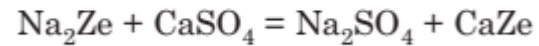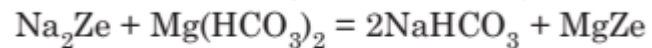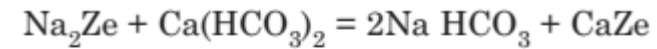Water purification methods - zeolites, ion-exchange resins and reverse osmosis; Fuels and combustion -
LCV, HCV, Bomb calorimeter (numericals), anti-knocking agents);
Corrosion- Protective coatings
(Sacrificial anodic protection, Impressed current cathodic protection and PVD); Applications of
computational methodologies

Zeolite or permutit process

- Zeolite is a Hydrated Sodium Alumino Silicate (HSAS), capable of exchanging reversibly its sodium ions for hardness producing ions in water.

- Natural zeolites are non-porous but synthetic zeolites are porous and possess gel structure

- Hard water is percolated through a bed of zeolite. The hardness causing ions are retained by the zeolite bed

$$Na_2Ze + Ca(HCO_3)_2 = 2Na\ HCO_3 + CaZe$$
$$Na_2Ze + Mg(HCO_3)_2 = 2NaHCO_3 + MgZe$$
$$Na_2Ze + CaSO_4 = Na_2SO_4 + CaZe$$
$$Na_2Ze + CaCl_2 = 2NaCl + CaZe$$
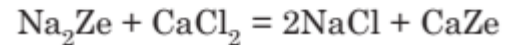
- After a while, Ze is completely converted to Ca and Mg Ze and needs to be regenerated

- 10% brine solution will regenerate the zeolite for further softening of hard water

Hard water in — Top distributor — Injector — Salt storage — Waste — Zeolite sand — Gravel — Soft water out
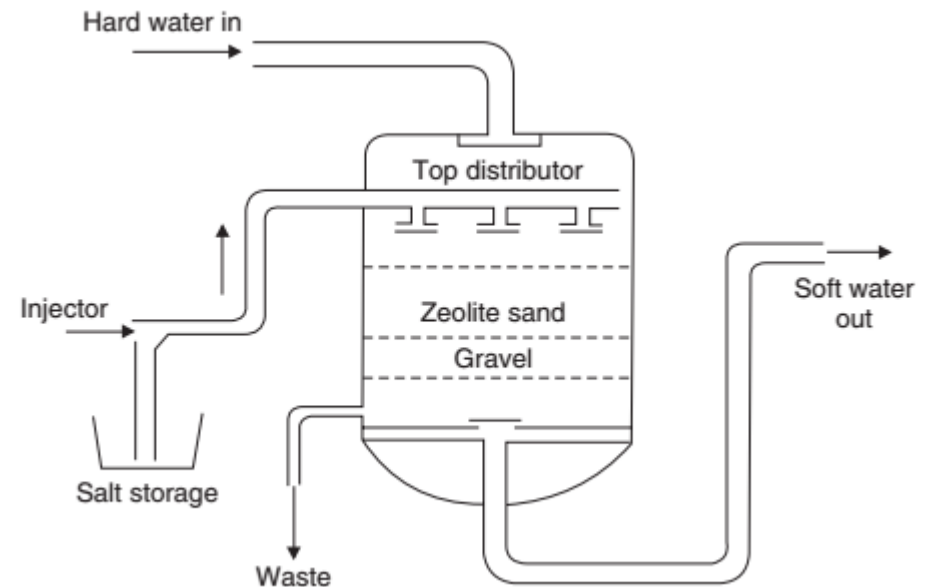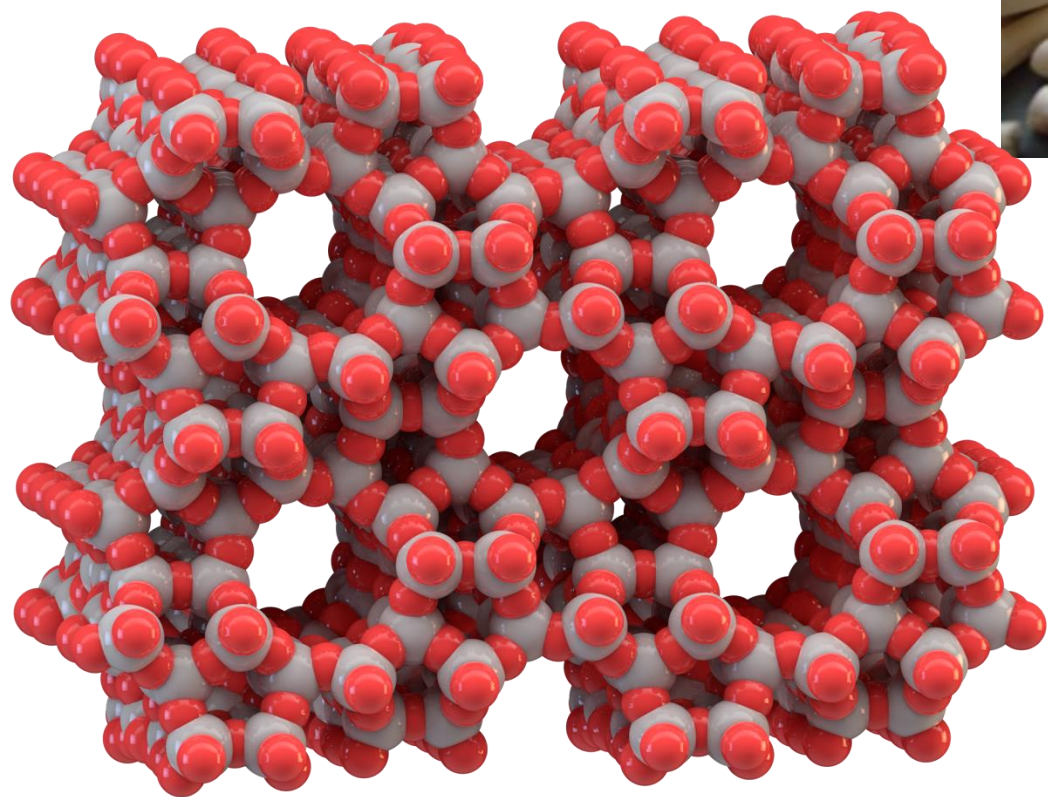
- **Limitations-** turbid water can cause clogging of the pores

