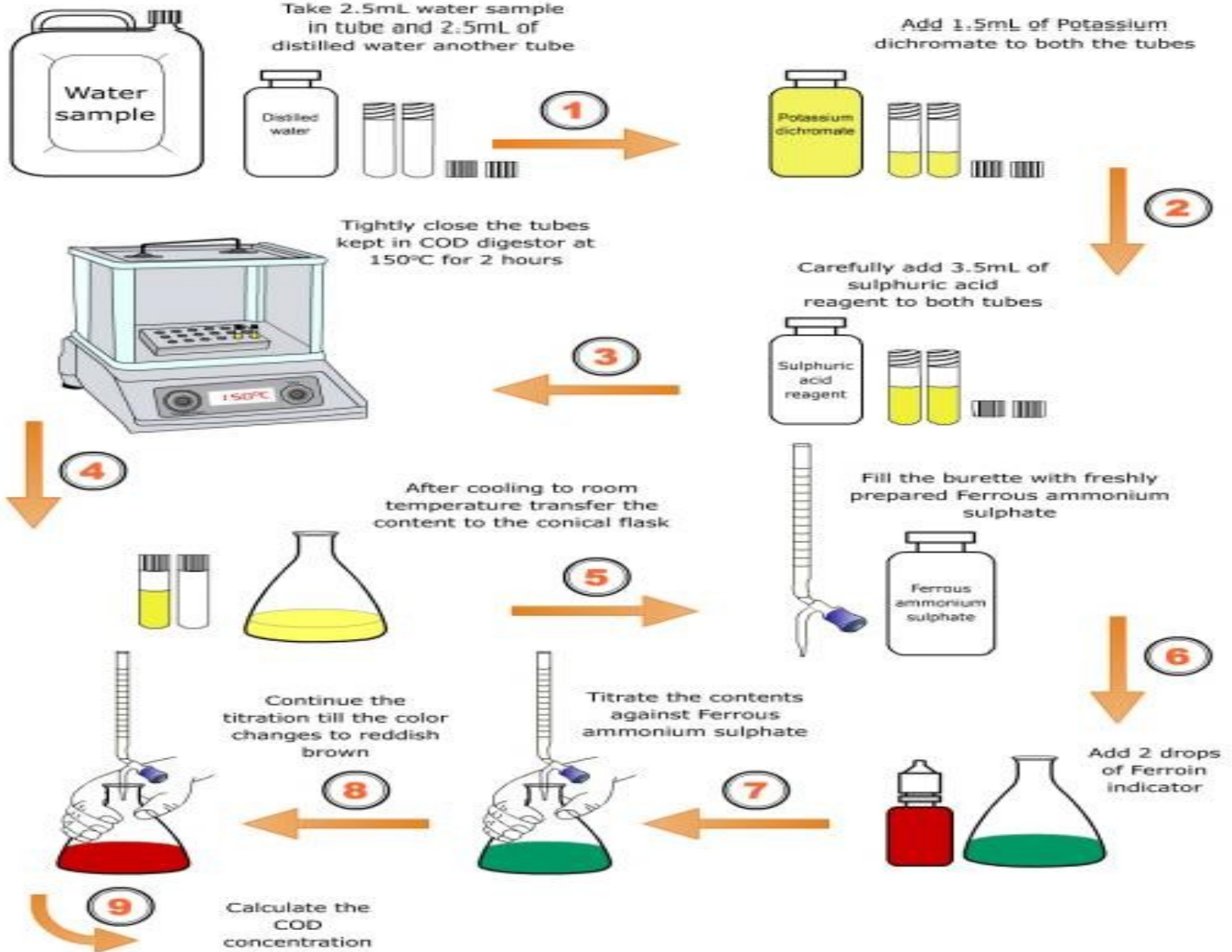
2. The mixture is refluxed (vaporized and condensed) for two hours. The oxidation of organic matter converts dichromate to trivalent chromium,



3. The mixture is titrated with ferrous ammonium sulphate (FAS) to measure the excess dichromate remaining in sample.

4. A blank sample of distilled water is carried through the same COD testing procedure as the wastewater sample.

PROCEDURE CHART



Calculations

COD is calculated from the following equation:

$$\text{COD} = \frac{8000(a-b) \times \text{Normality of Fe(NH}_4)_2(\text{SO}_4)_2}{V}$$

Where:

COD = chemical oxygen demand, mg/L

a = amount of ferrous ammonium sulphate
titrant added to blank, mL

b = amount of titrant added to sample, mL

V = volume of sample, mL

8000 = multiplier to express COD in mg/L of oxygen

GREEN CHEMISTRY

DEFINITION

Green Chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products .



