New added topics

Chemistry-I

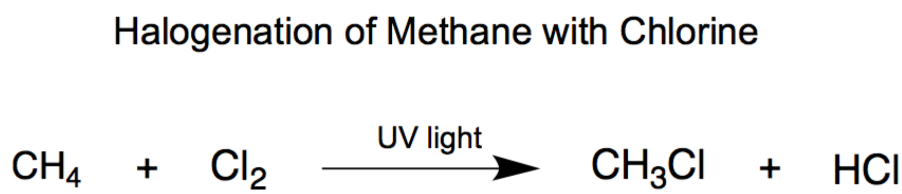
BTCH101-23

<u>Free radical substitution reaction (Unit-VI)</u>

Free radical substitution is a type of chemical reaction where a radical replaces another atom or group of atoms in a molecule. Radicals are highly reactive species with unpaired electrons. The most common example of free radical substitution is the halogenation of alkanes.

These reactions are relevant in organic chemistry, especially in the synthesis of halogenated organic compounds. It's important to note that free radical substitution reactions can be unpredictable and can result in side products.

For example: 1. Chlorination of Methane



Mechanism:

Free radical substitution reactions are take place by free radical as intermediate.

Three steps are involved in this:

- Chain initiation
- Chain propagation
- Chain termination

Initiation

(1) $Cl_2 \xrightarrow{\text{light}} 2Cl\cdot$

Propagation

(2) $Cl\cdot + CH_4 \longrightarrow HCl + \cdot CH_3$

(3) $CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$

Termination

(4) $2Cl\cdot \longrightarrow Cl_2$

$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$

$2\cdot CH_3 \longrightarrow CH_3CH_3$

2. Bromination of methane

"Mechanism" for Free Radical Substitution:

Step 1: Initiation – a radical is created, starting the reaction (UV light causes this to happen)

$Br_2 \rightarrow 2Br\bullet$

Step 2: Propagation – a radical reacts, creating a new radical to continue the reaction

$Br\bullet + CH_4 \rightarrow HBr + \bullet CH_3$

$\bullet CH_3 + Br_2 \rightarrow + CH_3Br + Br\bullet$

Step 3: Termination – two radicals react stopping chain reaction

$Br\bullet + Br\bullet \rightarrow Br_2$

$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$

$\bullet CH_3 + Br\bullet \rightarrow CH_3Br$

Free Radical Addition Reaction

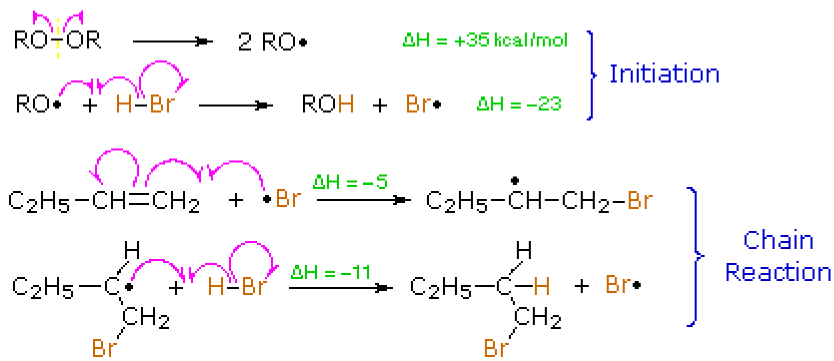
Free radical addition reactions involve the addition of radicals to unsaturated compounds, such as alkenes or alkynes. The addition occurs through a chain reaction mechanism involving initiation, propagation, and termination steps. Let's take the example of the free radical addition of hydrogen bromide. Free radical addition reactions are important in polymerization processes, where unsaturated monomers react to form polymers through the repeated addition of radicals across double or triple bonds.