- Coloured metal ions like Fe^{2+} or Mn^{2+} must be removed first, as they bind very firmly and cannot be removed easily from the zeolite

- Mineral acids can destroy the Ze bed and so must be neutralised before use

- **Advantages-** hardness comes down to around 10ppm

- The equipment is compact, less skill needed for maintenance, no sludge formation

- **Disadvantages-** the process introduces excess of sodium than the lime soda process

- The method only replaces Ca^{2+} and $Mg^{2+,}$ but leaves behind all the anions like HCO_3^- and CO_3^{2-}

- The HCO_3^- decomposes to give CO_2 which causes corrosion and CO_3^{2-} decomposes to NaOH which can cause caustic embrittlement

Ion exchange deionisation/demineralisation

- Ion exchange resins are synthetic insoluble, cross linked long chain organic polymers with a microporous structure
- The polymer chain contain functional groups for ion –exchange
- **Cation exchange resins** have **Acidic** functional groups (-COOH or $-SO_3H$) exchange H^+ with the **cations**
- **Anion exchange resins** have **Basic** functional groups (amines/imines based) exchange **anions** with OH^-
- **Usually styrene based polymers are utilised**

cation exchange resin

Anion exchange resin
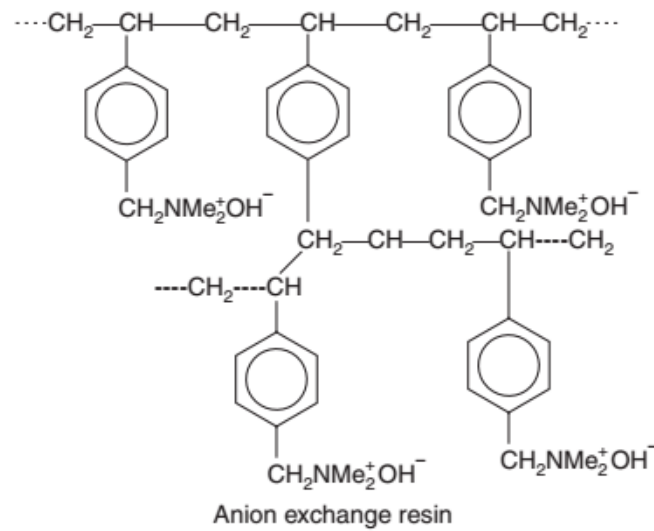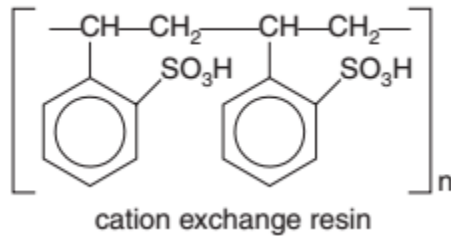
Water purification by Ion exchange
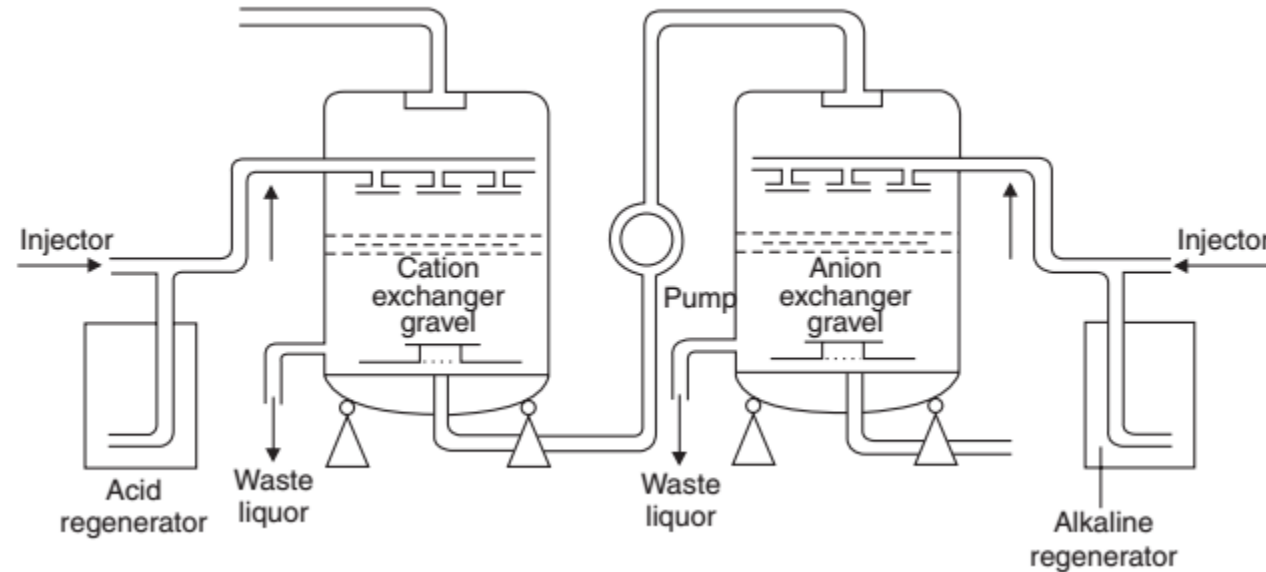
Hard water is passed first through the cation exchange column, removing all Ca2+ and Mg2+

$$2RH^+ + Ca^{2+}/Mg^{2+} \longrightarrow R_2Ca^{2+}/R_2Mg^{2+} + 2H^+$$
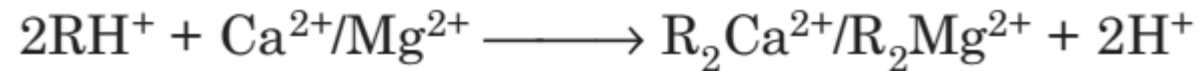
Then it is passed through the anion exchange column, removing all anions like SO_4^{2-}, Cl^-

$$ROH^- + Cl^- \longrightarrow R^+Cl^- + OH^-$$

Water is thus de-ionised (DI water)

