Module-7: Industrial applications

Water purification methods

- zeolites (principle, process, advantages and disadvantages),

- ion-exchange resins (double /mixed bed (principle, process, advantages and disadvantages),

- Reverse osmosis (principle, process, advantages and disadvantages),

Fuels and combustion

- -LCV, HCV, Bomb calorimeter (numerical)

Corrosion

- Prevention of Corrosion, cathodic protection (Sacrificial anodic protection and Impressed current cathodic protection).

Water Softening Methods

❖ Zeolite (Permutit process)

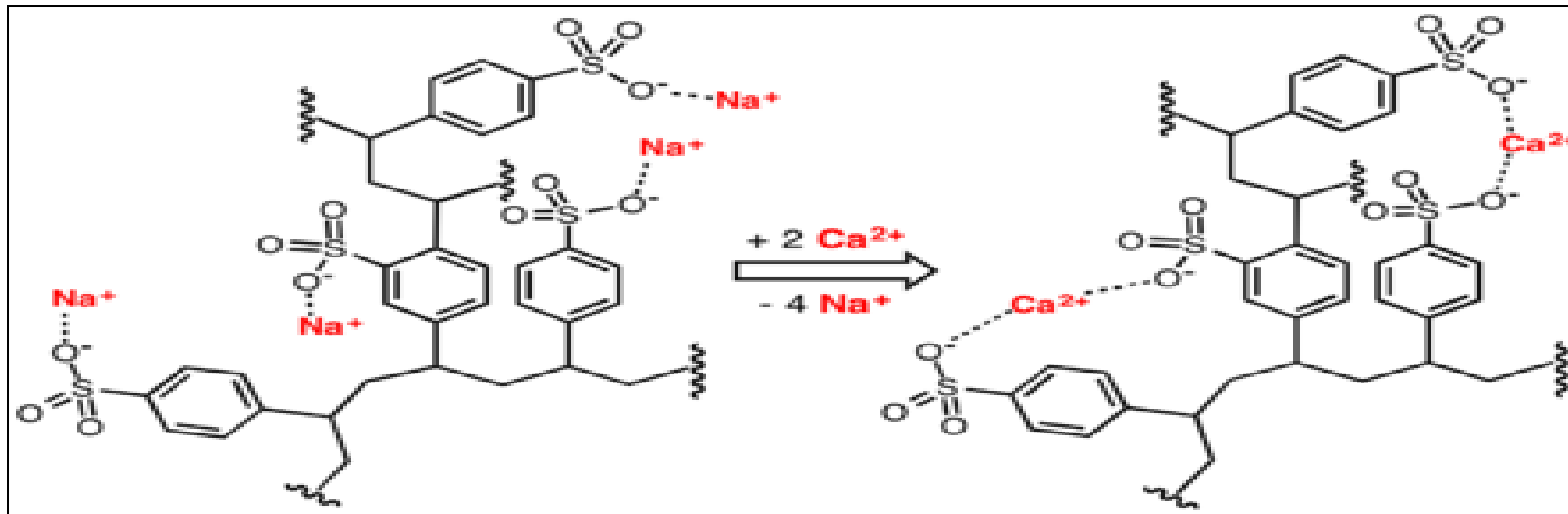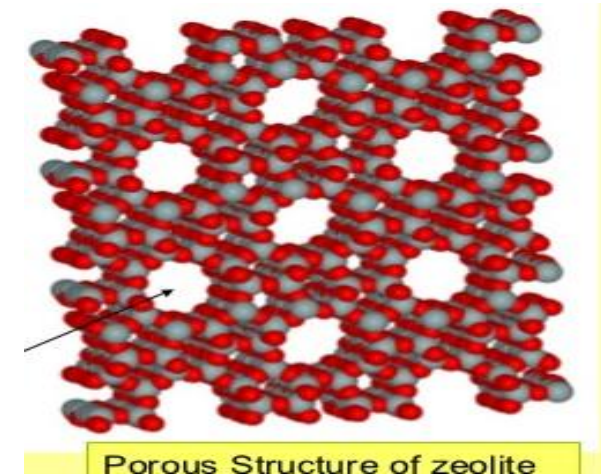❖ Ion-exchange

❖ Mixed bed ion-exchange

❖ Reverse Osmosis

Permutit or Zeolite Process

o   Zeolite is **hydrated sodium aluminium silicate** having a general formula, **$Na_2OAl_2O_3.xSiO_2.yH_2O$**.

o   It exchanges Na^+ ions for Ca^{2+} and Mg^{2+} ions.

o   Common Zeolite is $Na_2OAl_2O_3.3SiO_2.2H_2O$ known as natrolith.

o   Other gluconites, green sand (iron potassium phyllosilicate with characteristic green colour, a mineral containing Glauconite)etc. are used for water softening.

o   Artificial zeolite used for water softening is Permutit.

o   These are porous, glassy particles having higher softening capacity compared to green sand.

o   They are prepared by heating china clay (hydrated aluminium silicate), feldspar ($KAlSi_3O_8$-$NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) are a group of rock-forming tectosilicate minerals which make up as much as 60% of the earth's crust) and soda ash (Na_2CO_3)

Natural Zeolites:

1. Natrolite   - $Na_2O \cdot Al_2O_3\ 4SiO_2 \cdot 2H_2O$

2. Laumontite - $CaO \cdot Al_2O_3\ 4SiO_2 \cdot 4H_2O$

3. Harmotome - $(BaO \cdot K_2O) \cdot Al_2O_3\ 5SiO_2 \cdot 5H_2O$

- Capable of exchanging its Na ions

Porous Structure of zeolite

Permutit or Zeolite Process

o Method of softening:

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow 2\ NaHCO_3 + CaZe$$

$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow 2\ NaHCO_3 + MgZe$$

$$Na_2Ze + CaSO_4 \longrightarrow 2\ Na_2SO_4 + CaZe$$

$$Na_2Ze + CaCl_2 \longrightarrow 2\ NaCl + CaZe$$

o Regeneration of Zeolite:

$$CaZe\ (or)\ MgZe + 2\ NaCl \longrightarrow Na_2Ze + CaCl_2\ or\ MgCl_2$$

Brine solution

Softening of hard water by permutit process.
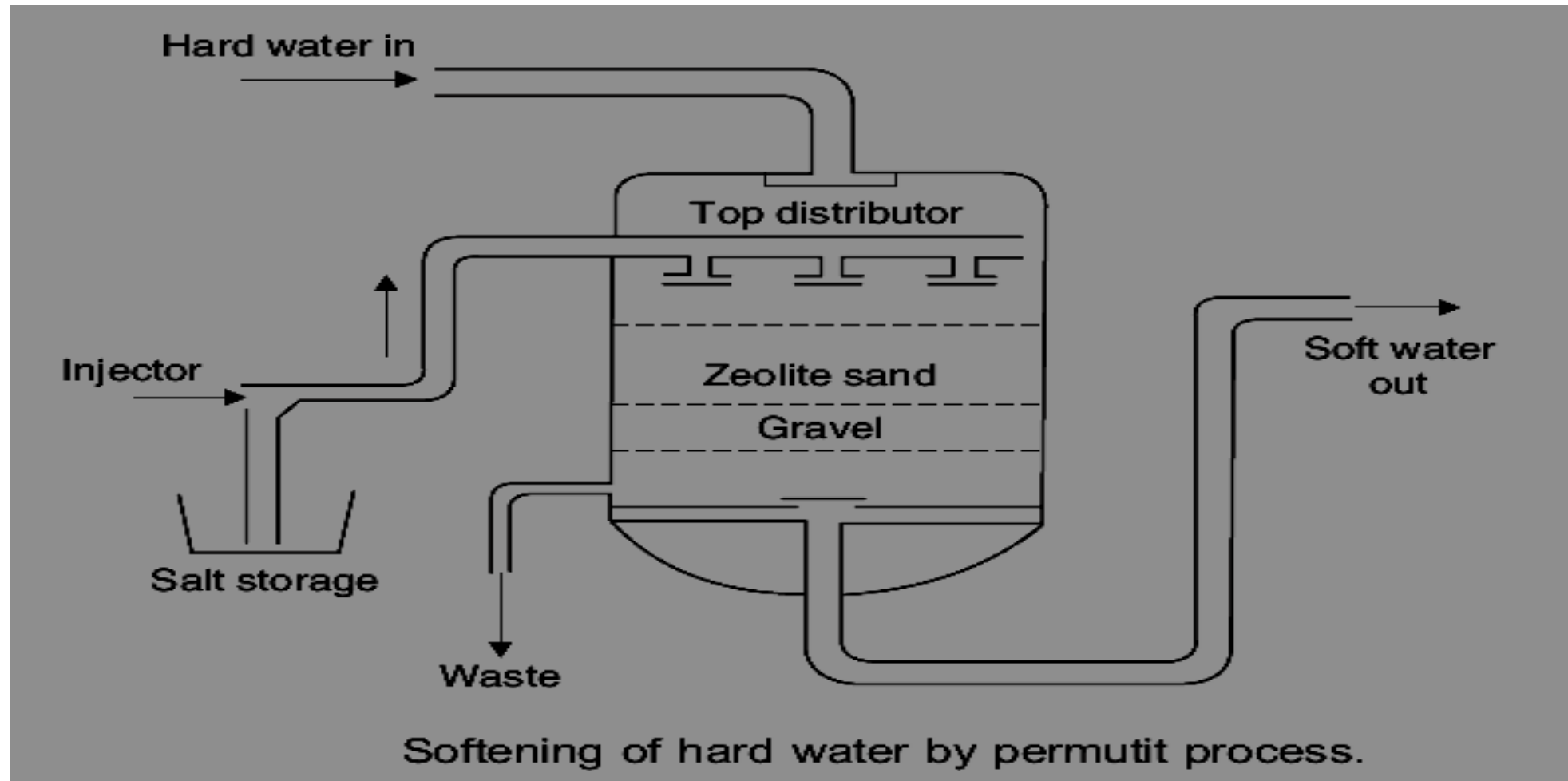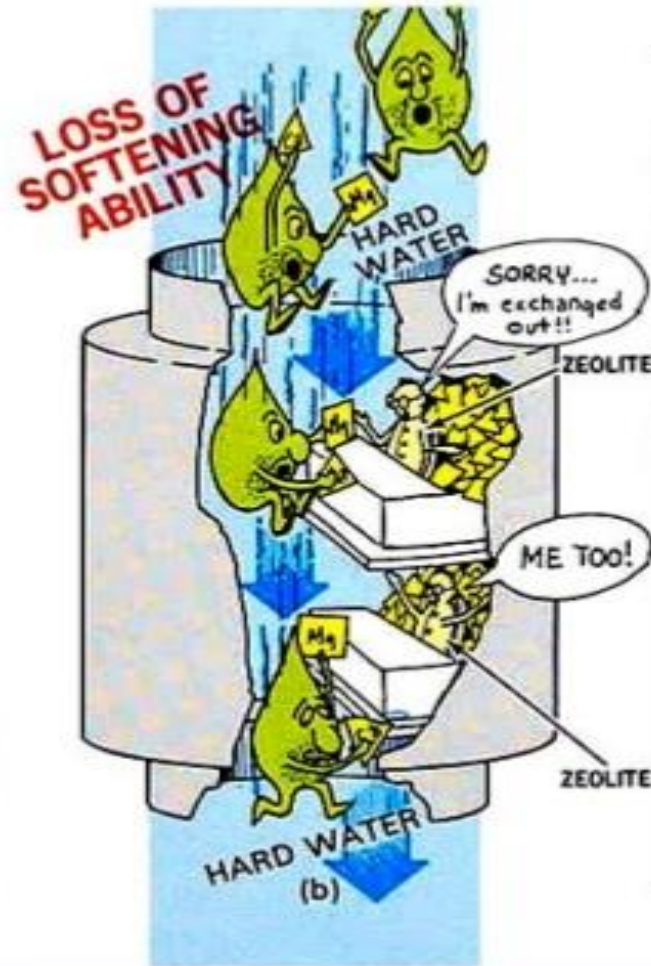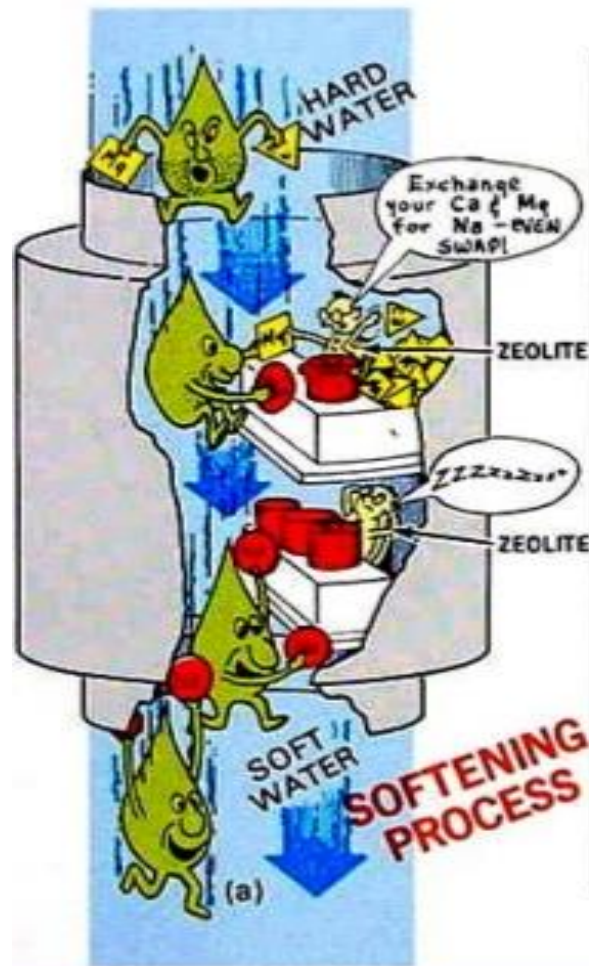
Zeolite Process

o Advantages:
  o Residual hardness of water is about 10 ppm only
  o Equipment is small and easy to handle
  o Time required for softening of water is small
  o No sludge formation and the process is clean
  o Zeolite can be regenerated easily using brine solution
  o Any type of hardness can be removed without any modifications to the process

o Disadvantages:
  o Coloured water or water containing suspended impurities cannot be used without filtration
  o Water containing acidic pH cannot be used for softening since acid will destroy zeolite.

Ion-Exchange Process

o Ion-exchange resins are cross linked long chain polymers with microporous structure

o Functional groups present are responsible for ion-exchange properties

o Acidic functional groups (-COOH, -SO_3H etc.) exchange H^+ for cations &

o Basic functional groups (-NH_2, =NH etc.) exchange OH^- for anions.