Green Chemistry Is About...

Reducing



Waste

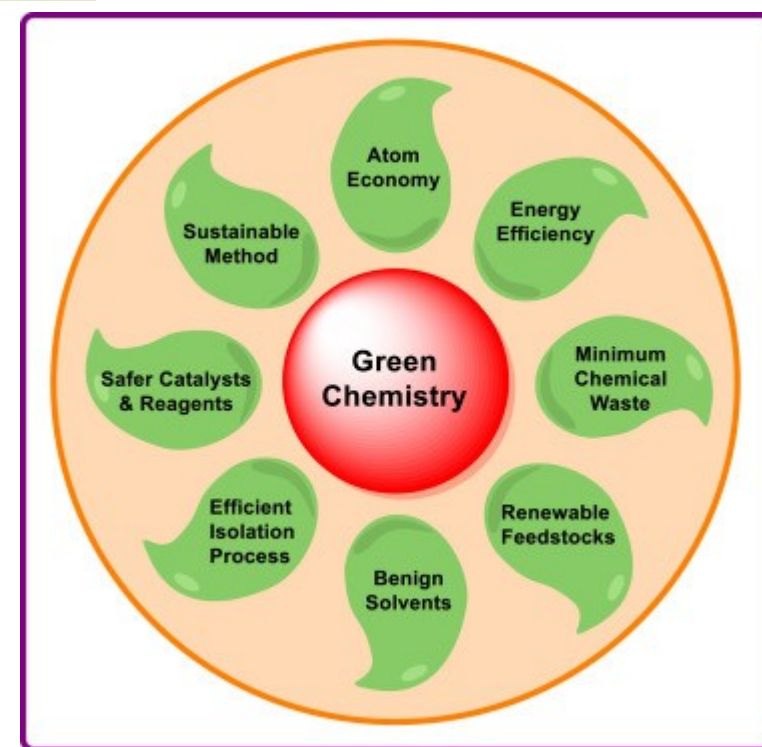
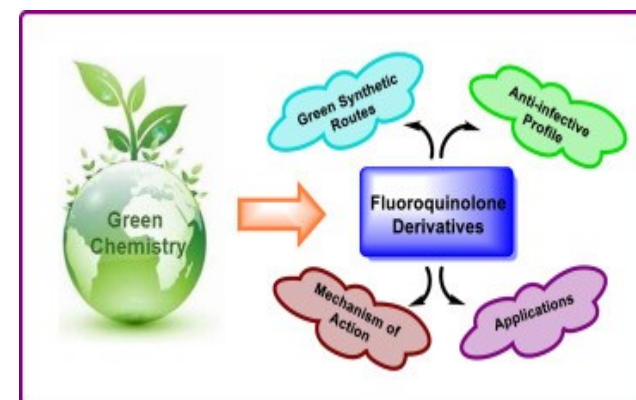
Materials

Hazard

Risk

Energy

Cost



INTRODUCTION



- Green chemistry is also known as environmentally benign chemistry or sustainable chemistry
- Paul Anastas and John Warner, who defined green chemistry as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
- Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for ‘greener’ chemical products.



INTRODUCTION



- Green chemistry looks at pollution prevention on the molecular scale and is an extremely important area of Chemistry due to the importance of Chemistry in our world today and the implications it can show on our environment.
- The Green Chemistry program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances.

INTRODUCTION



- Anastas and Warner formulated the twelve principles of green chemistry in 1998. These serve as guidelines for chemists seeking to lower the ecological footprint of the chemicals they produce and the processes by which such chemicals are made.
- The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.