Cation exchange

Filter bed

Anion exchange

D.M. Water

Hard water

Cation exchange reaction:

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

Anion exchange reaction:

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

$$R\overset{+}{N}H_3OH^- + Cl^- \rightleftharpoons R\overset{+}{N}H_3Cl^- + OH^-$$
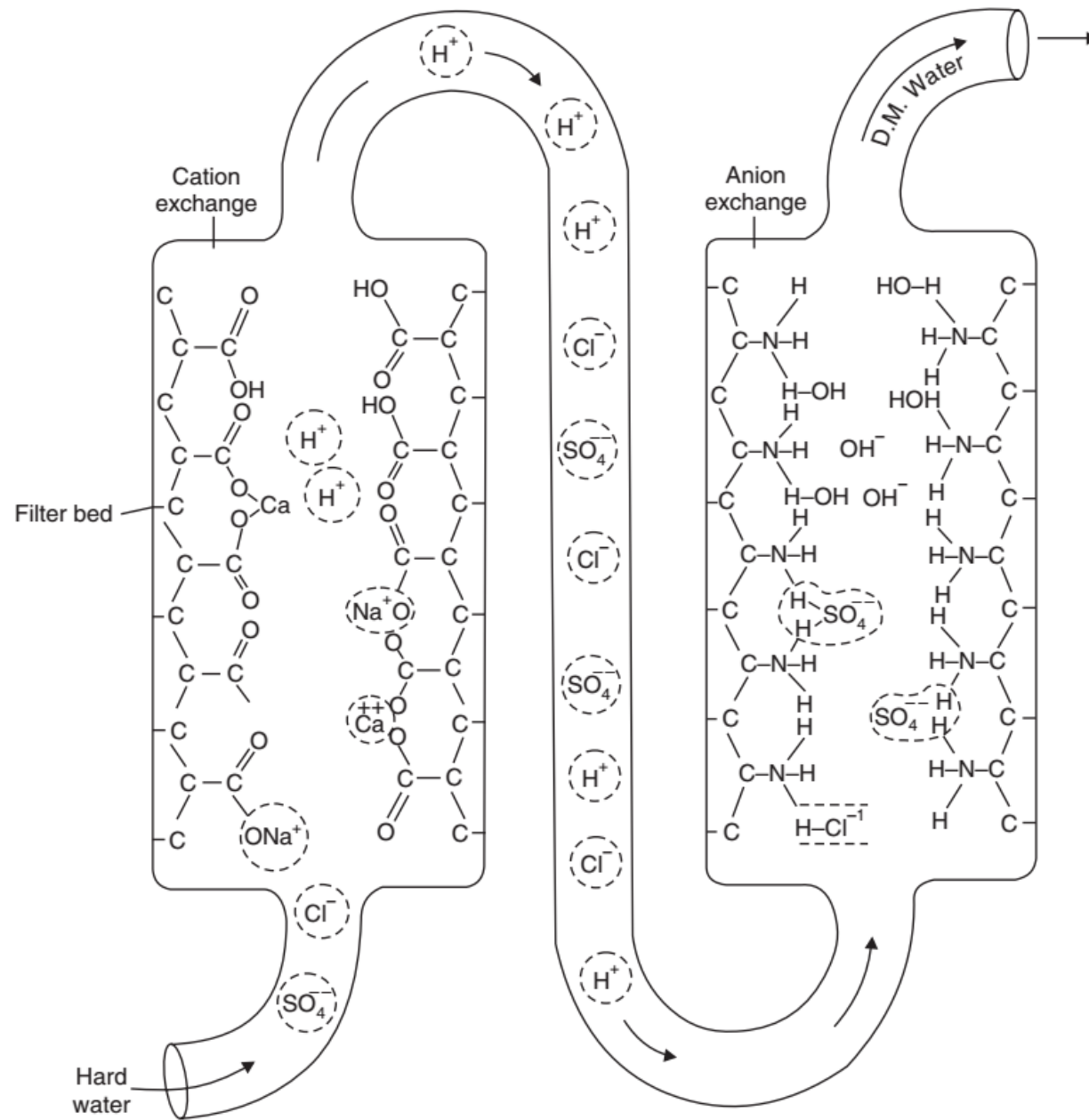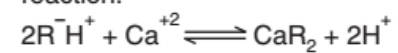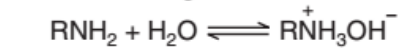
Regeneration of ion exchange resin

- After a while, the resin loses all its H$^+$ and OH$^-$ content and is exhausted and needs to be regenerated
- A cation exchange resin is regenerated by passing dil HCl or dil. H$_2$SO$_4$

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+}$$

- An anion exchange resin is regenerated by passing dil NaOH

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2ROH^- + SO_4^{2+}$$

- After regeneration, the resins are washed with DI water and the washings discarded

- **Advantages-** Highly acidic or alkaline water can be softened
- Softening upto 2ppm

- **Disadvantages-** expensive
- Turbidity can cause troubles

Mixed bed de-ioniser

- A single cylinder with an intimate mixture of cation and anion exchangers
- Hard water comes in contact very effectively, a number of times – equivalent to passing through a series of cation and anion exchangers
- Results in hardness less than 1ppm