A. Cation-exchange Resins(RH^+):
- Styrene divinyl benzene copolymers
- When sulphonated, capable of exchange H^+

cation exchange resin
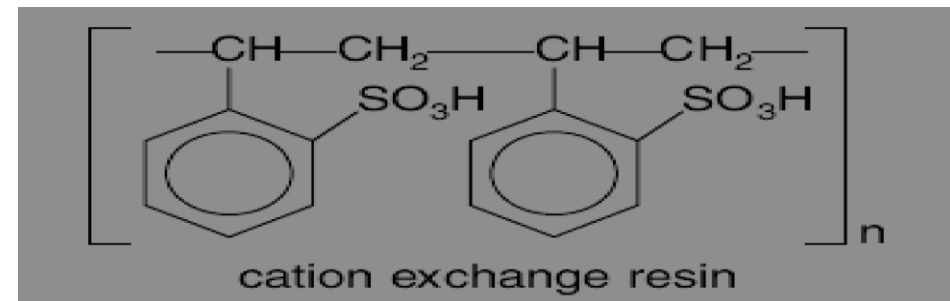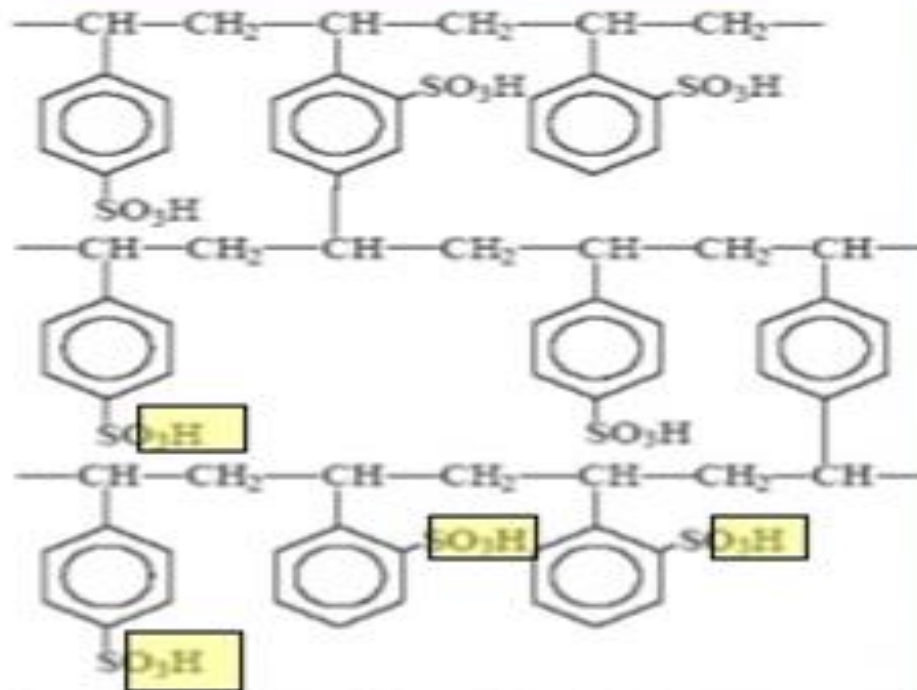
Ion-Exchange Process

B. Anion-exchange resins (R'OH):

- Styrene divinyl benzene copolymers or amine formaldehyde copolymers with NH_2, QN^+, QP^+, QS^+, groups.

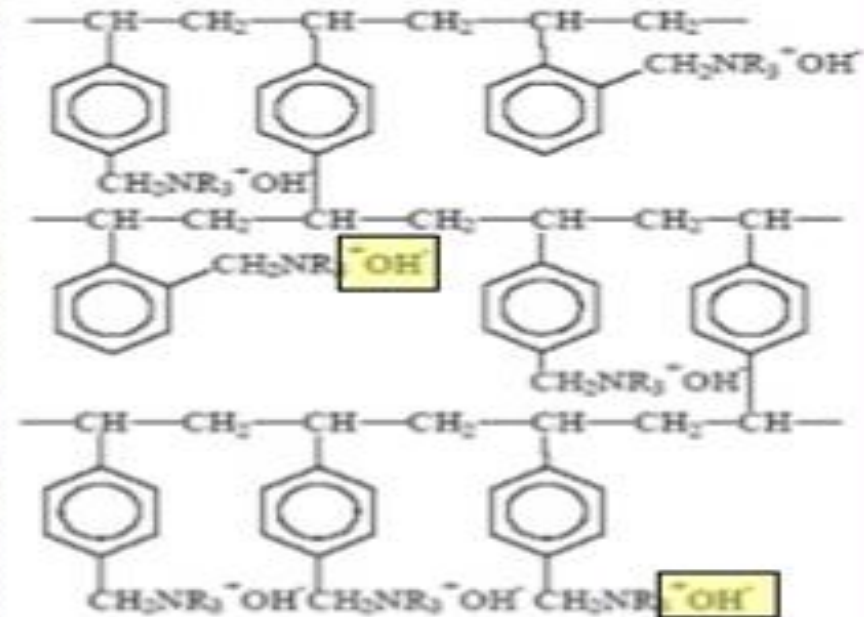- On alkali treatment, capable of exchange of OH^-

Anion exchange resin
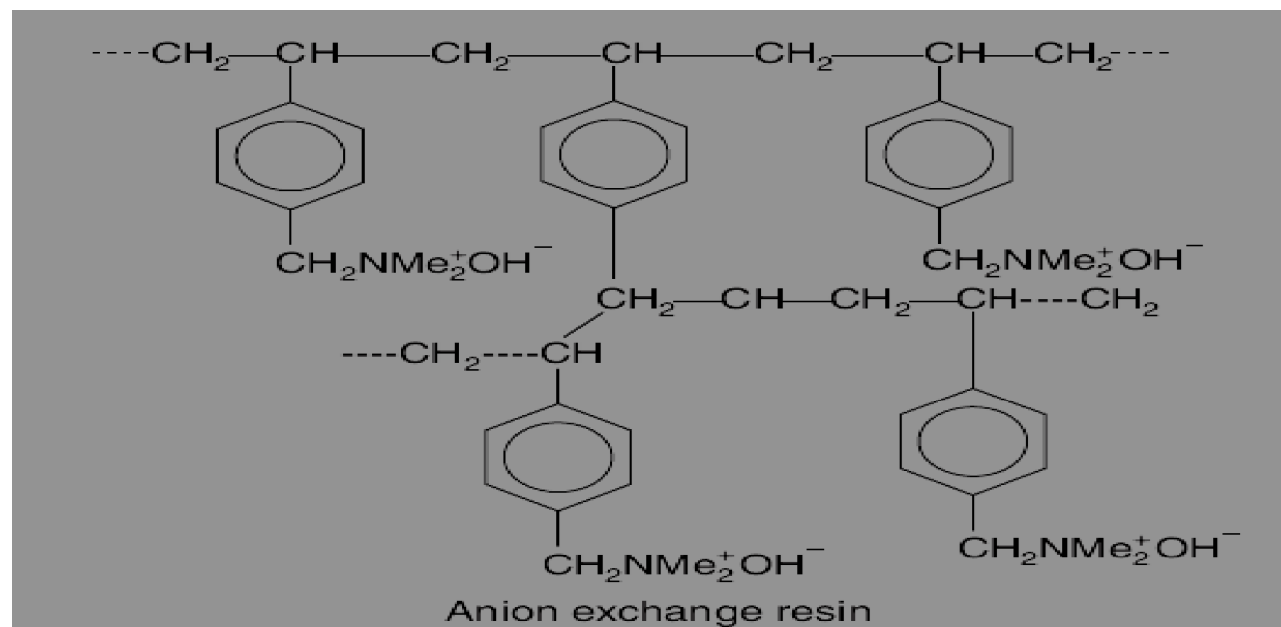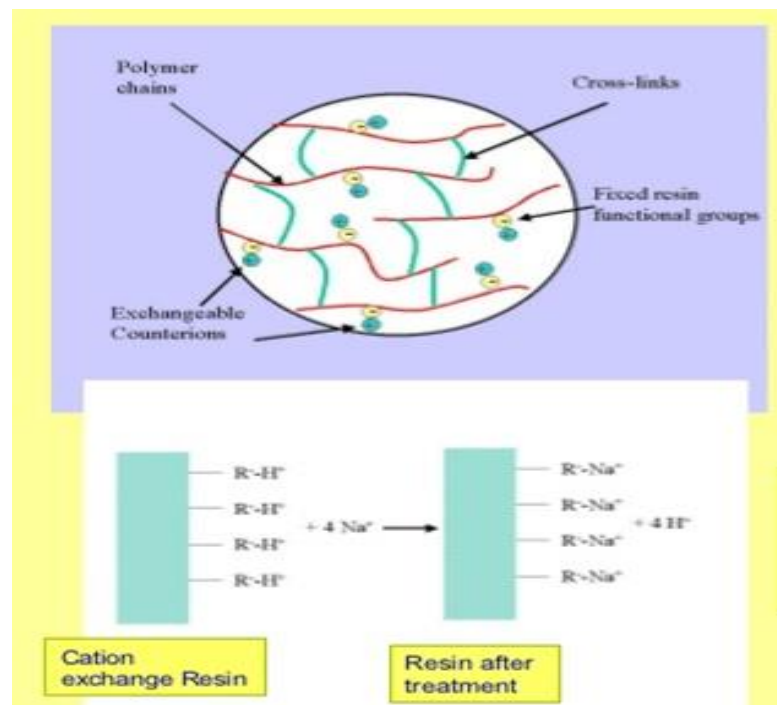
Structure of Cation and Anoin exchange resins

Ion exchange purifier or softener
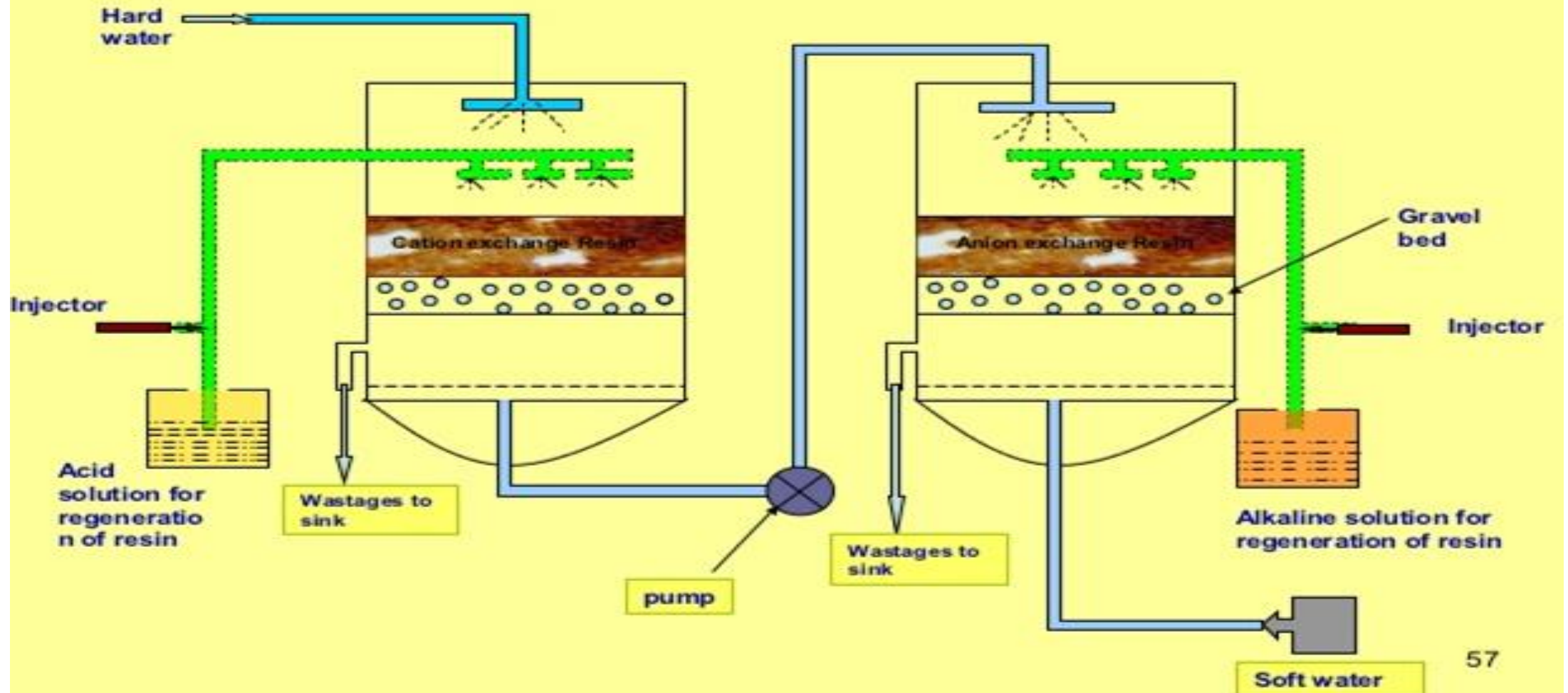
Ion-Exchange Process

The Process of Ion-exchange is:

$2\ RH^+ + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2\ H^+$ (Cation exchange)

$R'OH^- + Cl^- \longrightarrow R'^+ Cl^- + OH^-$ (anion exchange)

$2\ R'OH^- + SO_4^{2-} \longrightarrow R'_2\ SO_4^{2-} + 2\ OH^-$ (anion exchange)

$2\ R'OH^- + CO_3^{2-} \longrightarrow R'_2\ CO_3^{2-} + 2\ OH^-$ (anion exchange)

Finally, $\quad H^+ + OH^- \longrightarrow H_2O$
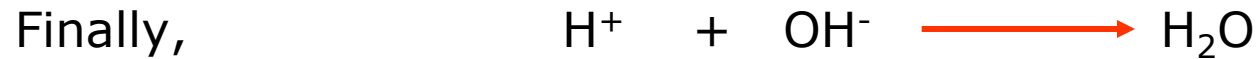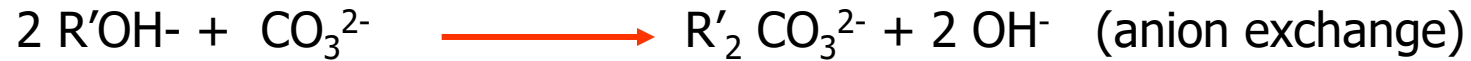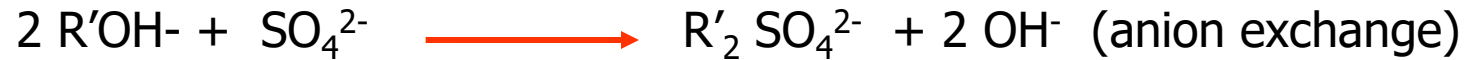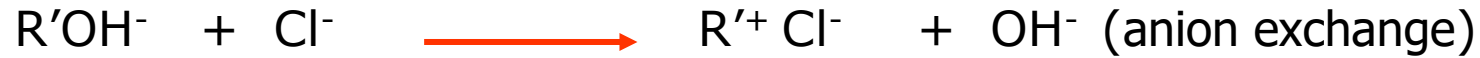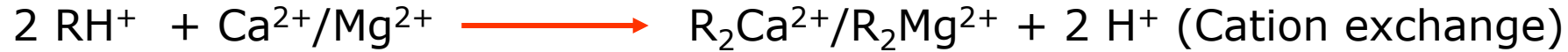
Regeneration of exhausted resins:

Saturated resins are regenerated:

$R_2Ca^{2+}/R_2Mg^{2+} + 2H^+ \longrightarrow 2\ RH^+ + Ca^{2+}/Mg^{2+}$ (cation) (Strong acid) (washings)

$R'_2\ SO_4^{2-} + 2\ OH^- \longrightarrow 2\ R'OH^- + SO_4^{2-}$ (Strong base) (washings)