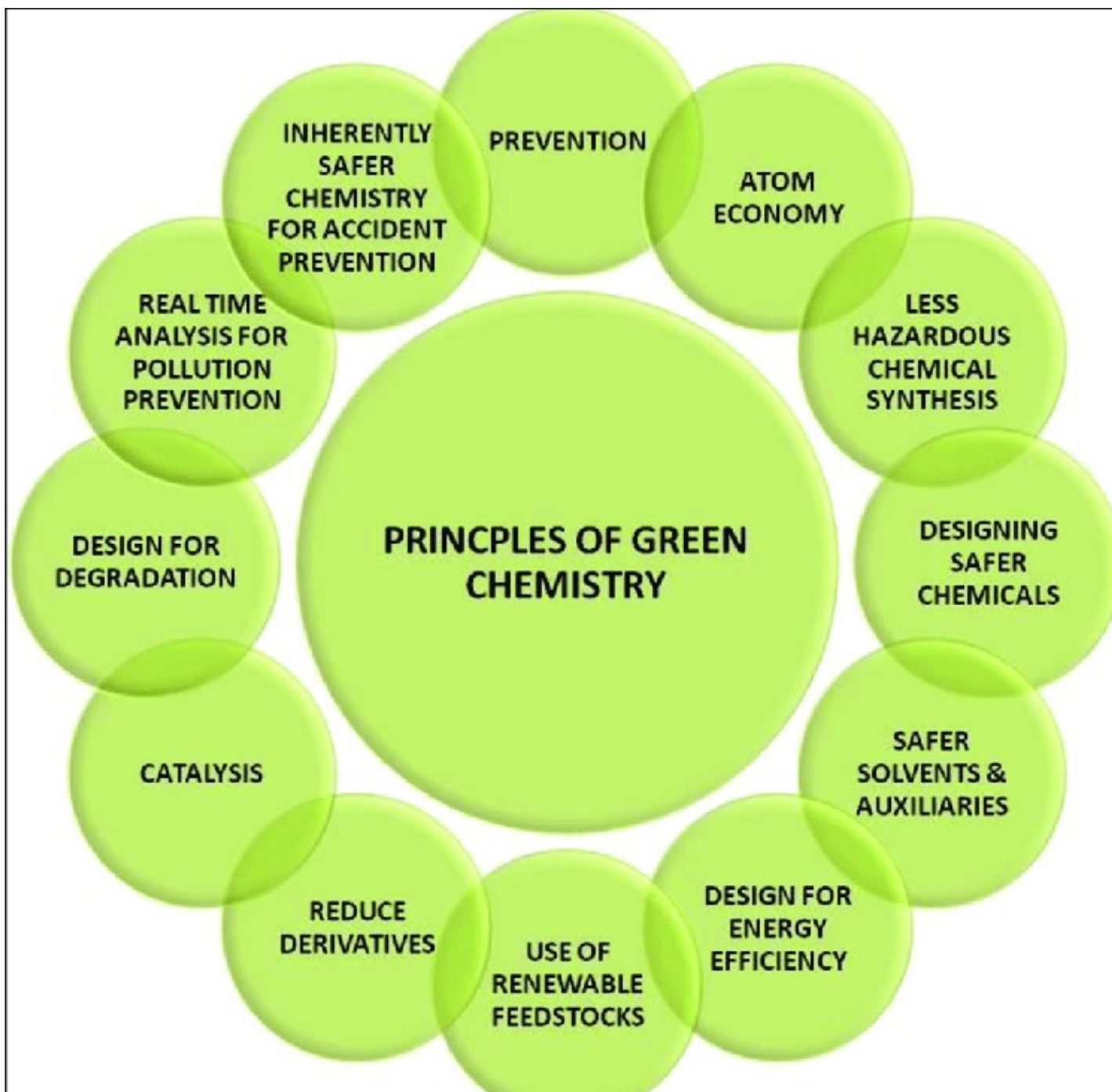
Green Chemistry By Paul T. Anastas and John C. Warner.



GREEN CHEMISTRY IS ABOUT



- – Waste Minimisation at Source
- – Use of Catalysts in place of Reagents
- – Using Non-Toxic Reagents
- – Use of Renewable Resources
- – Improved Atom Efficiency
- – Use of Solvent Free or Recyclable Environmentally Benign Solvent systems



12 PRINCIPLES OF GREEN CHEMISTRY

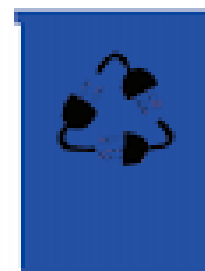
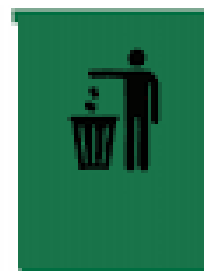
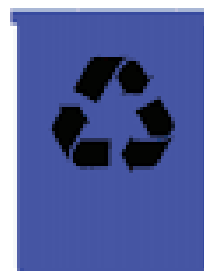


1. Prevention of Waste or by-products

- It is better to prevent waste than to treat or clean up waste after it is formed

WASTE PREVENTION

The Student Environmental Center at UC Santa Cruz



12 PRINCIPLES OF GREEN CHEMISTRY



2. Atom Economy

- Atom economy (atom efficiency) describes the conversion efficiency of a chemical process in terms of all atoms involved (desired products produced).