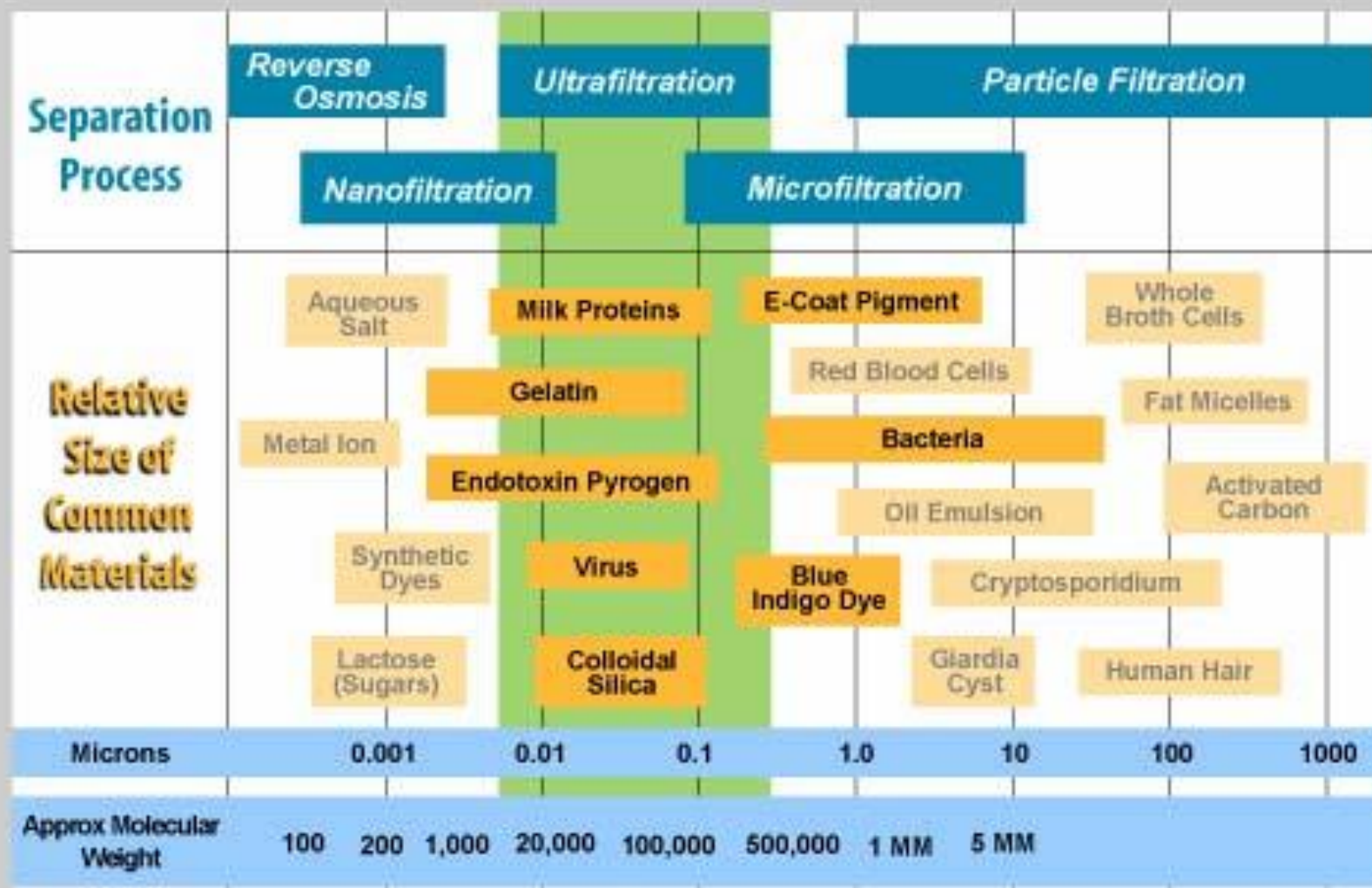# Ultrafiltration and nanofiltration for disinfection

- Filtration is a process of removing particulate matter from water by forcing the water through a porous media
- The size of materials that can be removed during filtration depends upon the size of the pores of the filter
- An ultrafiltration filter has a pore size around 0.01 micron
- A nanofiltration filter has a pore size around 0.001 micron
- Reverse osmosis filters have a pore size around 0.0001 micron

Ultrafiltration would remove large particles, macromolecules, bacteria, protozoa and may remove some viruses.
Ultrafiltration cannot remove dissolved substances unless they are first adsorbed (with activated carbon) or coagulated (with alum or iron salts).
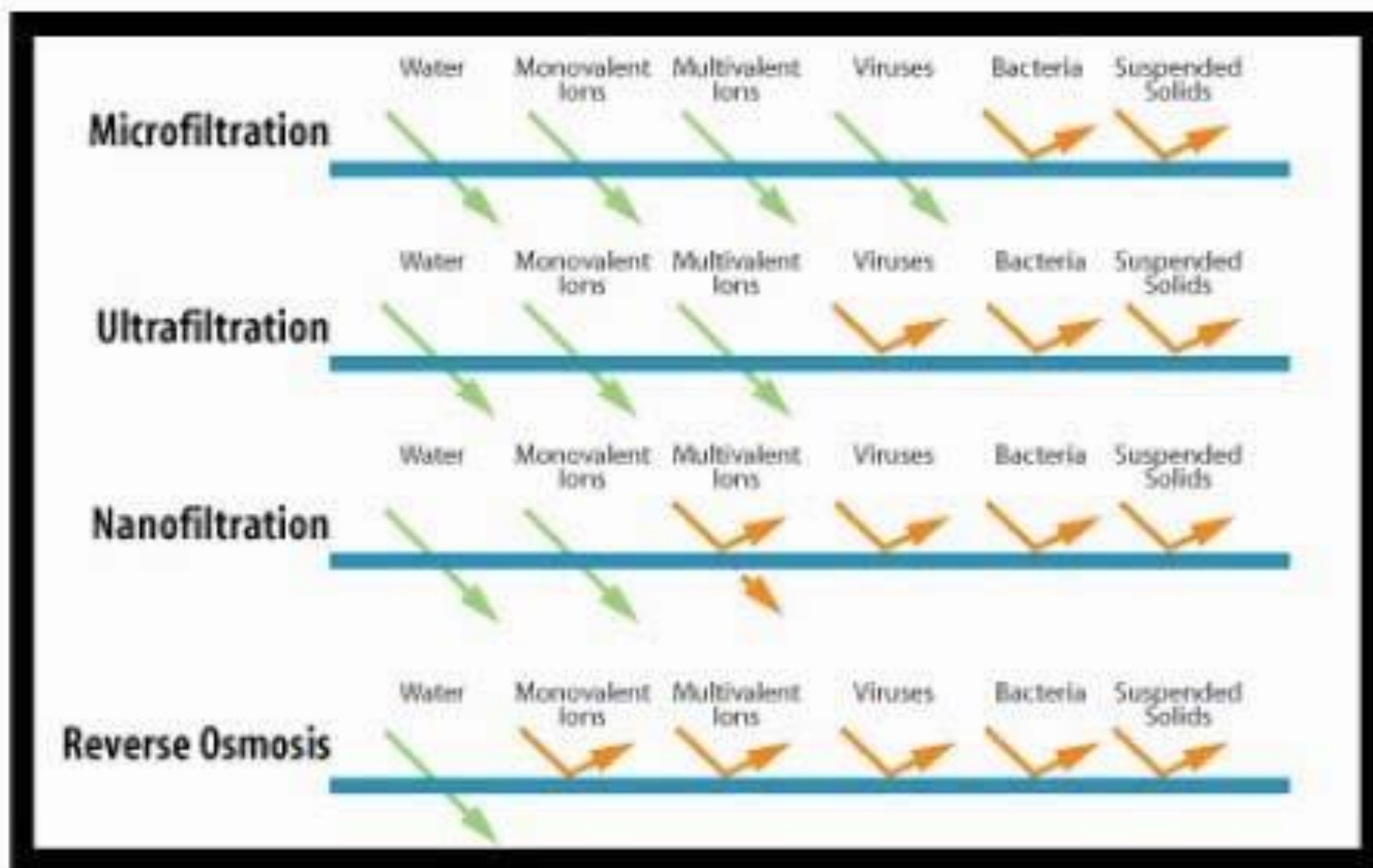
Nanofiltration removes most organic molecules, nearly all viruses, most of the natural organic matter and a range of salts. Nanofiltration removes divalent ions, which make water hard, so nanofiltration is often used to soften hard water.