Ion-Exchange Process

Demineralisation of water.
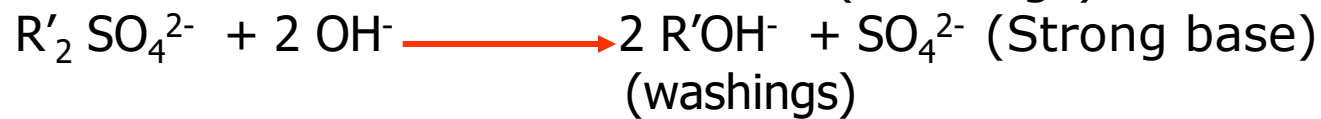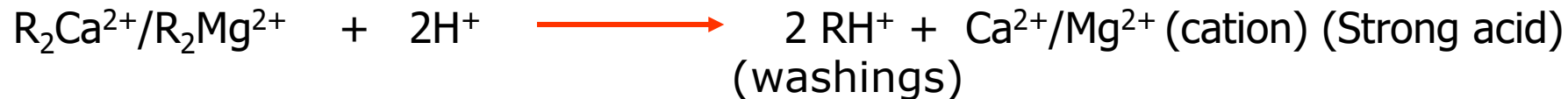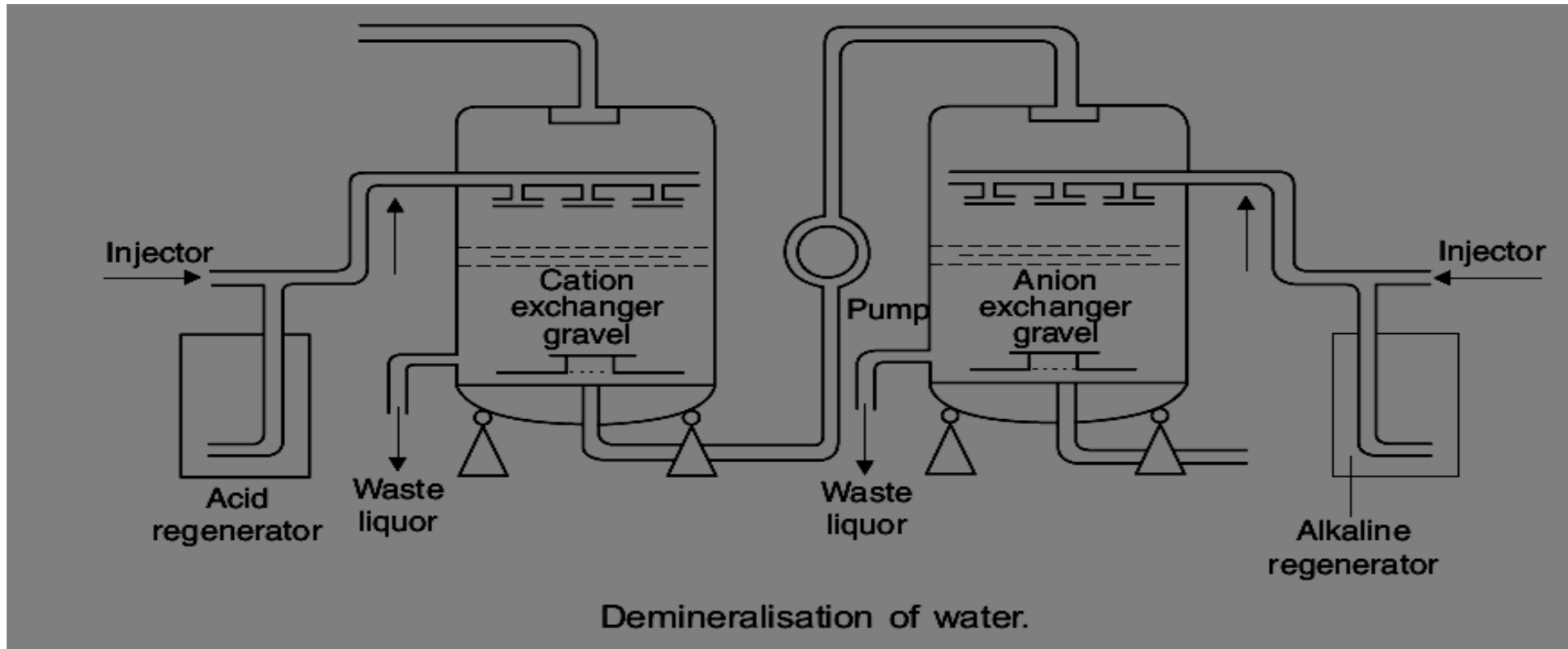
Note: Hard water should be first passed through the cation exchanger and then Anion exchanger to avoid hydroxides of Ca^{2+} and Mg^{2+} getting formed

Cation exchange reaction:

$$2R^-H^+ + Ca^{+2} \rightleftharpoons CaR_2 + 2H^+$$

Anion exchange reaction:

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3OH^-$$

$$R\overset{+}{N}H_3OH^- + Cl^- \rightleftharpoons R\overset{+}{N}H_3Cl^- + OH^-$$
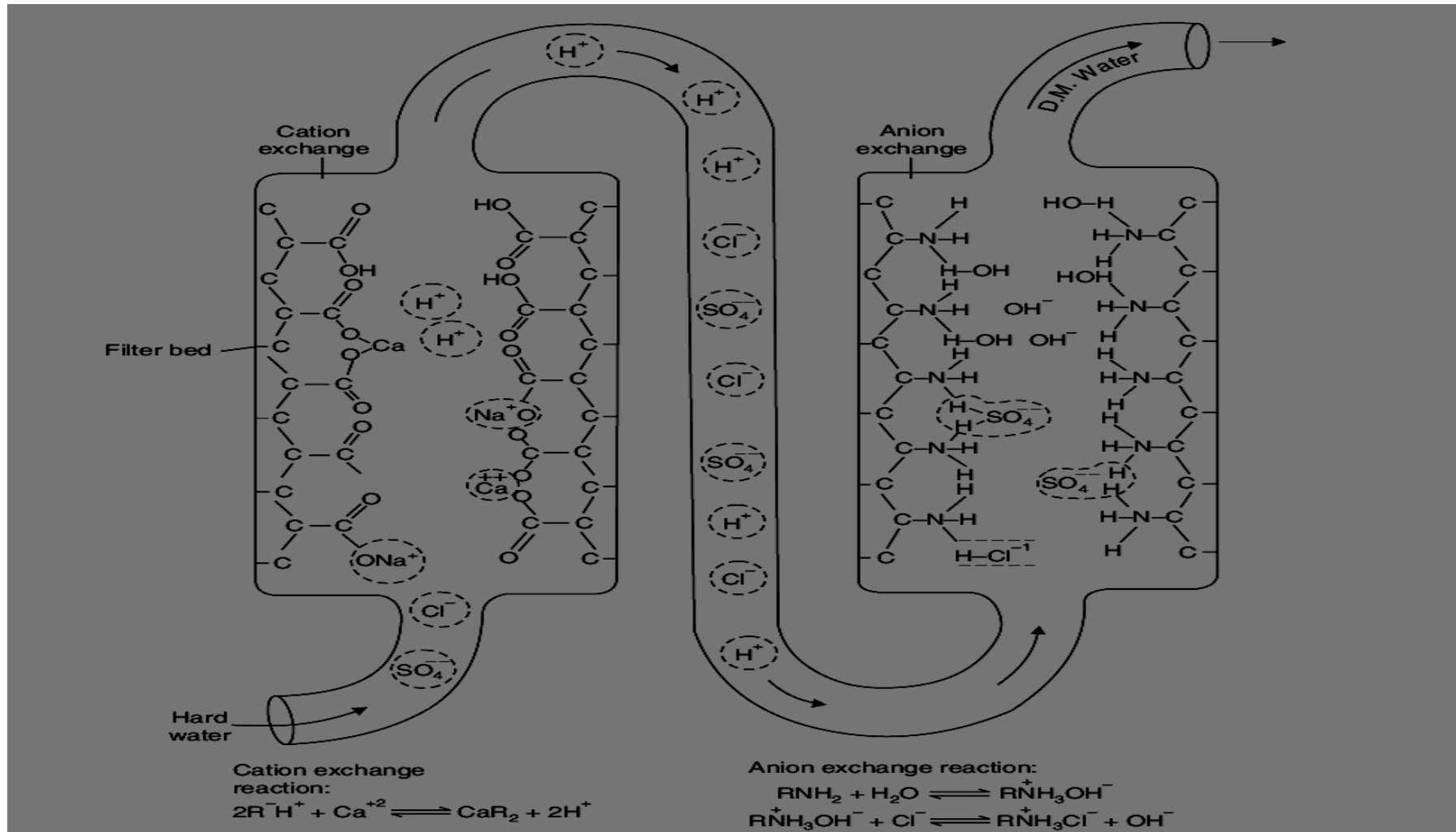
Mixed Bed Deionizer

Description and process of mixed bed deionizer

1. It is a single cylindrical chamber containing a mixture of anion and cation exchange resins bed

2. When the hard water is passed through this bed slowly the cations and anioins of the hard water comes in to contact with the two kind of resins many number of times

3. Hence, it is equivalent to passing the hard water many number of times through a series of cation and anion exchange resins.

4. The soft water from this method contains less than 1ppm of dissolved salts and hence more suitable for boilers

Hard water

Mixed bed deionizer

Anion exchange resin

Cation exchange resin

Mixed resin bed

Demineralised water
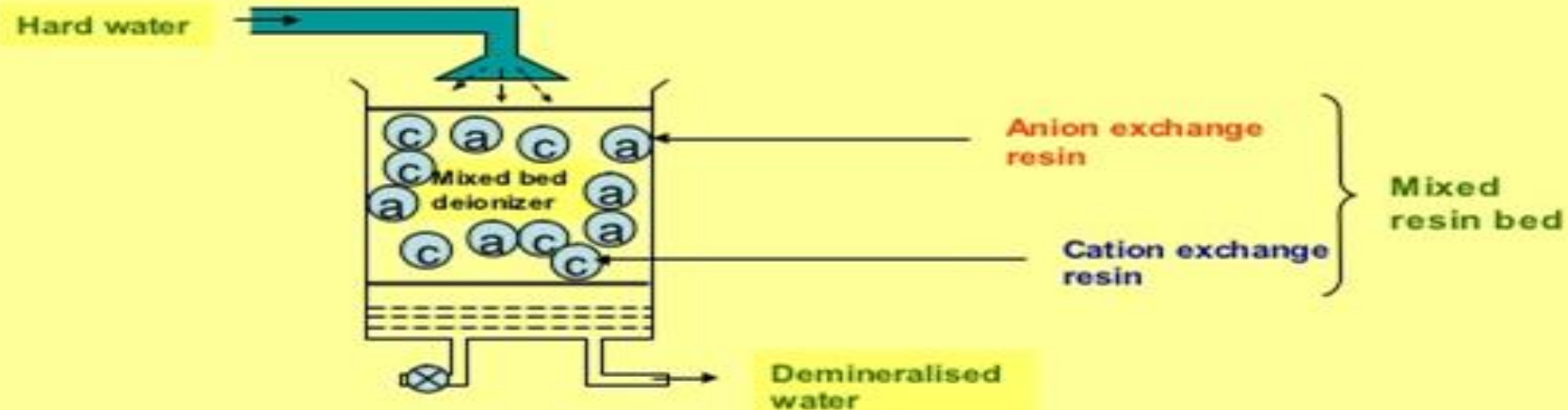
Regeneration of mixed bed deionizer

1. When the bed (resins) are exhausted or cease to soften the water, the mixed bed is back washed by forcing the water from the bottom in the upward direction

2. Then the light weight anion exchanger move to the top and forms a upper layer above the heavier cation exchanger

3. Then the anion exchanger is regenerated by passing caustic soda solution (NaOH) from the top and then rinsed with pure water

4. The lower cation exchanger bed is then washed with dil.H_2SO_4 solution and then rinsed.

5. The two beds are then mixed again by forcing compressed air to mix both and the resins are now ready for use
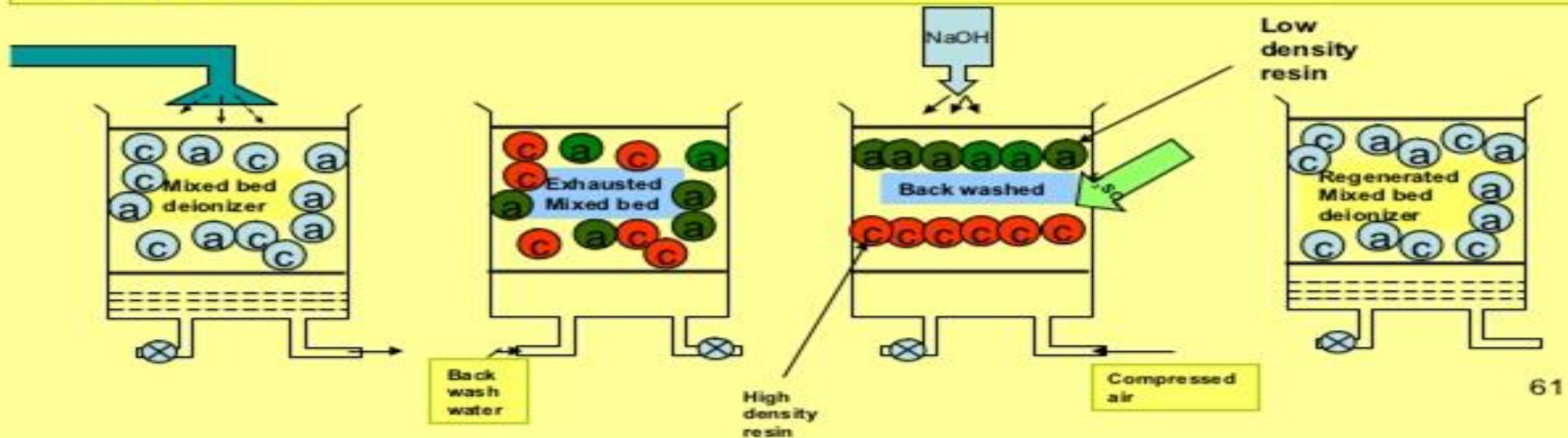
Advantages & Disadvantages

o   Advantages:

   - Can be used for highly acid and highly alkaline water

   - Residual hardness of water is as low as 2 ppm.

  - Very good for treating water for high pressure boilers

o   Disadvantages:

  - Expensive equipment and chemicals

  - Turbidity of water should be < 10 ppm. Otherwise output will

    reduce; turbidity needs to be coagulated before treatment.