Mol. weight of Desired product

$$\text{Atom Economy} = \frac{\text{Mol. weight of Desired product}}{\text{Mol. weight of all reactants}} \times 100$$



2. Atom Economy

- Atom economy describes the conversion efficiency of a chemical process in terms of all atoms involved (desired products produced).

- $$\text{Atom Economy} = \frac{\text{Mol. weight of Desired product}}{\text{Mol. weight of all reactants}} \times 100$$

- For the reaction, the atom economy should be maximum.

Atom Economy



e.g.

- **Rearrangement Reactions:**
- These reactions involves rearrangement of atoms that forms molecule. Hence, the atom economy of these reactions are 100%.

- **Addition Reactions:**
- These reactions involves addition of two or more molecules without elimination that forms molecule. Hence, the atom economy of these reactions are 100%

Efficiency Parameter



1. Reaction Yield

- $$\text{Reaction Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$
- The reaction should have high percentage of yield.

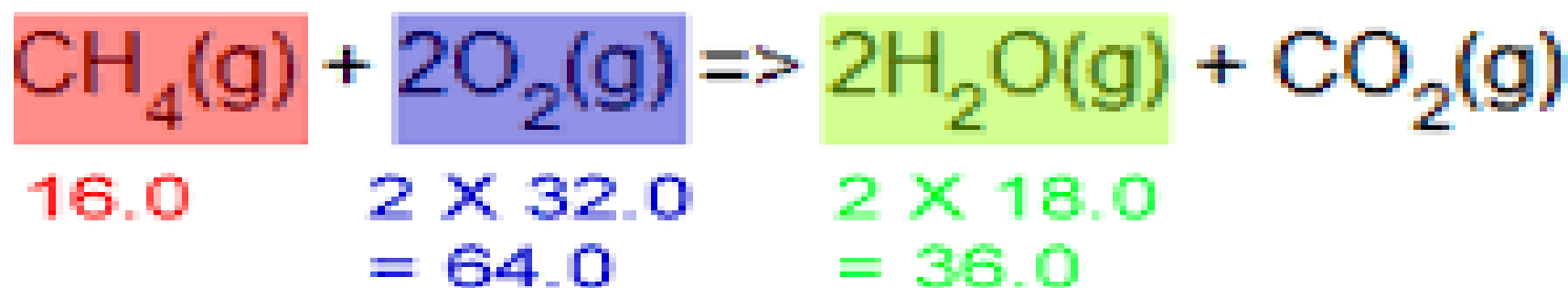


- Conversion factor:

Amount of reactant reacted

$$\text{Conversion} = \frac{\text{Amount of reactant reacted}}{\text{Amount of reactant taken}} \times 100$$

Atom Economy numericals



Total mass of
reactant atoms
= 16.0 + 64.0
= 80.0

Total mass of
desired product atoms
= 36.0

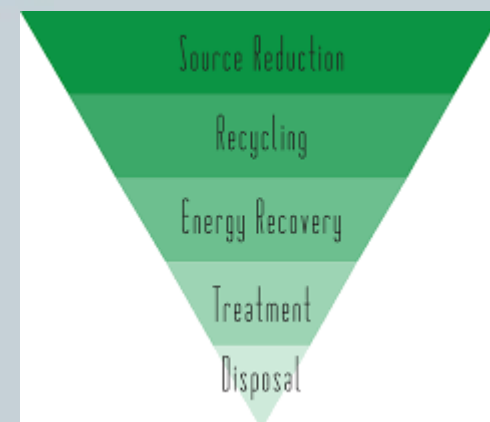
$$\text{Atom economy} = \frac{36.0}{80.0} \times 100$$
$$= 45.0\%$$

12 PRINCIPLES OF GREEN CHEMISTRY



3. Minimization of hazardous products

- Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.



12 PRINCIPLES OF GREEN CHEMISTRY



4. Designing Safer Chemicals

- Chemical products should be designed to effect their desired function while minimising their toxicity.