polysulfone and cellulose acetate are the most commonly used membrane materials

Separation Process

| Reverse Osmosis | Ultrafiltration | Particle Filtration |
| Nanofiltration | Microfiltration | |

Relative Size of Common Materials

- Aqueous Salt
- Milk Proteins
- E-Coat Pigment
- Whole Broth Cells
- Red Blood Cells
- Gelatin
- Fat Micelles
- Metal Ion
- Bacteria
- Endotoxin Pyrogen
- Activated Carbon
- Oil Emulsion
- Synthetic Dyes
- Virus
- Blue Indigo Dye
- Cryptosporidium
- Lactose (Sugars)
- Colloidal Silica
- Giardia Cyst
- Human Hair

Microns	0.001	0.01	0.1	1.0	10	100	1000

Approx Molecular Weight	100	200	1,000	20,000	100,000	500,000	1 MM	5 MM

Note: 1 micron (micrometer) = 4 x 10-5 inches = 1 x 104 Angstrom units
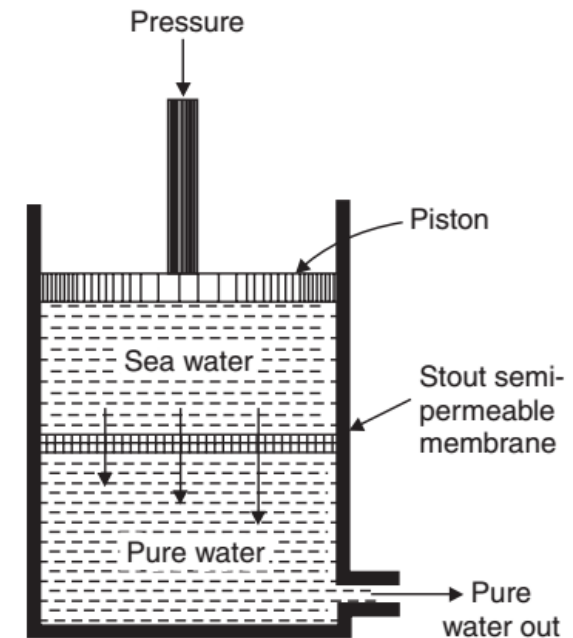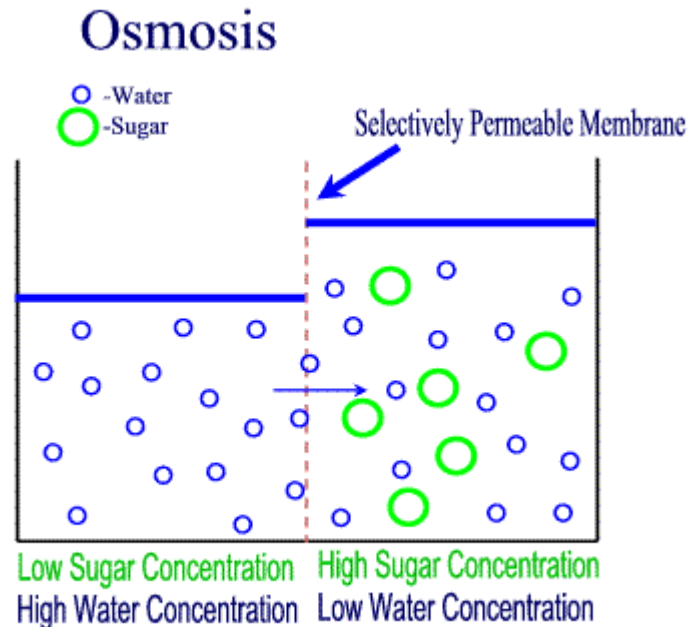
© 2004 - Koch Membrane Systems

Membrane Process Characteristics

Reverse osmosis

- **Osmosis** is the **spontaneous** net movement of solvent molecules through a semi-permeable membrane into a region of higher solute concentration, in the direction that tends to equalize the solute concentrations on the two sides.
- When pressure more than the osmotic pressure is applied from the concentrated solution, the flow of solvent reverses.
- In RO, pure water is separated from contaminants rather than removing the contaminants.
- Also known as super-filtration or hyper-filtration

Osmosis

O -Water
O -Sugar

Selectively Permeable Membrane

Low Sugar Concentration   High Sugar Concentration
High Water Concentration   Low Water Concentration