  - Needs skilled labour

Reverse Osmosis

Pressure

Piston

Sea water

Stout semi-permeable membrane

Pure water

Pure water out

Reverse osmosis cell
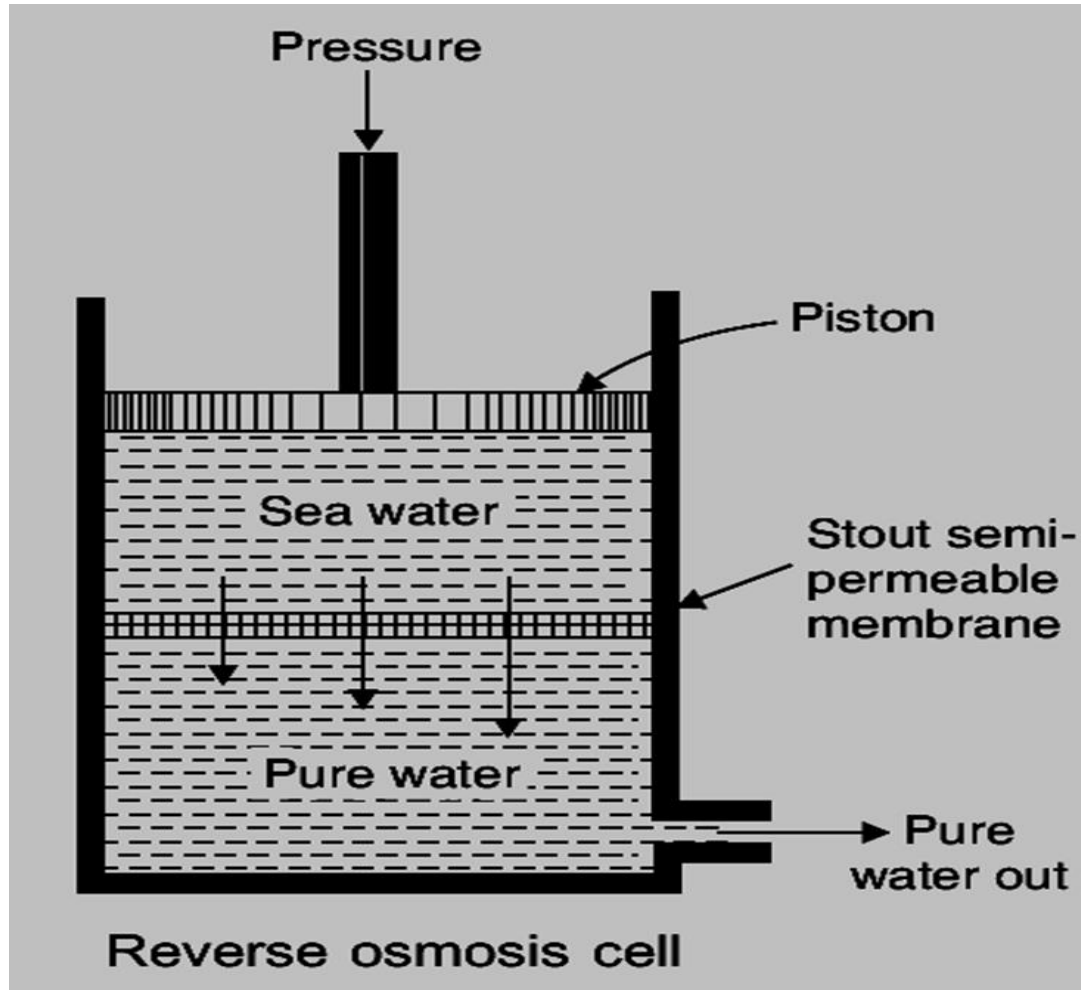
o When two solutions of unequal concentrations are separated by a Semipermeable membrane, solvent will flow from lower conc. to higher conc.

o This phenomenon can be reversed (solvent flow reversed) by applying hydrostatic pressure on the concentrated side

o In reverse osmosis, pressure of 15-40 kg/cm^2 is applied to sea water.

o The water gets forced through the semipermeable membrane leaving behind the dissolved solids.

Reverse Osmosis

TAP WATER (IN-COMING)

BACTERIA, PYROGENS, VIRUSES, PESTICIDES, HYDROCARBONS, RADIOACTIVE CONTAMINANTS, TURBIDITY, COLLOIDAL MATTER, CHLORINE, DETERGENTS, INDUSTRIAL WASTES, ASBESTOS, DISSOLVED SOLIDS: SODIUM, CALCIUM, MAGNESIUM, SULFATES, CADMIUM

MEMBRANE

PURE WATER (TO HOLDING TANK)

IMPURITIES (OUT TO DRAIN)

pressure

semipermeable membrane

salt water

fresh water

Precision Graphics

ADVANTAGES:

- Improves taste, odor and appearance
- Highly effective purification process. Will remove the pollutants listed above, and more!
- Consumes no energy
- Very convenient
- Flushes away pollutants, does not collect them
- Easy to keep clean
- Low production cost - gives you water of a guaranteed quality for pennies per gallon

Fuels and Combustion

- **<u>Fuel</u>** is a combustible substance, which on combustion produces a large amount of heat, which can be used for various domestic and industrial purposes.

Combustion:

- The process of combustion involves oxidation of carbon, hydrogen etc. of the fuels to CO_2, H_2O, and the difference in the energy of reactants and the products are liberated as large amount of heat energy which is utilized.

$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$
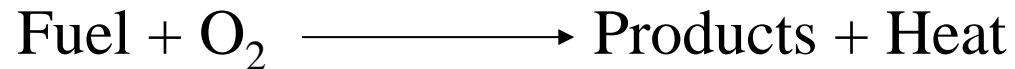
- The primary or main source of fuels are coal and petroleum oils, the amounts of which are dwindling day by day. These are stored fuels available in earth's crust and are generally called "fossil fuels".

Classification of Fuels


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                    Classification of Fuels
                              |
          ┌───────────────────┴───────────────────┐
          ↓                                       ↓
    Primary or                              Secondary or
     Natural                                  Derived
          |                                       |
   ┌──────┼──────┐                    ┌──────────┼──────────┐
   ↓      ↓      ↓                    ↓          ↓          ↓
 Solid  Liquid Gaseous             Solid      Liquid     Gaseous
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Primary or Natural			Secondary or Derived		
Solid	**Liquid**	**Gaseous**	**Solid**	**Liquid**	**Gaseous**
Wood Coal Dung	Crude oil	Natural gas	Coke Charcoal Petroleum-coke Coal-briquette	Tar Kerosene Diesel Petrol Fuel oil LPG Synthetic gasoline	Coal gas Water gas Oil gas Biogas Coke oven gas Blast furnace gas

Calorific value of fuels

- The most important property of fuel to be taken into account is its calorific value or the capacity to supply heat.

- The calorific value of a fuel can be defined as "the total quantity of heat liberated when a unit mass or volume of the fuel is burnt completely".

Units of heat

- Calorie - Calorie is the amount of heat required to raise the temperature of one gram of water through one degree centigrade.

- Kilocalorie (or) kilogram centigrade unit - This is the unit of metric system and is equal to 1000 calories. This may be defined as "the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade".

  - Thus 1 kcal = 1000 cal.

Units of heat

3. British thermal unit (B. Th. U.) - This is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit". This is English system unit.

$$1 \text{ B. Th. U.} = 252 \text{ cal} = 0.252 \text{ k cal.}$$

$$1 \text{ k cal} = 3.968 \text{ B. Th. U.}$$

4. Centigrade Heat Unit (C. H. U.) - This is the "quantity of heat required to raise the temperature of one pound of water through one degree centigrade".

$$\text{Thus, } 1 \text{ k cal} = 3.968 \text{ B. Th. U.} = 2.2 \text{ C. H. U.}$$

Units

Amount of heat required to raise the temp. of

- **<u>Calorie</u>**:   1g of water through 1^oC

- **<u>Kilocalories</u>** :   1Kg of water through 1^oC

- **<u>British Thermal</u>**

  <u>Unit (B. Th. U)</u> :   1pound of water through 1^oF

- **<u>Centigrade</u>**

  <u>Thermal Unit (C.T.U)</u> : 1pound of water through 1^oC

Higher or Gross Calorific Value (HCV or GCV)

Most of the fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted to steam

If the products of combustion are condensed to room temperature (15°C or 60°F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value"

So gross or higher calorific value may be defined as "the total amount of heat produced when one unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature"

Lower or Net Calorific Value (LCV)

In actual case of any fuel, the water vapour and moisture etc are not condensed and escapes as such along with hot combustion gases. Hence a lesser amount of heat is available. So, net or lower calorific value may be defined as "the net heat produced when unit mass / volume of the fuel is burnt completely and the products are permitted to escape".

Net or lower calorific value can be found from GCV value

$$NCV = GCV - \text{Latent heat of water vapour formed}$$

$$= GCV - \text{Mass of hydrogen} \times 9 \times \text{latent heat of steam}$$

1 part by mass of hydrogen produces 9 parts by mass of water.

The latent heat of steam is 587 k cal / kg or 1060 B. Th. U. / lb of water vapour formed at room temperature. (ie 15 °C)

Characteristics of a good fuel

1. High Calorific Value
2. Moderate Ignition Temperature
3. Low Moisture Content
4. Low non-combustible matter content
5. Moderate velocity of combustion
6. Products of combustion should not be harmful
7. Low Cost
8. Easy to transport
9. Combustion should be easily controllable
10. Should not undergo spontaneous combustion
11. Storage cost in bulk should be low
12. Size should be uniform (solid fuel) – Combustion is regular

Comparison between solid, liquid and gaseous fuel

Solid Fuels

Advantages

1. They are easy to transport
2. They are convenient to store, without any risk of spontaneous explosion
3. The cost of production is low
4. They posses moderate ignition temperature

Disadvantages

1. The ash content is high
2. Large production of heat wasted during combustion (low thermal energy)
3. Burn with clinker formation
4. Combustion operations can not be controlled easily
5. Cost of handling is high
6. Calorific value is lower as compared to liquid fuel
7. Require large excess of air for combustion
8. Can not be used in internal combustion engines

Liquid Fuels

Advantages

1. Posses high calorific value per unit mass than solid fuel
2. Burn without forming clinker, ash, dust etc.
3. Firing is easier and fire can be extinguished easily by stopping fuel supply
4. They are easy to transport through pipes
5. Can be stored indefinitely, without any loss
6. Flame can be controlled
7. Handling is easy
8. Clean in use and economic in labour
9. Loss of heat in chimney is low
10. They require less excess of air for complete combustion
11. Require less furnace space for combustion
12. Can be used in internal combustion fuels

Disadvantages

1. Cost of liquid fuel is relatively higher
2. Costly storage tanks are required
3. Greater risk of fire hazards
4. Gives bad odour
5. Specially designed burners and spraying apparatus are required
6. Choking of sprayers (during combustion) is a drawback of oil firing

Gaseous Fuels

Advantages

1. Conveyed easily through pipelines to the actual place of need
2. Lighted at moment of notice
3. High heat content, and helps to achieve higher temperatures
4. Combustion can be readily controlled
5. Burn without any smoke and ash less
6. Clean in use
7. Do not require any special burners
8. Burn without heat loss, due to convection currents
9. They burn even in slight excess of air supply
10. Free from solid and liquid impurities
11. Complete combustion without pollution is possible
12. High Calorific values
13. Can also be used as internal combustion engine

Disadvantages

1. Large storage tanks are needed for them
2. Highly inflammable, chances of fire hazards are high in their use
3. More costly compared to solid and liquid fuels

Determination of Calorific Value

Bomb calorimeter
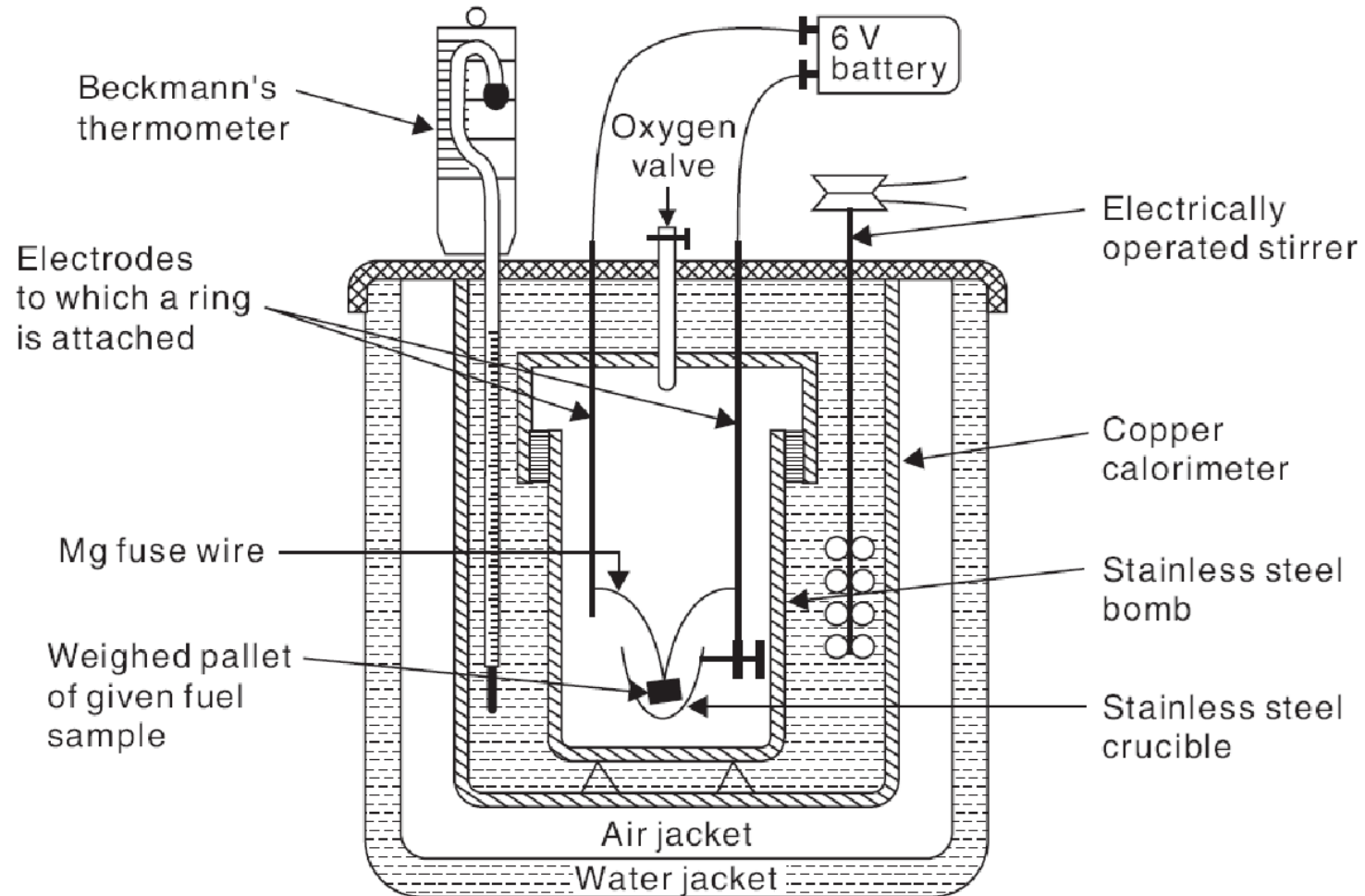
Calculation

m = mass of fuel pellet (g)

W = mass of water in the calorimeter (g)

w = water equivalent of calorimeter (g)

t_1 = initial temperature of calorimeter.

t_2 = final temperature of calorimeter.

HCV = gross calorific value of fuel.

$$L = HCV = \frac{(W + w)(t_2 - t_1)}{m} \ \text{cal/gm.}$$

Water Equivalent of the calorimeter is determined by burning a fuel of known calorific value (benzoic acid (HCV = 6,325 kcal/kg) and naphthalene (HCV = 9,688 kcal/kg)

If H is the percentage of hydrogen in fuel,
the mass of water produced from 1 g of fuel $= (9/100) \times H$
$= 0.09\ H$

Heat taken by water in forming steam = 0.09 H× 587 cal

(latent heat of steam = 587 cal/kg)

LCV = HCV – Latent heat of water formed

$$LCV = \left[HCV - \frac{9}{100}\ H \times 587 \right] \text{kcal/kg.}$$
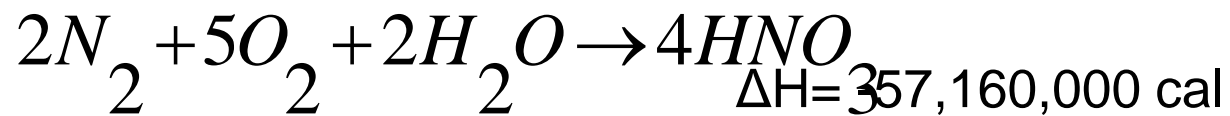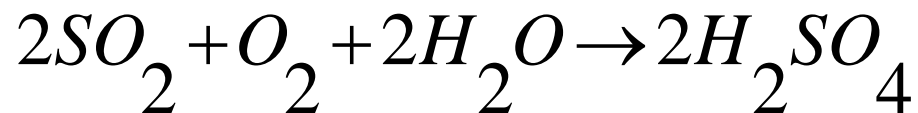$$= [HCV - 0.09\ H \times 587]\ \text{kcal/kg.}$$

Corrections

- **Fuse wire correction**. Heat liberated during sparking should be subtracted from heat liberated.

- **Acid correction**. Fuels containing Sulphur and Nitrogen if oxidized, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions).