Ex. **Thalidomide** was a widely used drug in the late 1950s and early 1960s for the treatment of nausea in pregnant women. It became apparent in the 1960s that thalidomide treatment resulted in severe birth defects in thousands of children.

12 PRINCIPLES OF GREEN CHEMISTRY



5. Safer Solvents & Auxiliaries

- “The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible, and innocuous when used”

5. Use Safer Solvents and Auxiliaries



12 PRINCIPLES OF GREEN CHEMISTRY



6. Design for Energy Efficiency

- Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized.
- If possible, synthetic methods should be conducted at ambient temperature and pressure.



12 PRINCIPLES OF GREEN CHEMISTRY



7. Use of Renewable Feedstock

- “A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.”



12 PRINCIPLES OF GREEN CHEMISTRY



8. Reduce Derivatives

- Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

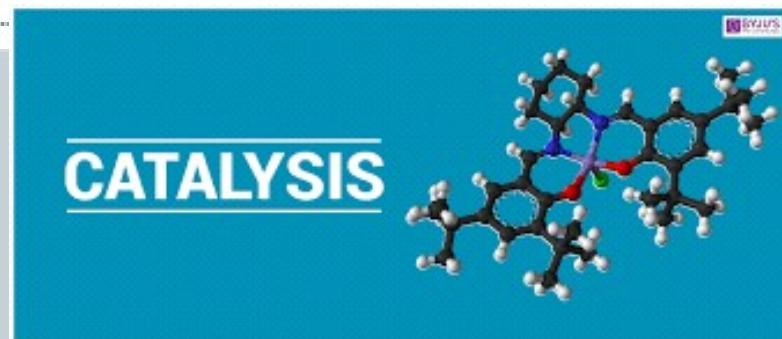
12 PRINCIPLES OF GREEN CHEMISTRY



8. Reduce Derivatives

- More derivatives involve
 - Additional Reagents
 - Generate more waste products
 - More Time
 - Higher Cost of Products
 - Hence, it requires to reduce derivatives.

12 PRINCIPLES OF GREEN CHEMISTRY



9. Catalysis

- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- e.g. Toluene can be exclusively converted into p-xylene (avoiding o-xylene & m-xylene) by shape selective zeolite catalyst.

12 PRINCIPLES OF GREEN CHEMISTRY



10. Designing of degradable products

- Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.



12 PRINCIPLES OF GREEN CHEMISTRY



11. New Analytical Methods

- “Analytical methodologies need to be further developed to allow for real-time, in-process monitoring
- and control prior to the formation of hazardous substances.”