Pressure

Piston

Sea water

Stout semi-permeable membrane

Pure water

Pure water out

Reverse osmosis - method

- Pressure applied is around 15 to 40 Kg /cm^2
- Both ionic and non-ionic impurities are left behind
- Membranes are made of cellulose acetate, poly methacrylate, polyamide polymers

Advantages

- All sorts of impurities are removed- ionic, non-ionic, high molecular organic matter, particles, dyes and bacteria
- Colloidal silica, which is not removed by other methods, is easily removed by RO
- Replacing the membrane is almost the only maintenance required
- Life of the membrane is high (~2 years) and can be replaced in minutes

Semipermeable membranes are fragile:

- Hard water can clog membrane
- Chlorine can destroy membrane
- Membrane must be rinsed regularly to prevent scaling
- Prefiltration usually required

Fuels and combustion

Fuels

- **Fuel is a combustible substance, containing carbon as the main constituent, which on proper burning gives large amount of heat that can be used for domestic and industrial purposes**

- During combustion of a fuel, atoms of C and H combine with oxygen to give CO_2 and H_2O

- These compounds have lesser energy than the fuel and hence the energy released during combustion is the difference in energy of the reactant and the products formed

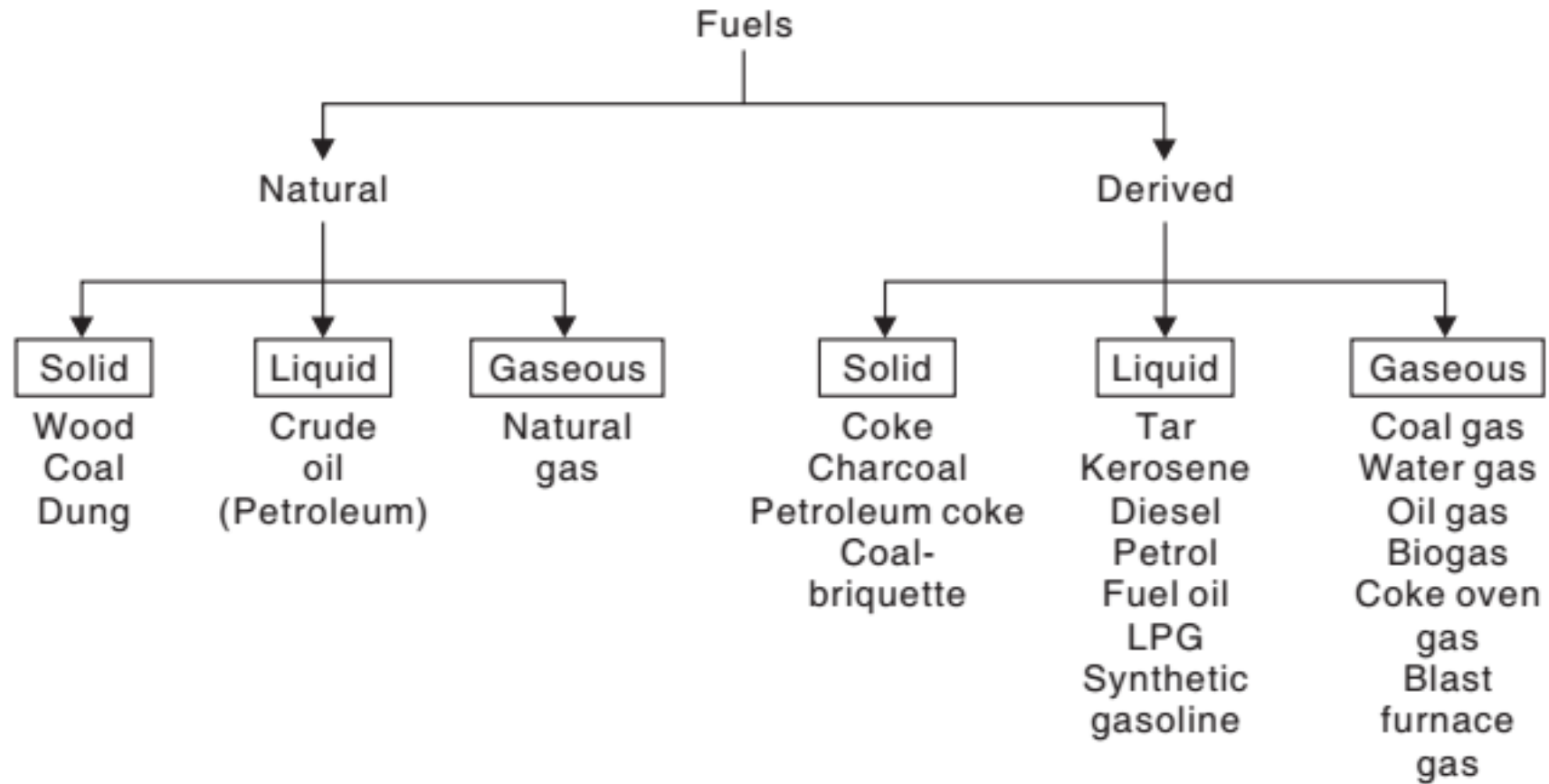$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$

- 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**

- **Expressed in cal/g or kcal/kg**

Characteristics of a good fuel

- It should have higher calorific value.

- Moderate ignition temperature.

- Low moisture content.

- Low non-combustible matter content

- A good fuel should burn with moderate rate of combustion.

- Products of combustion should not be harmful and polluting

- Should not undergo spontaneous combustion, but the combustion process should

  be easily controllable

- Should burn efficiently without much smoke

Classification of fuels

Fuels

Natural

Solid
Wood
Coal
Dung

Liquid
Crude
oil
(Petroleum)

Gaseous
Natural
gas

Derived

Solid
Coke
Charcoal
Petroleum coke
Coal-
briquette

Liquid
Tar
Kerosene
Diesel
Petrol
Fuel oil
LPG
Synthetic
gasoline

Gaseous
Coal gas
Water gas
Oil gas
Biogas
Coke oven
gas
Blast
furnace
gas

Units of Calorific Value

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

2. **Kilocalorie -** 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.