For example: addition of HBr to unsymmetrical alkene in the presence of peroxide

It is also known as Anti markonikov rule

$$C_2H_5\text{-}CH{=}CH_2 + HBr \xrightarrow{ROOR} C_2H_5\text{-}CH_2\text{-}CH_2Br$$

Mechanism:



Lime Soda Process (Unit-IV)

Lime soda process is an external treatment method employed for the softening hard water. It is a very cheap process because both lime and soda are easily available chemicals.

Principle of Lime soda process: The basic principle involved is the conversion of soluble impurities in to the insoluble impurities. Water is having the salts of Ca and Mg present in water that makes it hard. So lime and soda convert these soluble impurities in to insoluble precipitates. By this process soluble magnesium and calcium salts are removed as calcium carbonate and magnesium hydroxide precipitated.

$Ca(OH)_2$= Lime

Na_2CO_3= Soda

Chemical reactions

- ✓ In case of temporary water hardness the following reactions are take places:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + MgCO_3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$$

- ✓ In case of permanent water hardness the following reactions are take places:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

$$MgSO_4 + Na_2CO_3 \rightarrow MgCO_3 + Na_2SO_4$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$$

Lime soda process is of two types

- Cold lime soda process
- Hot lime soda process

- ❖ Cold lime soda process: In the cold lime soda process the reactions take place at normal temperature. The raw water is passed into a tank with a static continuous flow, at the same time a calculated amount of chemical mixture of lime and soda ash are also added a static continuous flow and then thoroughly mixed with a stirrer in this mixture tank. Afterward this water is allowed to settle. When the settlement becomes complete the water is passed by continuous up-flow process into another tank which is called filter bed. The cold lime soda process is not suitable for all purposes. It is limited for those purposes where partially softened water needed because this process fails to precipitate completely all the hardness forming salts. The cold lime soda process is used for municipal water and cooling water softener systems. The reason in case of municipal purpose, it is not necessary to remove all water hardness forming ions. Same way cooling water should be free from temporary water hardness. In this process it is possible to remove magnesium water hardness nearly completely but calcium hardness may be remains more than 40ppm.