- **Cooling correction**. The rate of cooling of the calorimeter from maximum temperature to room temperature is noted. From this rate of cooling (i.e., dt°/min) and the actual time taken for cooling (t min) then correction (dt × t) is called cooling correction and is added to the (t2 . t1) term.

$$L = \frac{(W+w)\,(t_2 - t_1 + \text{Cooling Correction}) - (\text{Acid} + \text{Fuse Correction})}{\text{Mass of the fuel } (x)}$$

Corrections: For accurate results the following corrections are also incorporated:

(a) Fuse wire correction: As Mg wire is used for ignition, the heat generated by burning of Mg wire is also included in the gross calorific value. Hence this amount of heat has to be subtracted from the total value.

(b) Acid Correction: During combustion, sulphur and nitrogen present in the fuel are oxidized to their corresponding acids under high pressure and temperature.

$$S + O_2 \rightarrow SO_2 \qquad \Delta H = \text{-144,000 cal}$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3 \qquad \Delta H = \text{-57,160,000 cal}$$

The corrections must be made for the heat liberated in the bomb by the formation of H_2SO_4 and HNO_3. The amount of H_2SO_4 and HNO_3 is analyzed by washings of the calorimeter.

For each ml of 0.1 N H_2SO_4 formed, 3.6 calories should be subtracted.

For each ml of 0.1 HNO_3 formed, 1.429 calories must be subtracted.

(C) Cooling correction: As the temperature rises above the room temperature, the loss of heat does occur due to radiation, and the highest temperature recorded will be slightly less than that obtained. A temperature correction is therefore necessary to get the correct rise in temperature.

If the time taken for the water in the calorimeter to cool down from the maximum temperature attained, to the room temperature is x minutes and the rate of cooling is dt/min, then the cooling correction = x × dt. This should be added to the observed rise in temperature

1. 0.72 gram of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3º to 29.1ºC. If the calorimeter contains 250 grams of water and its water equivalents is 150 grams, calculate the HCV of the fuel. Give your answer in kJ/kg.

Here m= 0.72 g, W = 250g, w= 150g, t_1 = 27.3ºC, t_2 = 29.1ºC.

HCV of fuel (Q) = $\frac{(W + w)\ (t_1 - t_2)}{m}$

= (250 + 150) × (29.1-27.3)/0.72 cal/g

=400g x1.8 ^{0}cx 4.2joule.g^{-1}. c^{-1}/0.72g

=4200 joule/gram   (1000g= 1kg)

=4200kJ/kg

Specific heat of water = s (1 calorie/gram °C = 4.2 joule/gram °C)

A sample of coal has C=93%, H=6% and ash=1%. When coal is tested in bomb calorimeter, the following are the data:

- Weight of burnt coal=0.92g,

- weight of water taken=550g,

- water equivalent to bomb calorimeter=2200g,

- rise in temperature=2.42 ^{0}C,

- fuse wire correction=10 cal,

- acid correction=50 cal.

Calculate gross and net calorific value of the coal assuming the latent heat of condensation of steam as 587 cal/g

2. On burning 0.83 of a solid fuel in a bomb calorimeter , the temperature of 3,500g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385g and 587.0 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific value.

$$\text{Gross calorific value} = \frac{(W + w)\ (t_2 - t_1)}{x}$$

$$= \frac{(3500 + 385) \times 2.7}{0.83}\ \text{cal/g} = 12{,}638\ \text{cal/g}$$

$$\text{NCV} = [\text{GCV} - 0.09\ H(\%) \times 587]$$

$$= (12{,}638 - 0.09 \times 0.7 \times 587)\ \text{cal/g}$$

$$= (12{,}638 - 37)\ \text{cal/g}$$

$$= 12{,}601\ \text{cal/g}$$

Dulongs Formula

The approximate calorific value of a fuel can be determined by knowing the amount of constituents present:

Gross or higher calorific value (HCV) from elemental constituents of a fuel.

$$H = 34500 \text{ kcal/kg}; C = 8080 \text{ kcal/kg}; S = 2240 \text{ kcal/kg}$$

Oxygen present in the fuel is assumed to be present as water (fixed hydrogen).

Available Hydrogen   = Total hydrogen - Fixed hydrogen
                        = Total hydrogen - 1/8 mass of oxygen in fuel.

Dulongs formula for calorific value from the chemical composition of fuel is,

$$HCV = \frac{1}{100}\left[8080\, C + 34500\left(H - \frac{O}{8}\right) + 2240\, S\right] \text{kcal/kg}$$

Corrosion

Corrosion

Any process of deterioration and consequent loss of solid metallic material, through an unwanted chemical or electrochemical attack by its environment

$$\text{Metal} \underset{\substack{\text{Extraction of} \\ \text{Metals}}}{\overset{\substack{\text{Corrosion} \\ \text{(Oxidation)}}}{\rightleftharpoons}} \text{metallic compounds + Energy}$$

Types

- Dry or Chemical Corrosion

- Electrochemical Corrosion

Dry or Chemical Corrosion

1. Oxidation Corrosion

1. Corrosion by other gases

1. Liquid Metal Corrosion

Oxidation Corrosion

Oxygen present in the atmosphere attacks the metal surface

– formation of oxide layers

$$2M \longrightarrow 2M^{n+} + 2n\ e^-$$

$$\frac{n}{2} O_2 + 2n\ e^- \longrightarrow n\ O^{2-}$$

$$2M + \frac{n}{2} O_2 \longrightarrow 2\ M^{n+} + n\ O^{2-} \text{ (or) } MO$$

Mechanism

Nature of the Oxide

– When oxidation starts, a thin layer of oxide film will be formed on the surface and the nature of the film decides the further action!
i.e. Porous film or non-porous film

Factors Influencing Corrosion

Nature of the

Metal

Position in galvanic series

Overvoltage

Relative areas of anode and cathode

Purity of the metal

Physical state of the metal

Nature of the surface film

Passive character of the metal

Solubility of corrosion products

Environment

Temperature

Humidity

Presence of impurities in atmosphere

Suspended particles

pH

Silicates

Conductance

Formation of O_2 conc. cell

Flow velocity

Forms of Corrosion

Example	Types of Corrosion
	Uniform Corrosion • Generally occurs due to direct chemical attacks
	Galvanic Corrosion • An electrochemical action that occurs between two dissimilar metals which are in contact with other.
	Concentration Cell Corrosion • It occurs when two metal surfaces are in contact with different concentrations of the same solution.
	Pitting Corrosion • A kind of localized corrosion that occurs with pits at underneath surface formed due to corrosion product accumulation.

Crevice Corrosion

- It occurs when metals are in contact with nonmetals.

Filiform Corrosion

- It occurs on painted surfaces due to penetration of coated surface by moisture in the form of filaments.

Intergranular Corrosion

- It occurs on grain boundaries of a metal or alloy.

	Stress Corrosion Cracking • It occurs due to applied loads, residual stresses or a combination of both.
	Corrosion Fatigue • A special case of stress corrosion that occurs due to combined effects of cyclic stress and corrosion.
	Fretting Corrosion • It is a rapid corrosion, occurs at the interface between highly loaded metal surfaces due to vibratory motions.
	Erosion Corrosion • It occurs due to combination of a chemical environment with high fluid-surface velocities.

➢ Crevice Corrosion
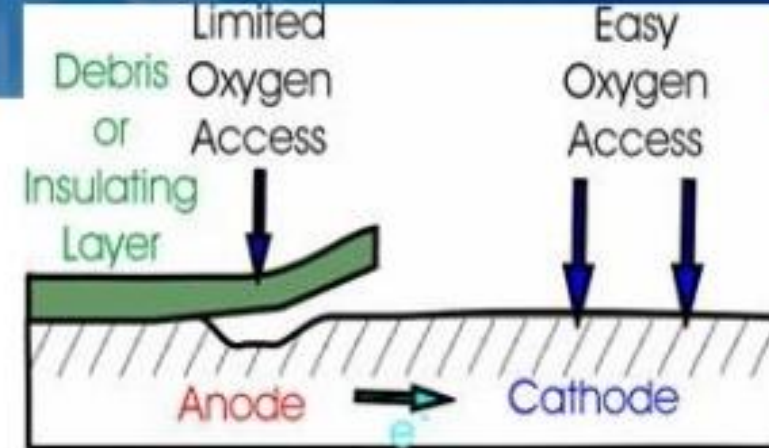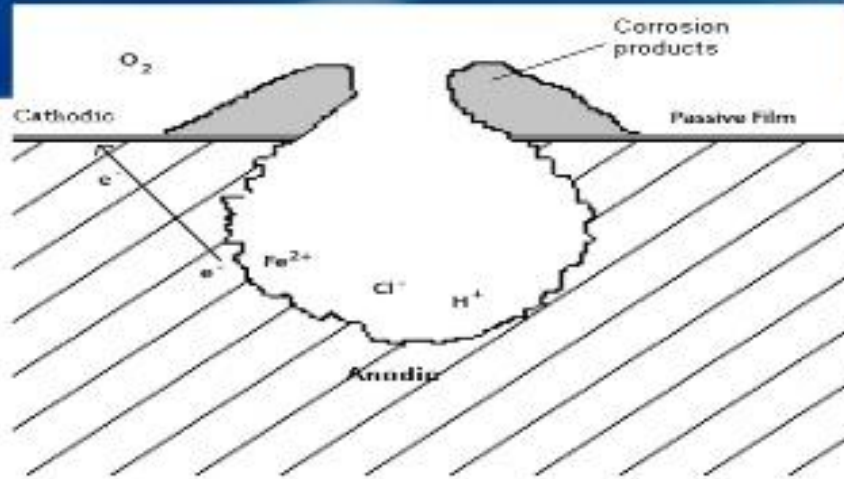
This is a concentration cell in action. Notice how the damage occurs in out of sight places.

Control of Corrosion

Corrosion can be controlled by:

a)   Proper designing
b)   Proper selection of metal or alloy
c)   Use of pure metals
d)   Use of alloys
e)   Cathodic protection
f)   Anodic protection
g)   Use of inhibitors
h)   Changing the environment
i)   Application of protective coatings

Cathodic Protection

Cathodic protection:

Principle is to make the base metal to be protected as cathode by connecting to a highly anodic metallic plate.

Two methods of cathodic protection are known:

i) Sacrificial anodic protection

ii) Impressed current cathodic protection

i) Sacrificial anodic protection:

o   The metallic structure to be protected is connected through a metal wire to a more anodic metal.

o   This will induce corrosion at the anodic metal.

o   Thus the more anodic metal sacrifices itself and gets corroded protecting the metallic structure.

o   Sacrificial anodes known are Zn, Mg, Al and their alloys.

o   Applications are: protection of underground pipelines, ship hulls and other marine devices, water tanks.

Sacrificial anodic protection

Sacrificial anodic protection - concept
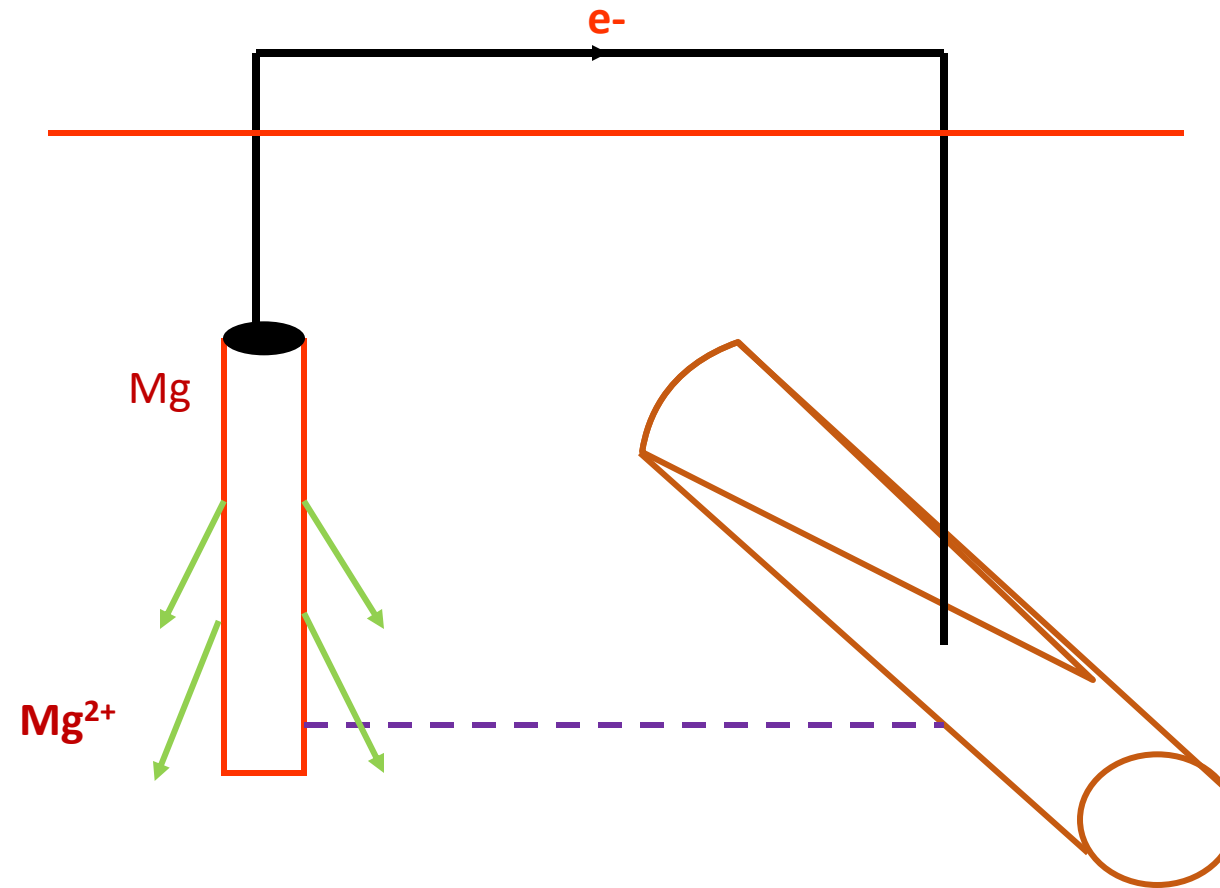
Sacrificial Anodes

- **Galvanization of Steel**

- **Dip steel sheet in molten zinc. Get a pretty thin coating.**

- **Zinc will be anode. Steel exposed by crack is the cathode. Since we have a huge anode having to be served by a small cathode, corrosion rate will be slow.**

Tiny cathode (steel)

Larger Area (Zinc)
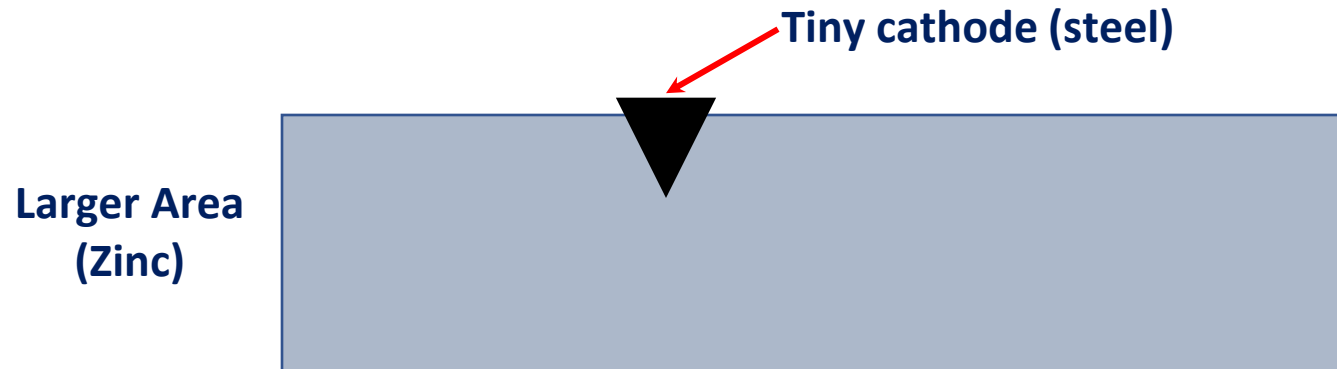
An example of a unfavorable area ratio. Bad deal: huge cathode, tiny anode