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 B. Th. U. = 252 cal = 0.252 k cal.
     1 k cal = 3.968 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".
   Thus, 1 k cal = 3.968 B. Th. U. = 2.2 C. H. U.

1 calorie = 4.187 Joule

GCV/HCV– Gross / Higher calorific value

- **"Amount of heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion have been cooled to room temperature".**

- Most of the fuels used are hydrocarbon based.

- When the products are cooled to room temperature, the steam present condenses, releasing its latent heat of vapourisation

- If the products of combustion are condensed to room temp., the **latent heat of condensation of steam also gets included in the measured heat.** Hence higher (or) gross calorific value

NCV/LCV– Net / Lower calorific value

- **Amount of heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion have been allowed to escape".**

- In practice, water vapor are not condensed but allowed to escape. Hence lesser amount of heat is available.

- **LCV = HCV – Latent heat of water vapor produced**
- **= HCV – (Mass of hydrogen in the fuel x 9 x Latent heat of steam)**

Determination of Calorific Value by Bomb calorimeter
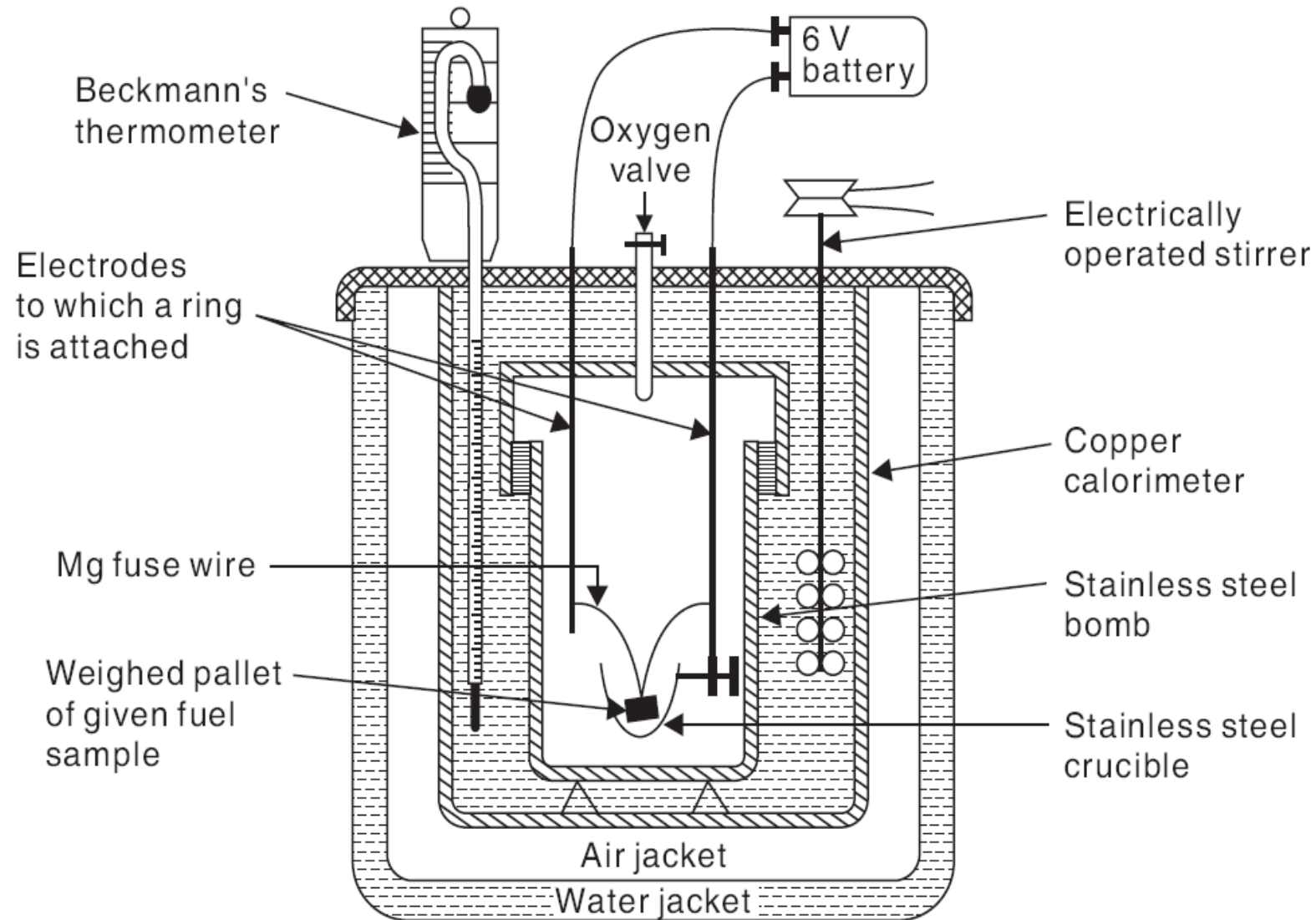
Bomb calorimeter

- Used to find calorific value of solid and liquid fuels

- The bomb consists of lid which can give a gas-tight seal

- The lid also has two electrodes and an oxygen inlet valve

- To one of the electrodes a ring is attached in which a crucible is supported

- The bomb is placed in a copper calorimeter

- A known mass of fuel is completely burnt in excess of oxygen and heat liberated is absorbed by the surrounding water and the brass calorimeter

- The increase in temperature of the calorimeter and water is noted

- Calorific value is calculated based on fact that heat lost by burning the fuel is equal to the heat gained by the water and the calorimeter

- The heat quantity calculated is GCV because the products of combustion remain inside the calorimeter and brought down to ambient temperature

Calculation

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

$$\text{H}_2 + \tfrac{1}{2}\,\text{O}_2 \longrightarrow \text{H}_2\text{O}$$
2 kg   18 kg
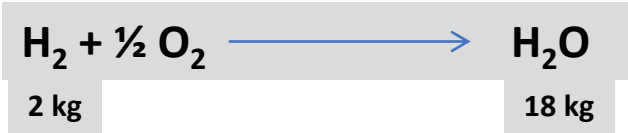
Where

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.