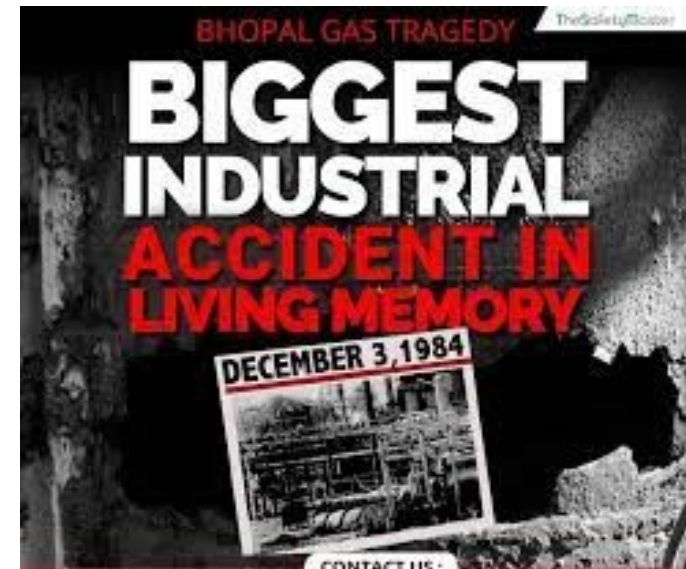


12. Safer Chemicals For Accident Prevention

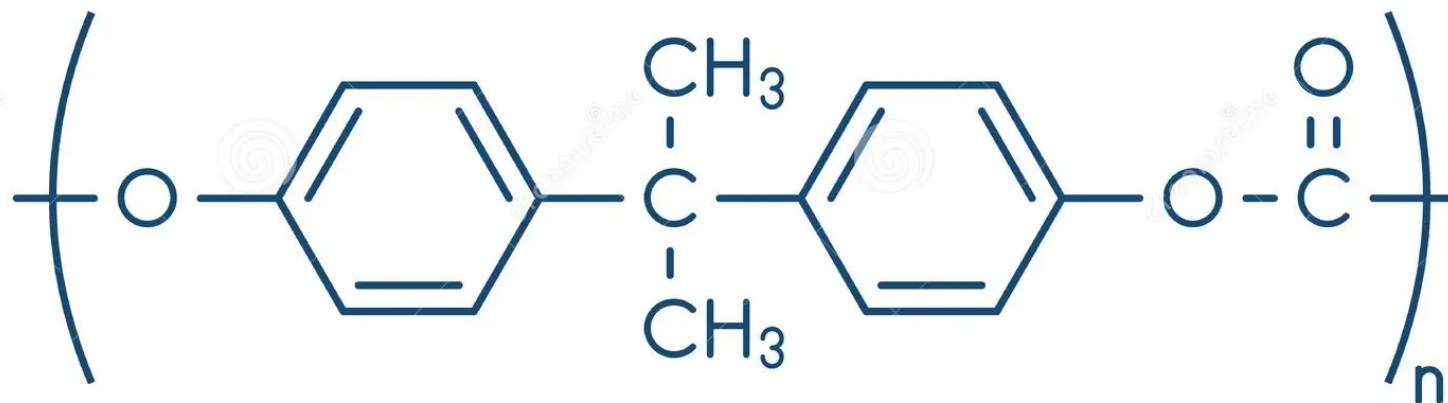
- “Analytical Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.”



Bhopal gas tragedy (Accident prevention)