Another Example

Zinc is attached to the steel hull of the vessel

Table 17.2   The Galvanic Series

	Platinum
	Gold
	Graphite
	Titanium
	Silver
	⌈316 Stainless steel (passive)
	⌊304 Stainless steel (passive)
	⌈Inconel (80Ni–13Cr–7Fe) (passive)
	⌊Nickel (passive)
	⌈Monel (70Ni–30Cu)
Increasingly inert (cathodic) ↑	Copper–nickel alloys
	Bronzes (Cu–Sn alloys)
	Copper
	⌊Brasses (Cu–Zn alloys)
	⌈Inconel (active)
	⌊Nickel (active)
	Tin
	Lead
Increasingly active (anodic) ↓	⌈316 Stainless steel (active)
	⌊304 Stainless steel (active)
	⌈Cast iron
	⌊Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

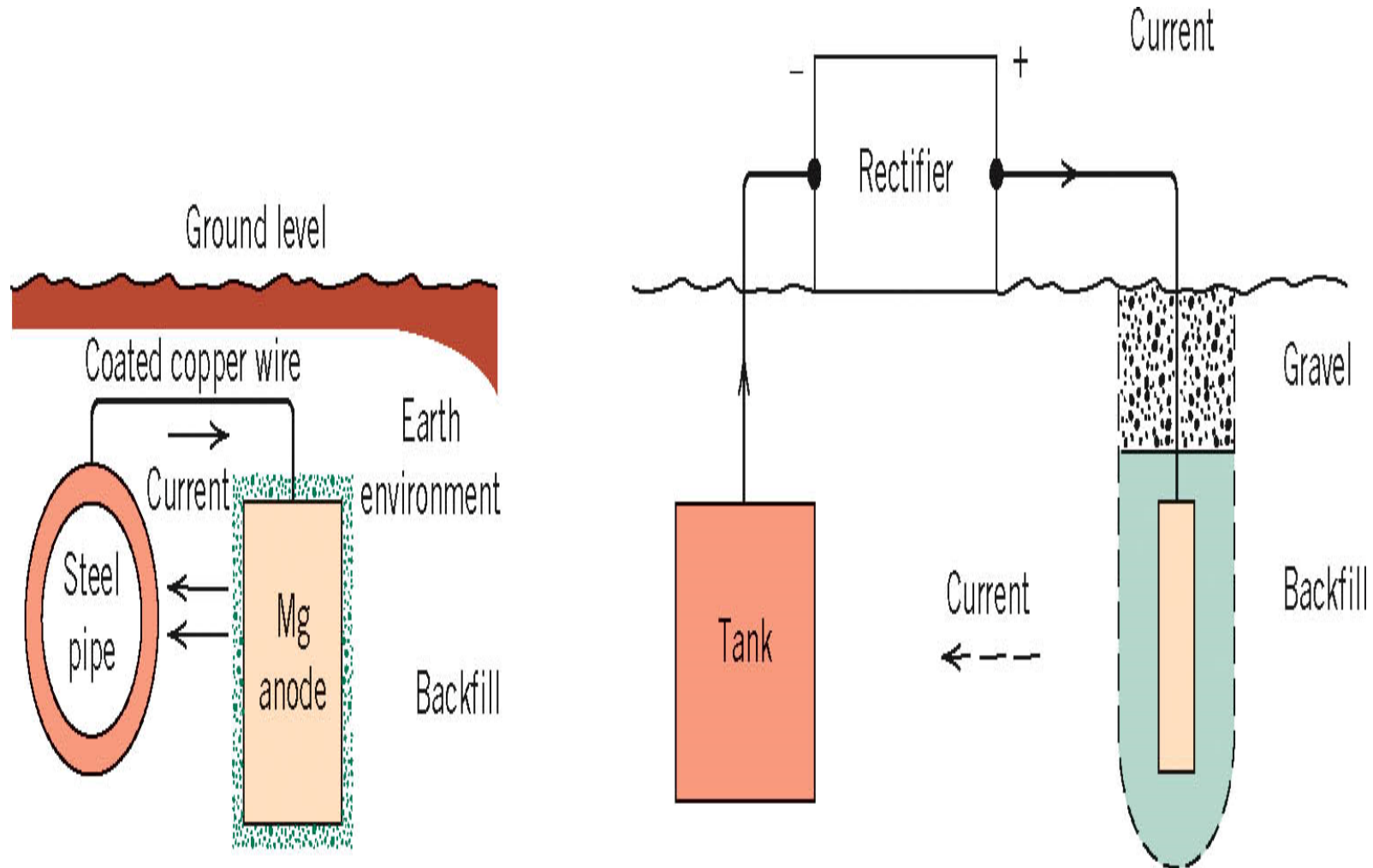| Electrode		Electrode reaction	E^0/V
Au	Gold	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.43
Ag	Silver	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Cu	Copper	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
H	Hydrogen	$H^+ + e^- \rightleftharpoons H$	0
Pb	Lead	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
Sn	Tin	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
Ni	Nickel	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
Cd	Cadmium	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.40
Fe	Iron	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
Zn	Zinc	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
Ti	Titanium	$Ti^{2+} + 2e^- \rightleftharpoons Ti$	−1.63
Al	Aluminium	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
Mg	Magnesium	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
Na	Sodium	$Na^+ + e^- \rightleftharpoons Na$	−2.71
K	Potassium	$K^+ + e^- \rightleftharpoons K$	−2.93
Li	Lithium	$Li^+ + e^- \rightleftharpoons Li$	−3.05

Sacrificial Anode for a Pipeline
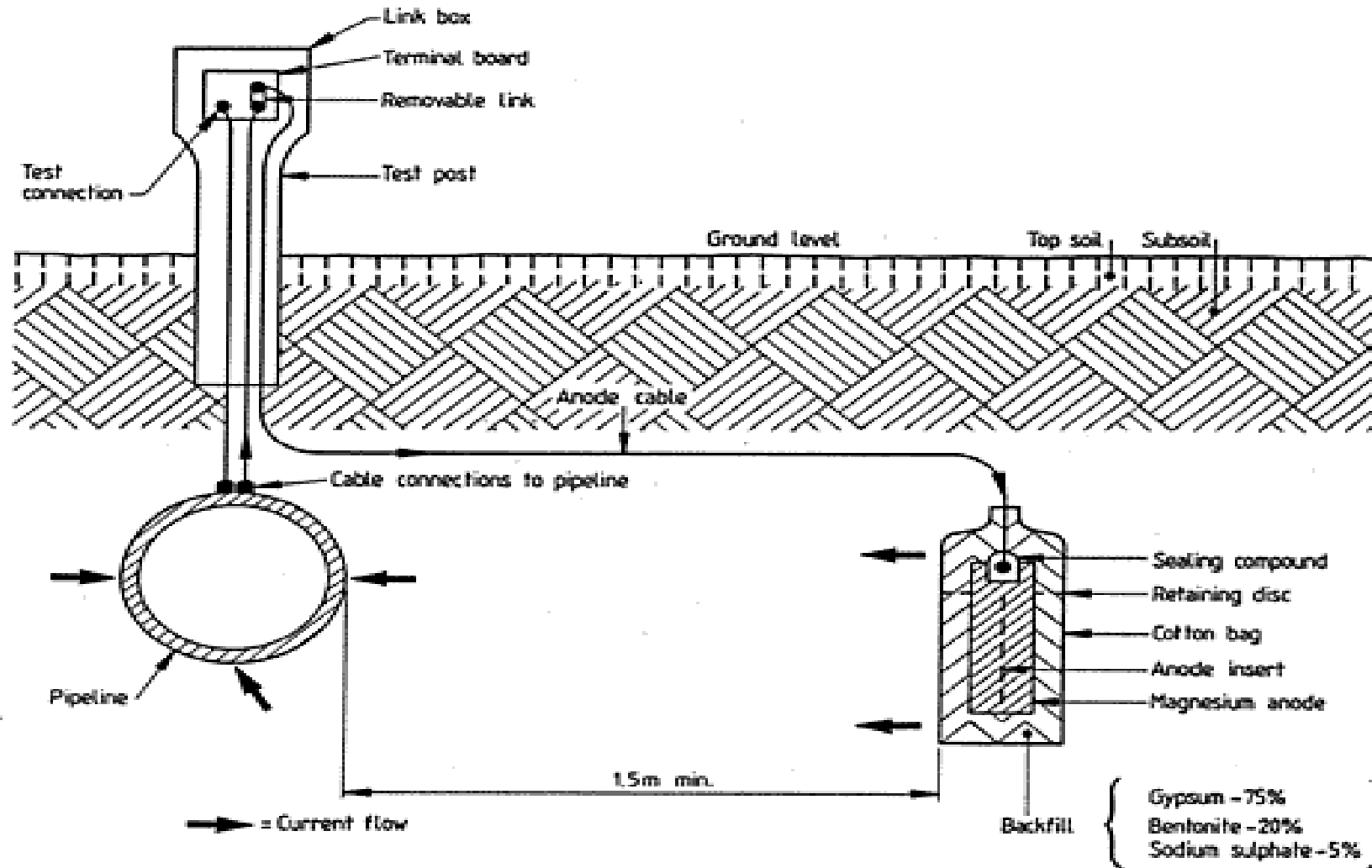
ii) Impressed current cathodic protection:

o Impressed direct current is applied in the opposite direction to the corrosion current to nullify it.

o Usually, one terminal of a battery is connected with an insoluble anode e.g. graphite electrode is immersed in black fill containing coke, gypsum, bentonite and sodium sulphate for good electrical conductivity.

o The other terminal is connected to the metallic structure to be protected.

o Since the current is impressed on the metallic structure, it acts as cathode and thus gets protected.

o This method is usually used to protect underground water pipe lines, oil pipe lines, transmission lines, ships etc.

Impressed current cathodic protection

Corrosion current of equal magnitude but opposite in direction applied to nullify corrosion current

Copper plating:

- Anode reaction: $Cu\ (s) \rightarrow Cu^{2+}\ (aq.) + 2\ e$
- Cathode reaction: $Cu^{2+}\ (aq.) + 2\ e \rightarrow Cu\ (s)$
- Electrolyte: Aqueous $CuSO_4$ solution

Nickel plating:

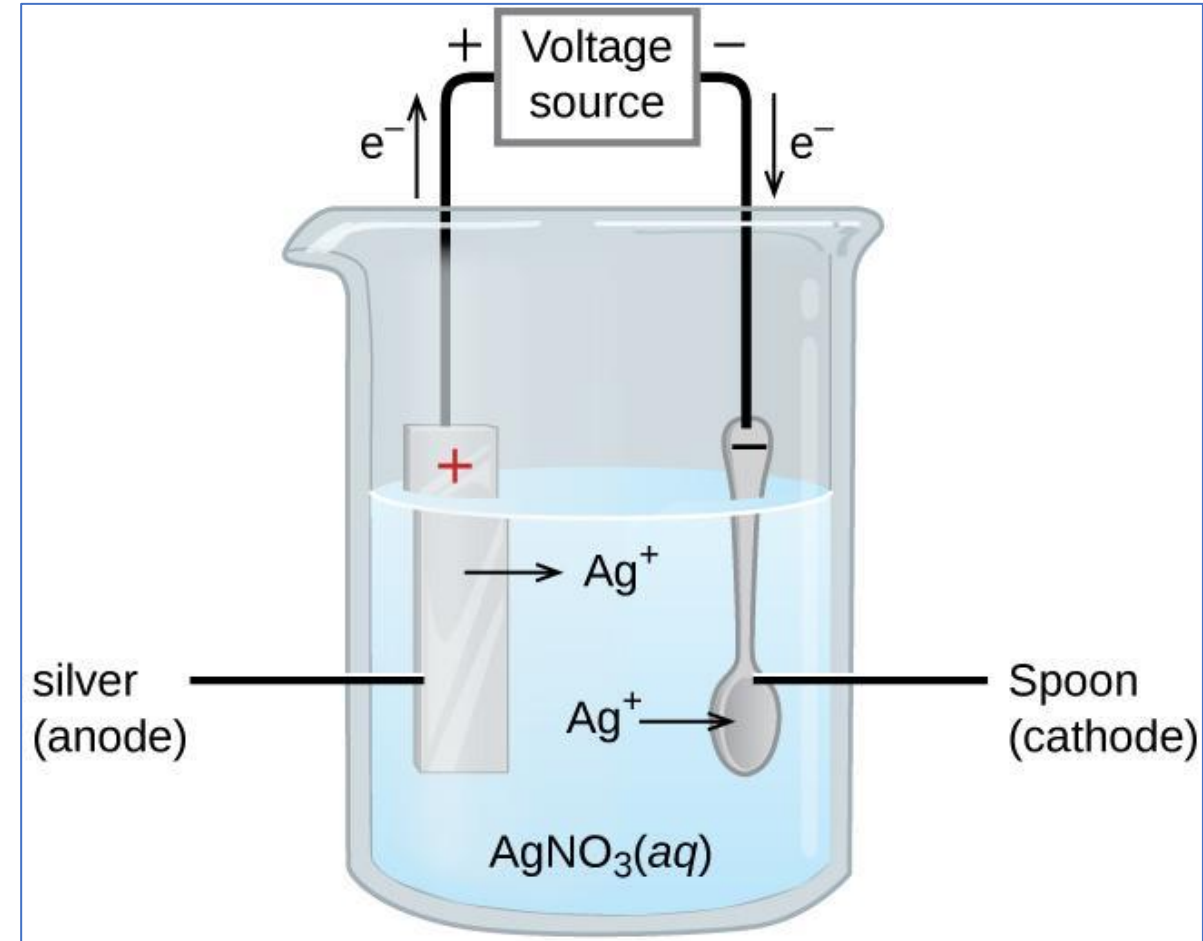- Anode reaction: $Ni\ (s) \rightarrow Ni^{2+}\ (aq.) + 2\ e$
- Cathode reaction: $Ni^{2+}\ (aq.) + 2\ e \rightarrow Ni\ (s)$
- Electrolyte: Aqueous $NiSO_4$ solution

Gold plating:

- Anode reaction: $Au\ (s) \rightarrow Au^+\ (aq.) + e$
- Cathode reaction: $Au^+\ (aq.) + e \rightarrow Au\ (s)$
- Electrolyte: Aqueous $K[Au(CN)_2]$ solution

Silver plating:

- Anode reaction: $Ag\ (s) \rightarrow Ag^+\ (aq.) + e$
- Cathode reaction: $Ag^+\ (aq.) + e \rightarrow Ag\ (s)$
- Electrolyte: Aqueous $AgNO_3$ solution

Silver plating:

- Anode reaction: $Ag\ (s) \rightarrow Ag^+\ (aq.) + e$
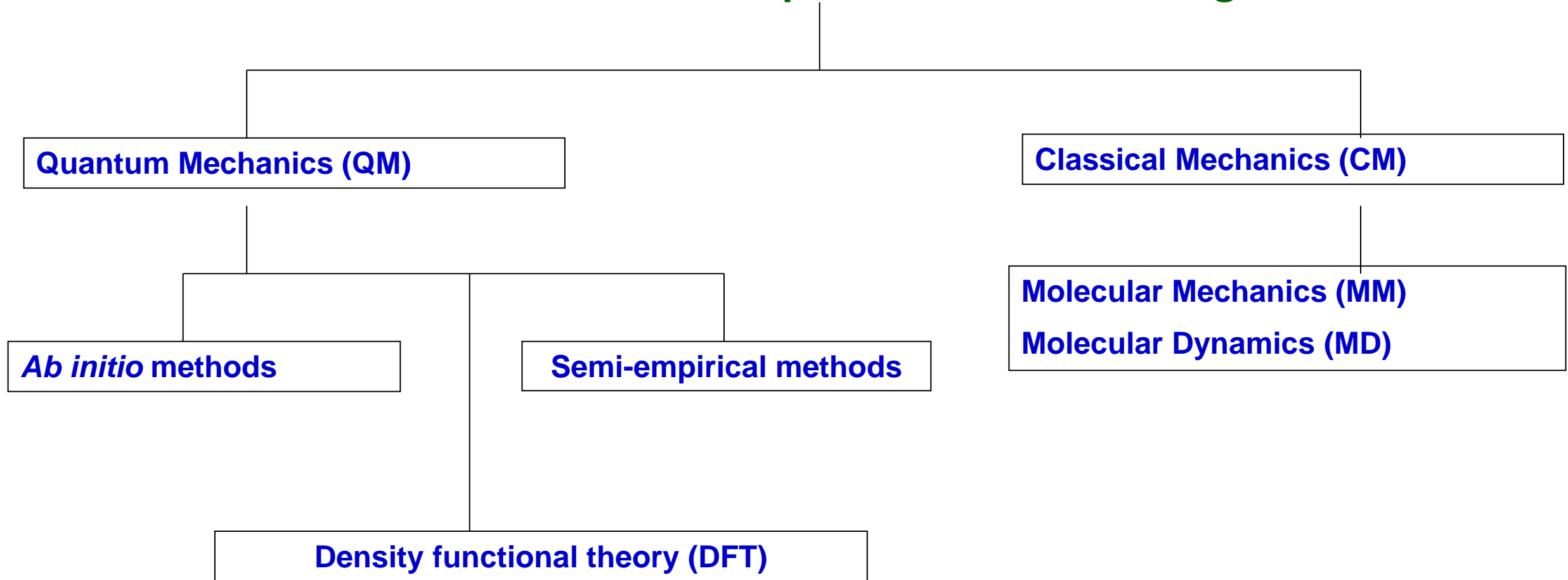- Cathode reaction: $Ag^+\ (aq.) + e \rightarrow Ag\ (s)$
- Electrolyte: Aqueous $K[Ag(CN)_2]$ solution

Computational chemistry is the use of computers to solve the equations of a theory or model for the properties of a chemical system.
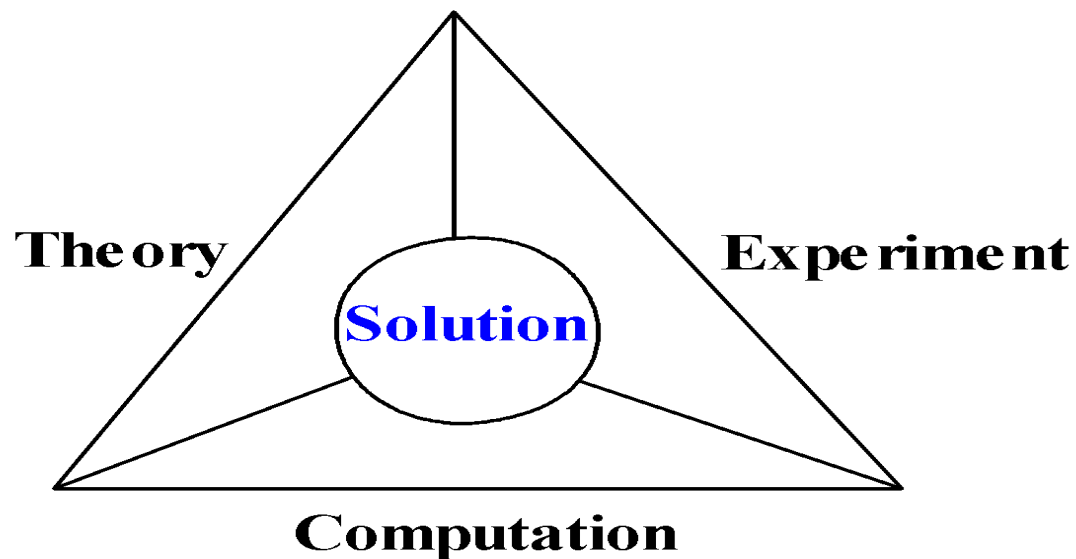
- The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn *"for his development of the density-functional theory"* and John A. Pople *"for his development of computational methods in quantum chemistry"*.
- Martin Karplus, USA, Michael Levitt, USA and Arieh Warshel, USA "for the development of multiscale models for complex chemical systems"

Overview of computational methodologies

Quantum Mechanics (QM)

Classical Mechanics (CM)

***Ab initio* methods**

Semi-empirical methods

Molecular Mechanics (MM)

Molecular Dynamics (MD)

Density functional theory (DFT)

Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

- **H** is the quantum mechanical Hamiltonian for the system (an operator containing derivatives)
- **E** is the energy of the system
- **Ψ** is the wave function (contains everything we are allowed to know about the system)
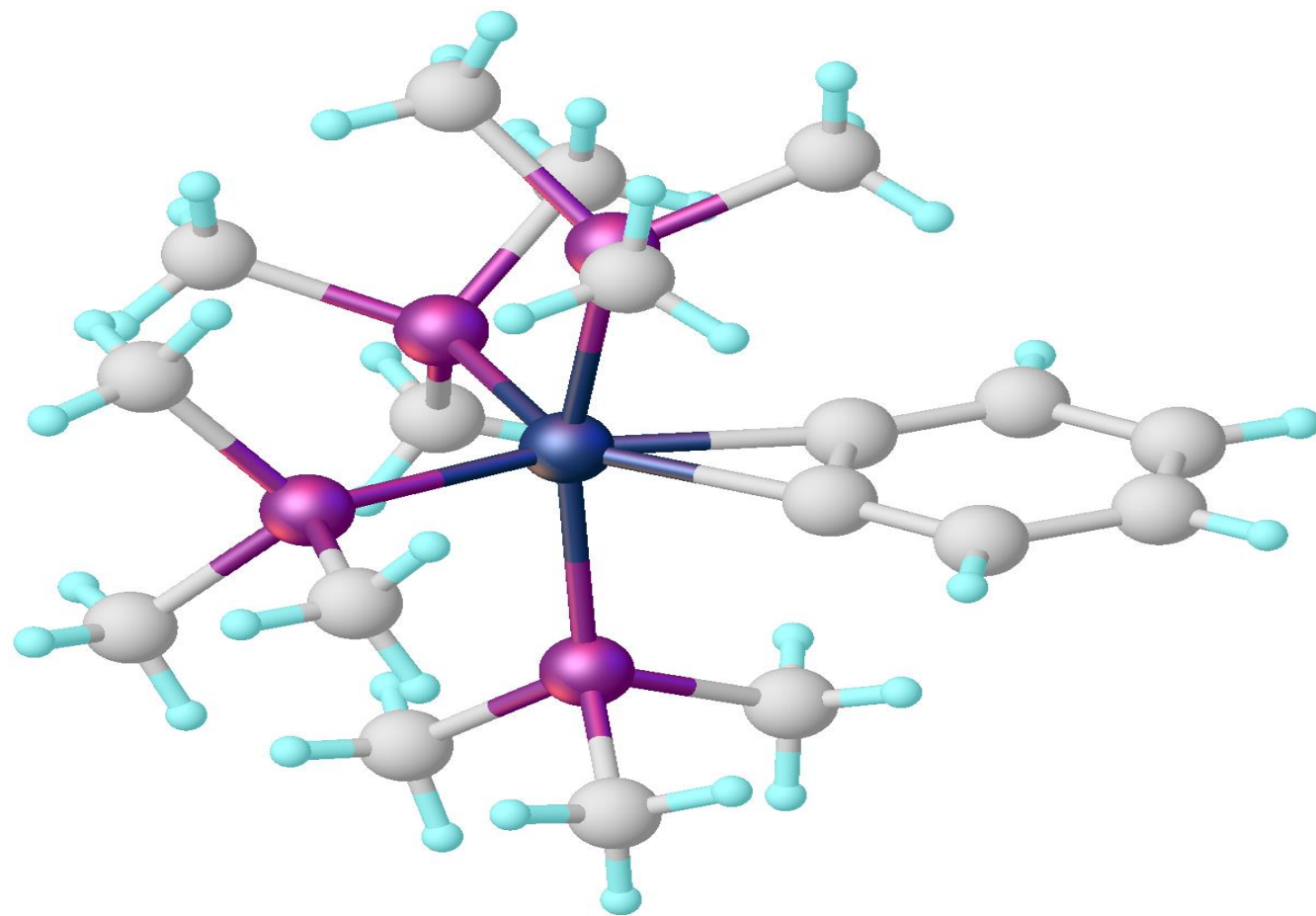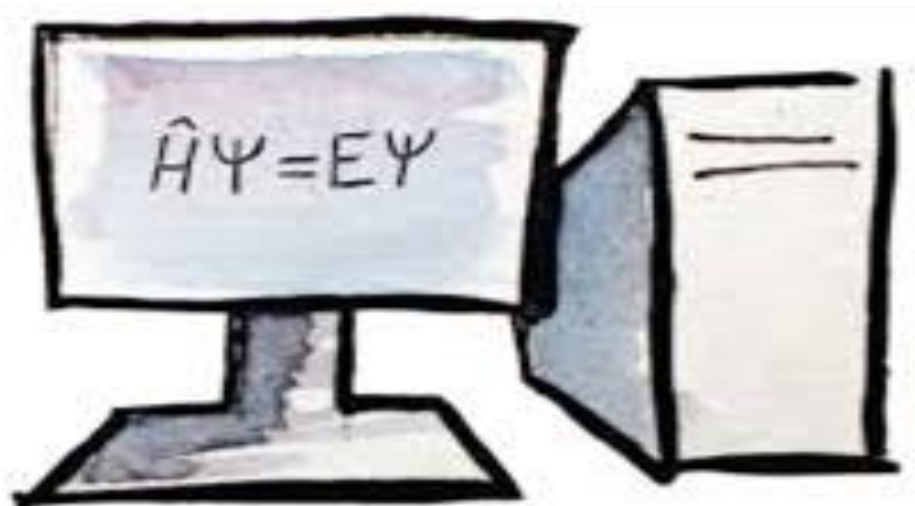- $|\Psi|^2$ is the probability distribution of the particles

Ab-initio methods

o The term "*Ab Initio*" is Latin for **"from the beginning"**. Computations of this type are derived directly from theoretical principles, with no inclusion of experimental data.

o Mathematical approximations are usually a simple functional form for a an approximate solution to A wave function! (**The Shrödinger Equation**).

o These methods try to compute an accurate as possible many electron wavefunction which then automatically leads to an accurate total energy.

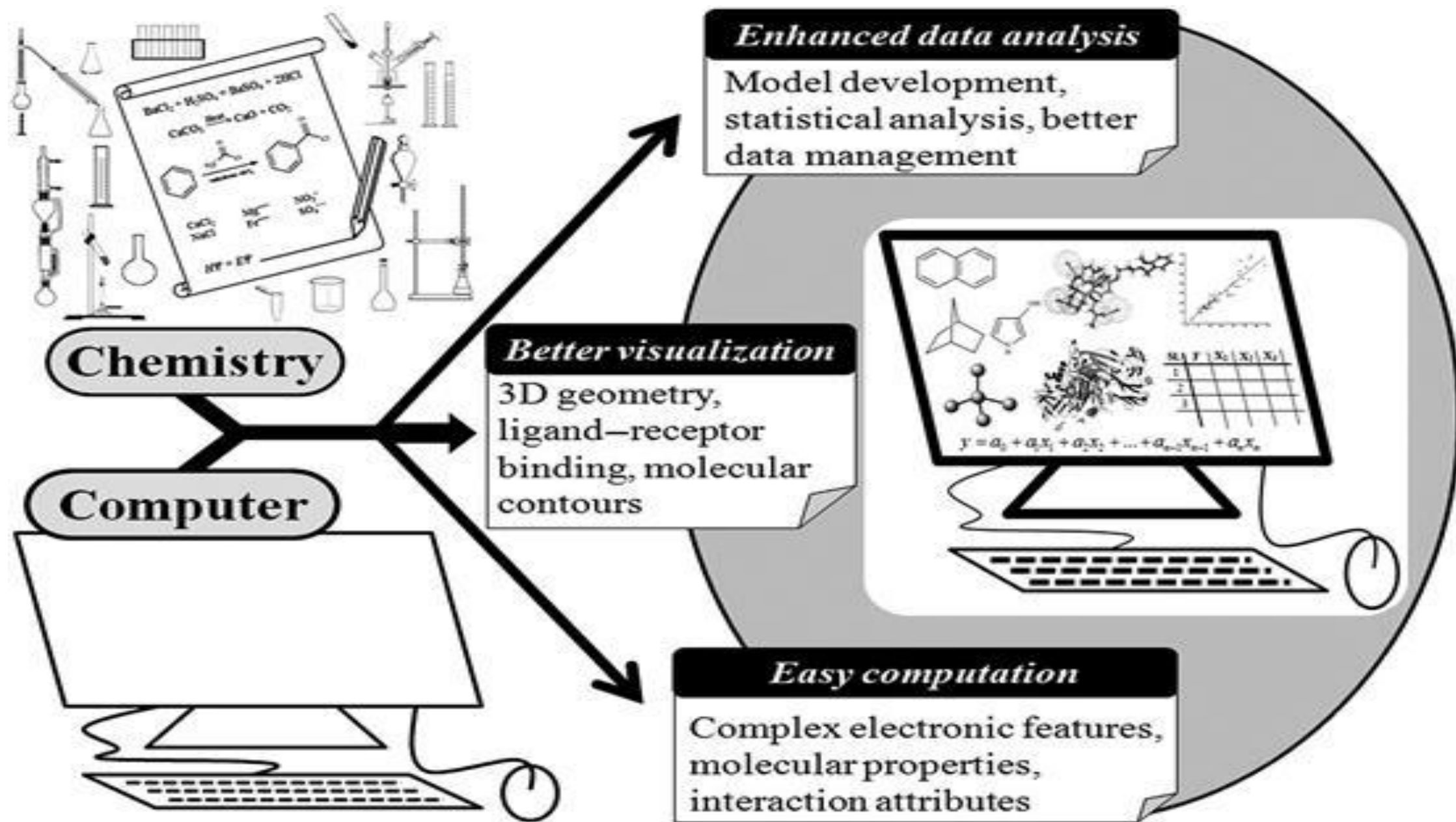o **Accuracy can be systematically improved.**

Semi-empirical methods

o It uses approximations from empirical (experimental) data to provide the input into the quantum chemical models.

o **Accuracy depends on parameterization.**

- DFT allows getting information about the energy, the structure and the molecular properties of molecules at lower costs. It goes with electron density instead of wave function. Accuracy varies with functionals, however, there is no systematical way to improve the accuracy.

- Molecular mechanics uses classical physics and empirical or semi-empirical (predetermined) force fields to explain and interpret the behavior of atoms and molecules. Generally not very accurate.

- Molecular dynamics is a computer simulation technique that allows one to predict the time evolution of a system of interacting particles (atoms, molecules, etc.)