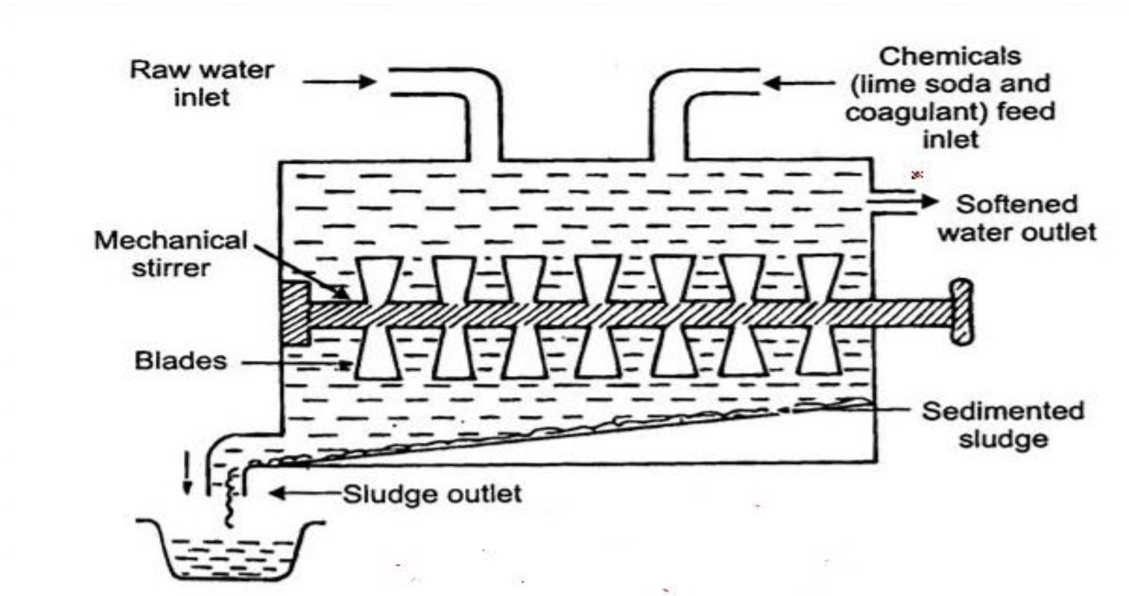


Figure 1:Cold lime soda process

Hot lime soda process: In the hot lime soda process the reactions take place at higher temperature near about boiling point of water. Temp. Range is 94-100 °C. The chemical mixing process is same as the cold lime soda process, but steam is applied in mixture tank. As a result precipitation becomes almost complete very quickly. This process is more effective than cold lime soda process. The hot lime soda process water softener systems are exclusively used for boiler purpose. In this process it is possible to remove magnesium water hardness completely and calcium hardness may be remains very low. Moreover dissolved corrosive gases also removed by this hot lime soda process.

Parts of Hot lime soda process

1. **Reaction Tank**
2. **Sedimentation Tank**
3. **Sand Filter**

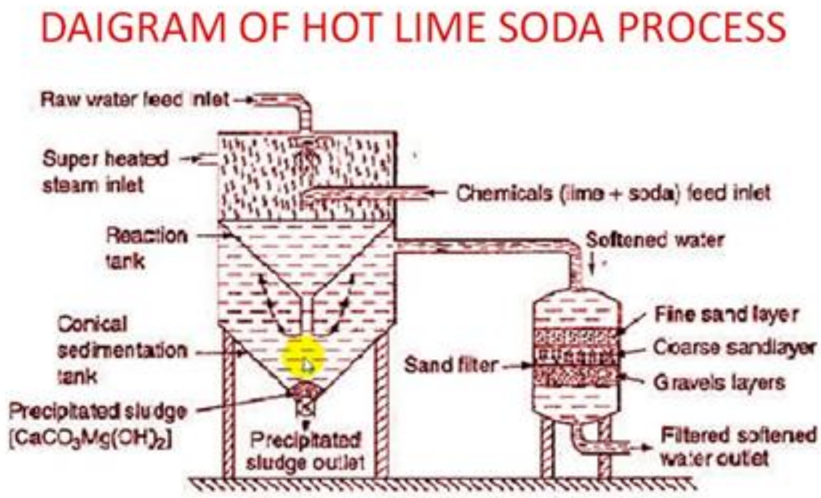


Figure 1:Hot lime soda process

Difference between Cold and Hot lime soda process

Cold lime soda process	Hot lime soda process
1. It is carried out at room temperature (25-30°C)	1. It is carried out at high temperature (95-100°C)
2. It is a slow process	2. It is a rapid process
3. Use of coagulant is a necessary	3. No coagulant required
4. Filtration is not easy	4. Filtration is easy as viscosity of water is low
5. Residual hardness is 60 ppm	5. Residual hardness is 15—30 ppm
6. Dissolved gases are not removed	6. Dissolved gases are removed
7. It has low softening capacity	7. It has high softening capacity

Disadvantages of lime soda process:

- For efficient and economical softening, careful operation and skilled supervision is required.
- Disposal of large amount of sludge poses a problem.
- This can remove hardness up to 15 ppm which is not good for boilers.

Advantages of Hot Lime Soda Process

1. The reaction between hardness producing substance and lime soda proceeds at a faster rate
2. The precipitates and sludges formed are settled at the bottom easily and hence No coagulants are required
3. The dissolved gases such as CO_2 escapes and the water becomes free from dissolved gases
4. It produces soft water with the residual hardness of 15-30ppm in contrast to the cold lime soda process which produces soft water with 50-60ppm of residual hardness

Hot lime soda Plant consists of three parts

1. **Reaction tank**: water, chemicals and steam are mixed
2. **Conical sedimentation tank** : sludge settles down
3. **Sand filter** : complete removal of sludge from the soft water is ensured