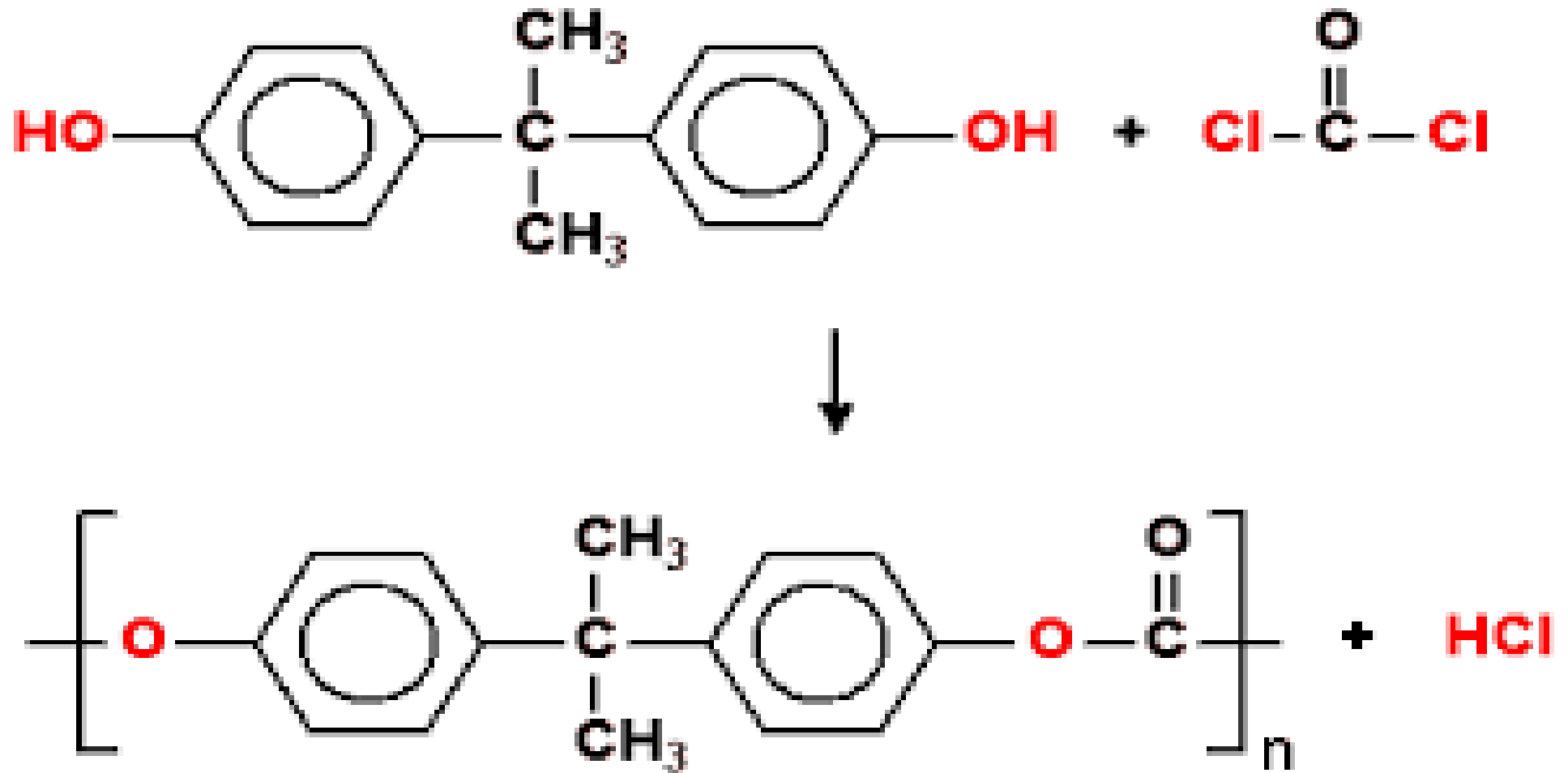


Synthesis of Polycarbonate



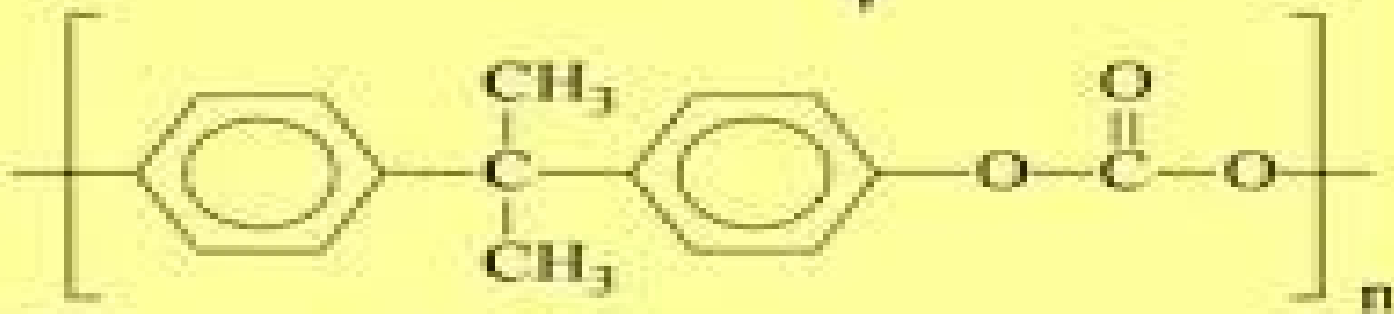
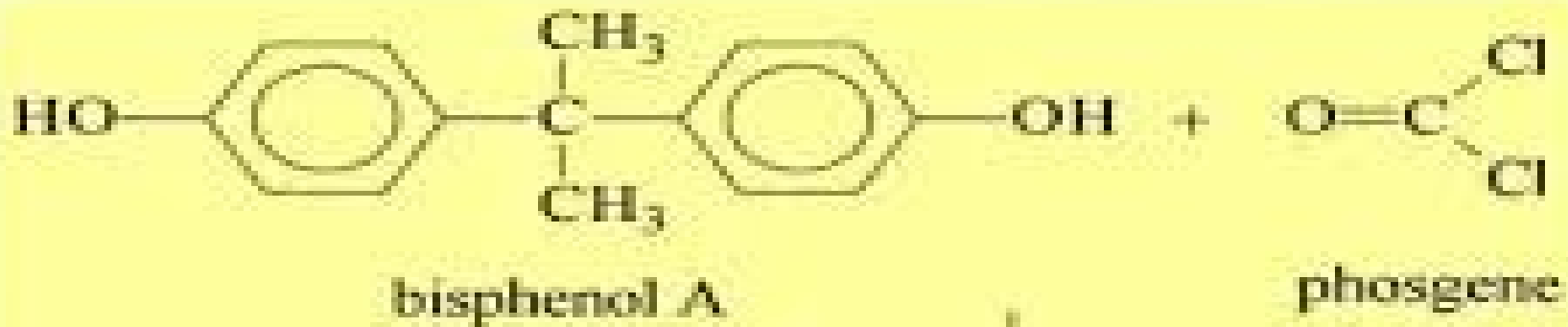
polycarbonate