Doing Chemistry with Computers

$$\hat{H}\Psi = E\Psi$$

Enhanced data analysis
Model development, statistical analysis, better data management

Better visualization
3D geometry, ligand—receptor binding, molecular contours

Easy computation
Complex electronic features, molecular properties, interaction attributes

Chemistry

Computer

$$y = a_0 + a_1 x_1 + a_2 x_2 + \ldots + a_{n-1} x_{n-1} + a_n x_n$$

Using computational chemistry software you can in particular perform:

o   **Electronic structure predictions**

o   **Geometry optimizations or energy minimizations**

o   **Conformational analysis and potential energy surfaces (PES)**

o   **Frequency calculations**

o   **Finding transition structures and reaction paths**

o   **Molecular docking: Protein – Protein and Protein-Ligand interactions**

o   **Electron and charge distributions calculations**

o   **Calculations of rate constants for chemical reactions: Chemical kinetics**

o   **Thermochemistry - heat of reactions, energy of activation, etc.**

o   **Calculation of many other molecular and physical and chemical properties**

o   **Orbital energy levels and electron density**
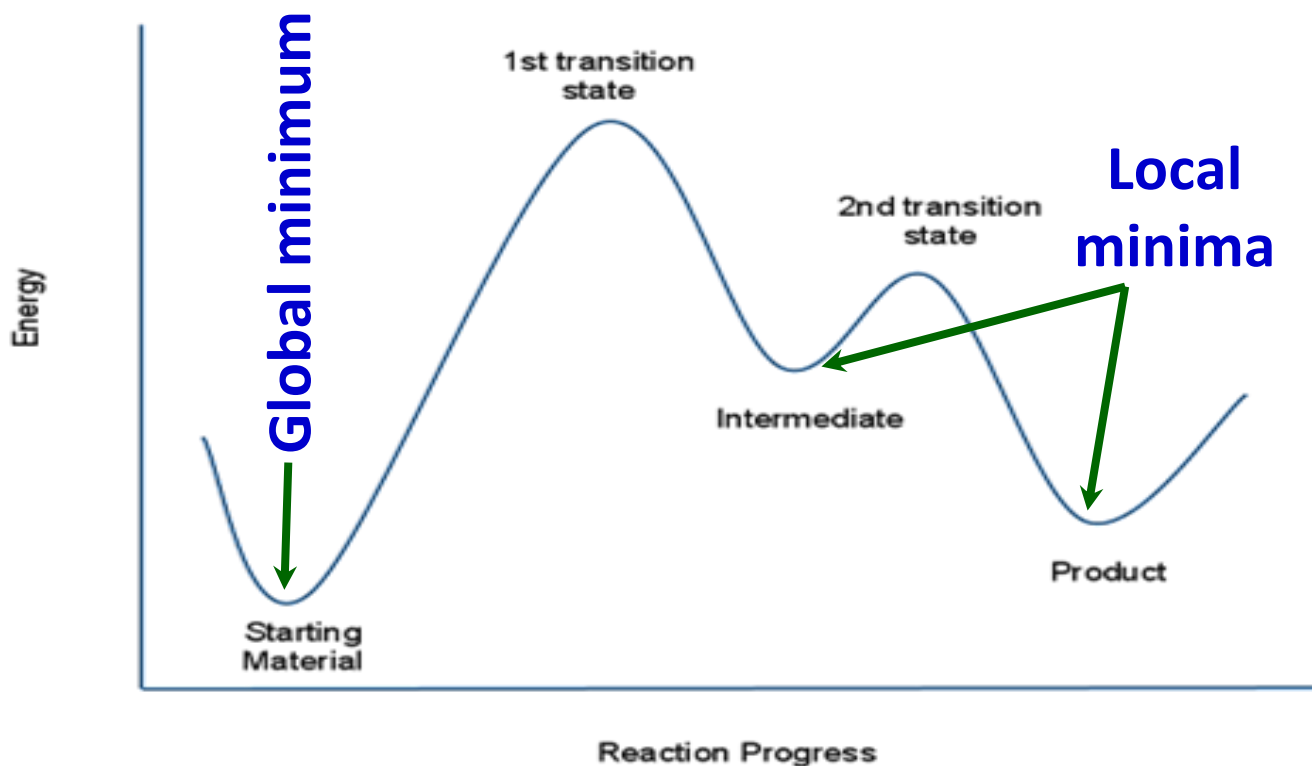
o   **Electronic excitation energy**

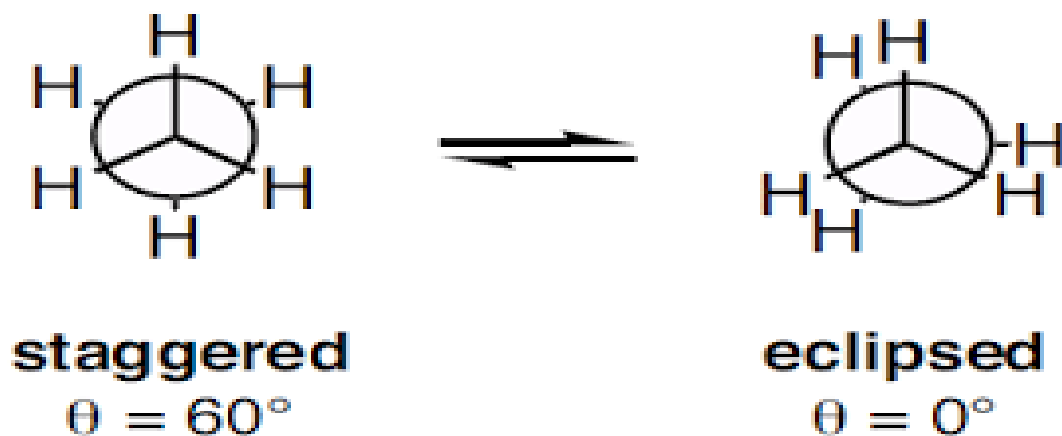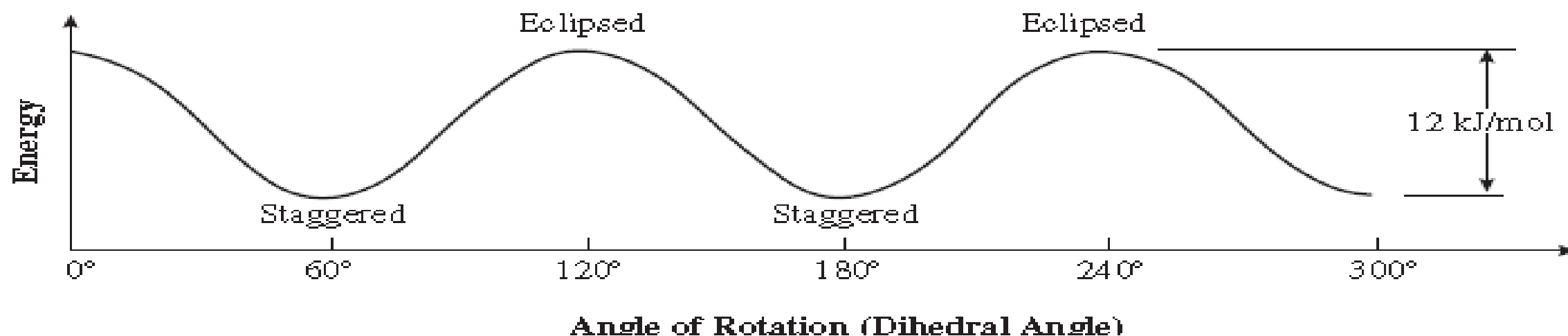# Potential Energy Surfaces and Mechanism
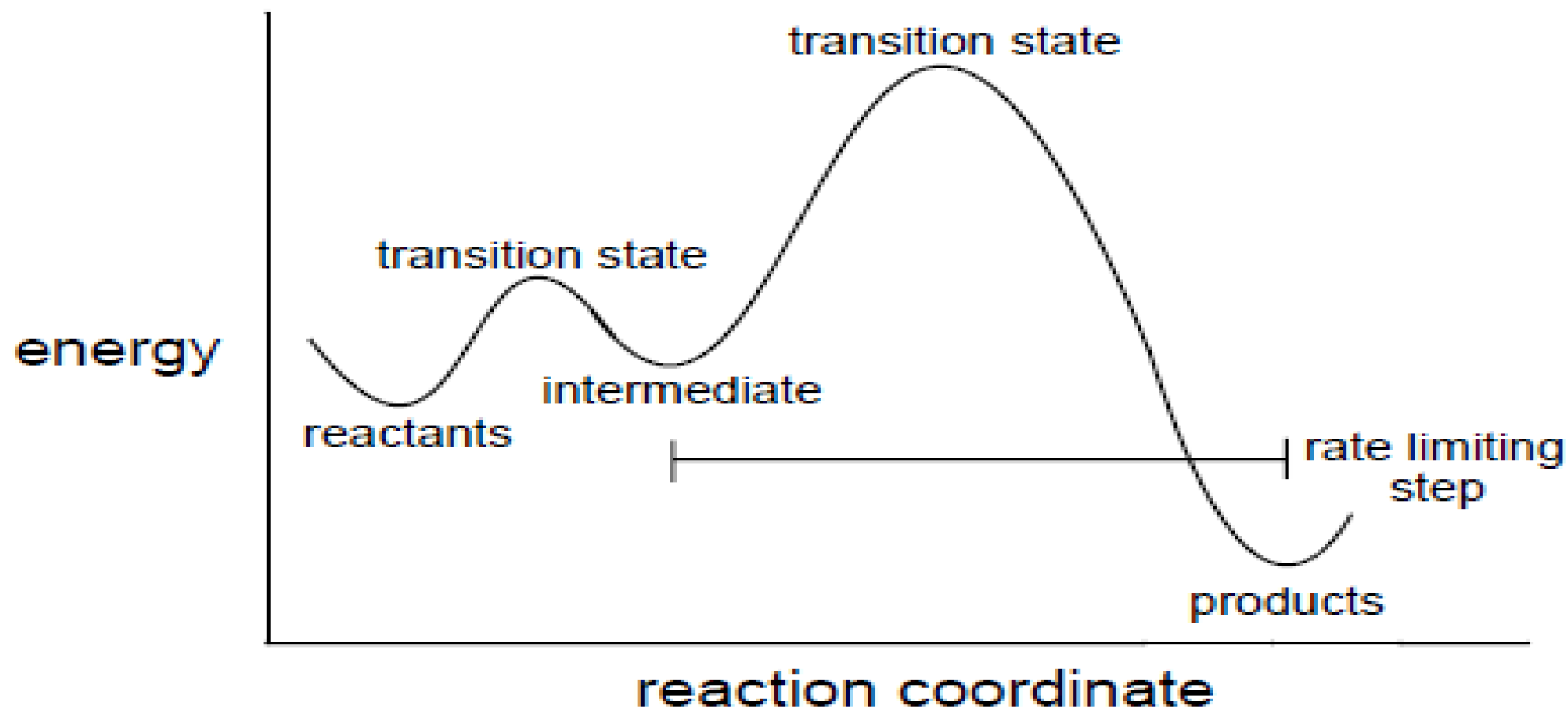
Conformational Analysis

➢ **Identification of all possible minimum energy structures (conformations) of a molecule is called conformational analysis.**

➢ **Conformational analysis is an important step in computational chemistry studies as it is necessary to reduce time spent in the screening of compounds for properties and activities.**

➢ **The identified conformation could be the local minimum, global minimum, or any transition state between the minima.**
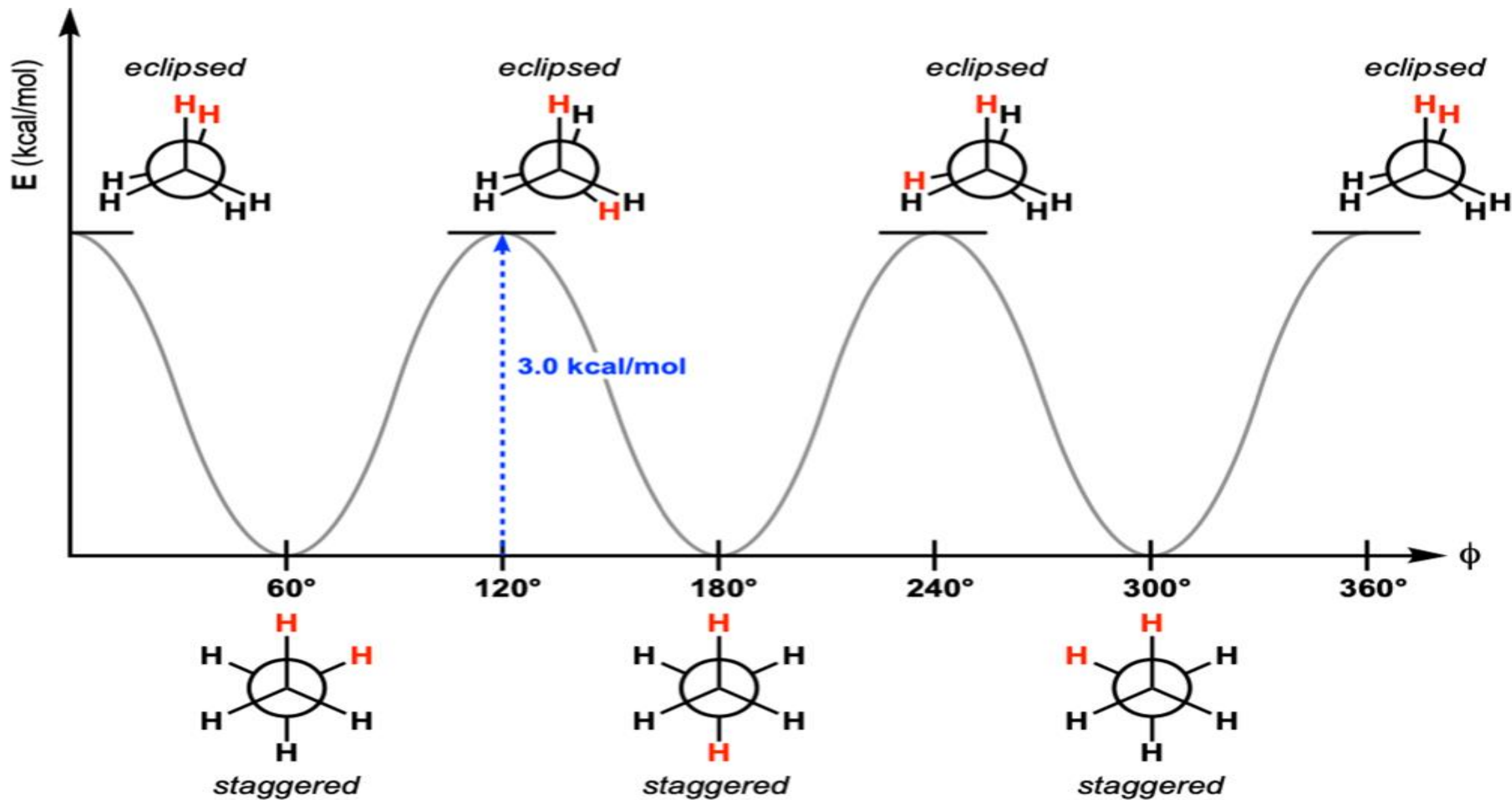
➢ **Out of the several local minima on the potential energy surface of a molecule, the lowest energy conformation is known as the global minimum.**

Ethane Conformations

Energy vs. Angle of Rotation (Dihedral Angle)

Eclipsed — Eclipsed (12 kJ/mol)

Staggered — Staggered

0°   60°   120°   180°   240°   300°

staggered
$\theta = 60°$

eclipsed
$\theta = 0°$

The torsional energy of ethane is lowest in the staggered conformation. The eclipsed conformation is about 3.0 kcal/mol (12.6 kJ/mol) higher in energy. At room temperature, this barrier is easily overcome, and the molecules rotate constantly.

Conformations of Cyclohexane