Traditional method of synthesis of polycarbonate



Traditional method of synthesis of polycarbonate

POLYCARBONATE SYNTHESIS

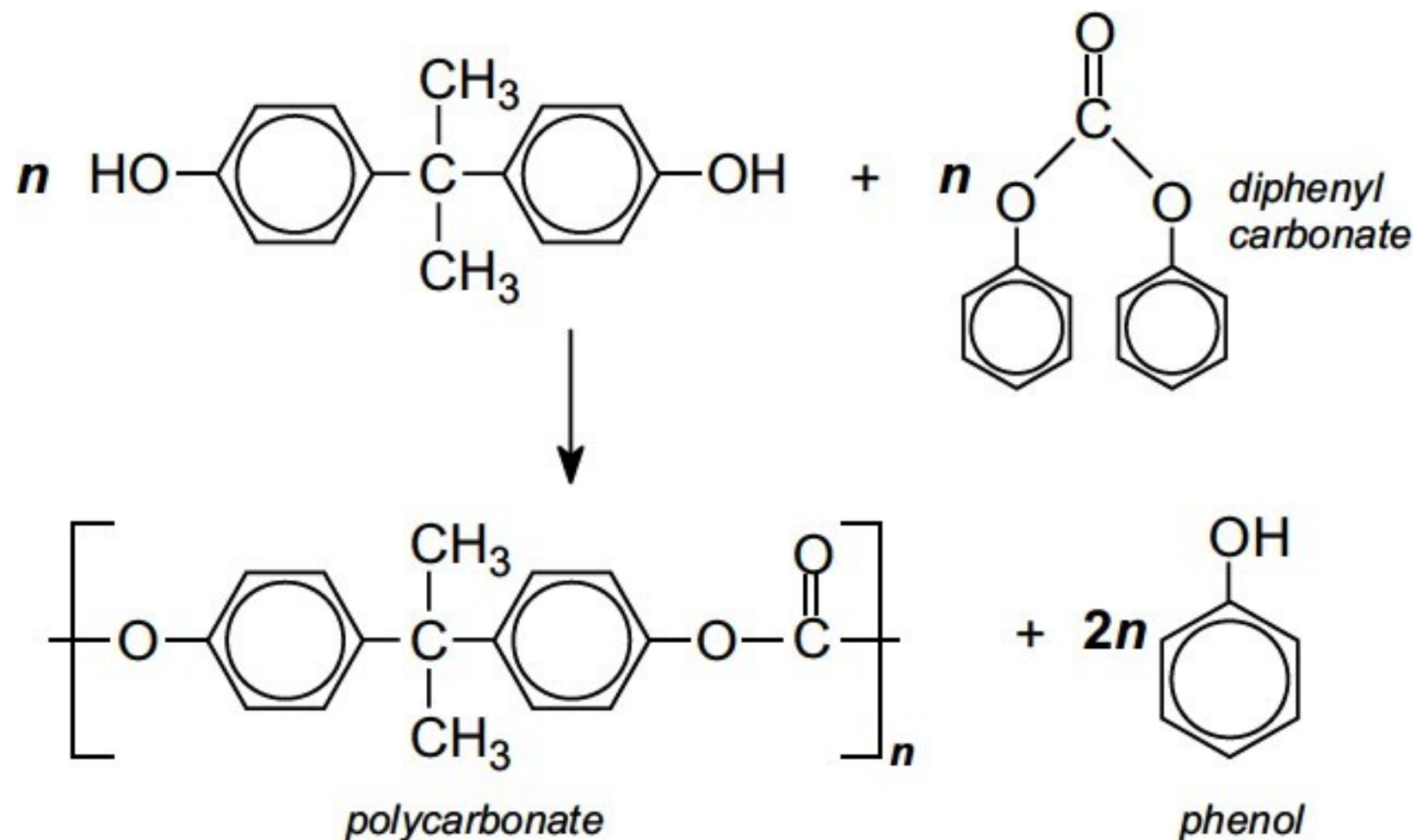


bisphenol A polycarbonate

Drawbacks of traditional synthesis

- Use of dangerous phosgene
- Formation of CH_2Cl_2 in large amount and it is difficult to separate
- Presence of Cl impurities in polycarbonate.

Green synthesis of polycarbonate



Advantages of green method

- It eliminates use of phosgene which is hazardous.
- The reaction is carried out in molten condition thereby eliminating use of solvent methylene chloride which is carcinogenic.

Thank
you!!!