S = specific heat capacity of water

- The water equivalent of the calorimeter is related to its heat capacity, is determined by burning a fuel of known calorific value. E.g benzoic acid (HCV = 6,325 kcal/kg) or naphthalene (HCV = 9,688 kcal/kg)

- The NCV of a fuel can be calculated if the percentage of hydrogen in the fuel is known

- Since 2 kg of H produces 18 kg of steam, x kg would produce $9x$ kg of steam

- If 100 kg of fuel contains x kg of H, then 1 kg of the fuel would produce $0.09x$ kg of steam

- Latent heat of steam is 587 kcal/kg

- Hence NCV = HCV – latent heat of water formed

  = HCV – $0.09x$ (587) kcal/kg

5. Corrections

Fuse wire correction :   Heat liberated during sparking should be subtracted from the total heat obtained.

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: time taken to cool water in calorimeter from max temperature to room temperature is noted. From the rate of cooling (dt °/min) and actual time for cooling (t min) the cooling correction of dt x t is added to the raise in temperature (to account for heat transfer from calorimeter to its environment)

$$L = HCV = \frac{(W+w).S.(t_2-t_1+cooling\ correction)\ -(Acid+fuse\ correction)}{m}$$ cal/g

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

$$= [HCV - 0.09\ H \times 587]\ \text{cal/kg.}$$

remember units

Amount of Hydrogen content (kg)in fuel

Example 1. *A sample of coal contains:*

$$C = 93\%, H = 6\% \text{ and ash} = 1\%$$

Calculate the gross and net calorific V value of the coal from the following data:

Weight of coal burnt (m) = 0.92 g

Weight of water taken (w) = 550 g

Water equivalent of bomb calorimeter (W) = 2,200 g.

Rise in temperature $(t_2 - t_1)$ = 2.42°C; Fuse wire correction = 10 cal.

Acid correction = 50 cal

Sol. $HCV = \dfrac{(W + w)\,(t_2 - t_1) - [\text{acid} + \text{fuse}]\,\text{correction}}{m}$

$$= \dfrac{(2{,}200 + 530) \times 2.42 - [50 + 10]}{0.92}\ \text{cal/g}$$

$$= 7168.5 \text{ cal/g}$$

Net Calorific Value (NCV)   = HCV- (0.09H *L) cal/g
= 7168.5 – (0.09 *6*587)
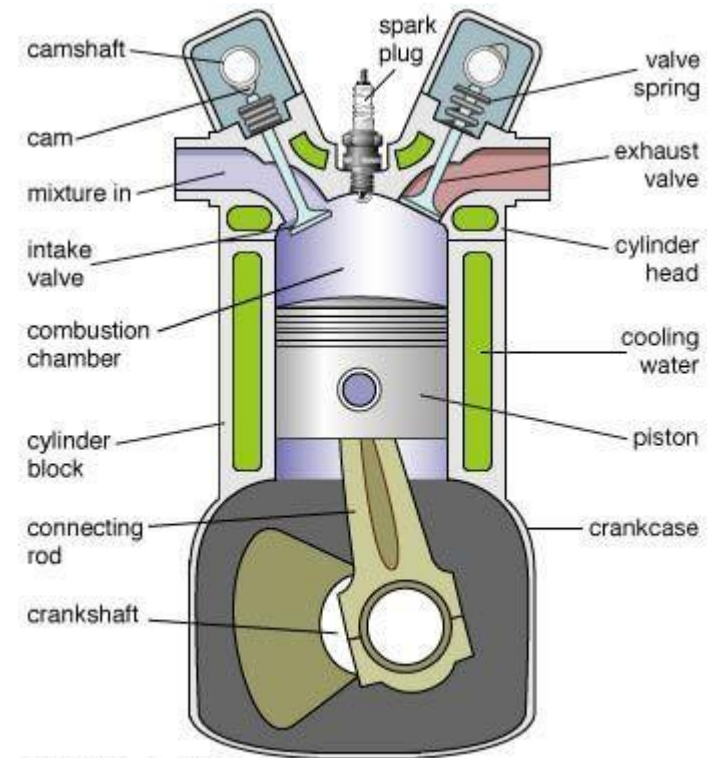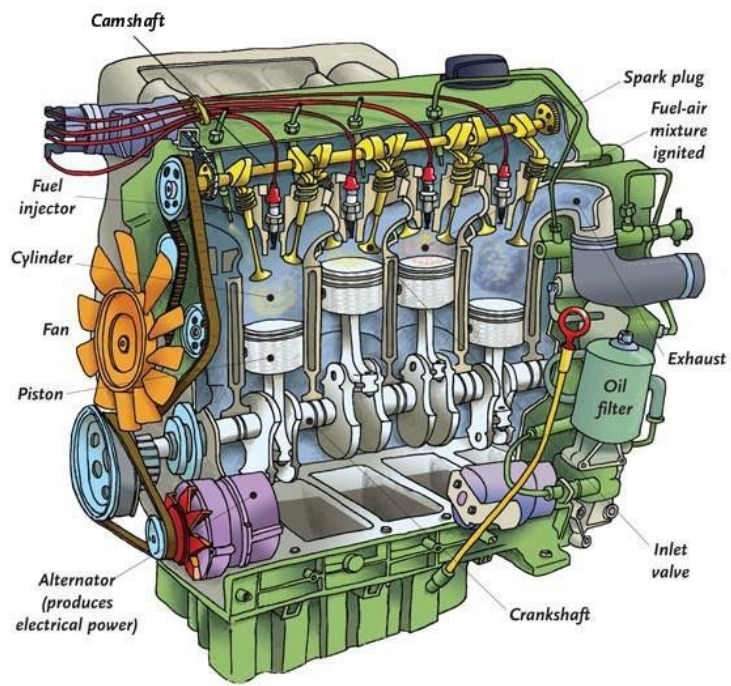= **6,851.5 cal/g**

Example 3. *On burning 0.83 g of a solid fuel in bomb calorimeter, the temperature of 3,500 g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385 g and 587 cal/g, respectively. If the fuel contains 0.77% H, calculate HCV and NCV.*
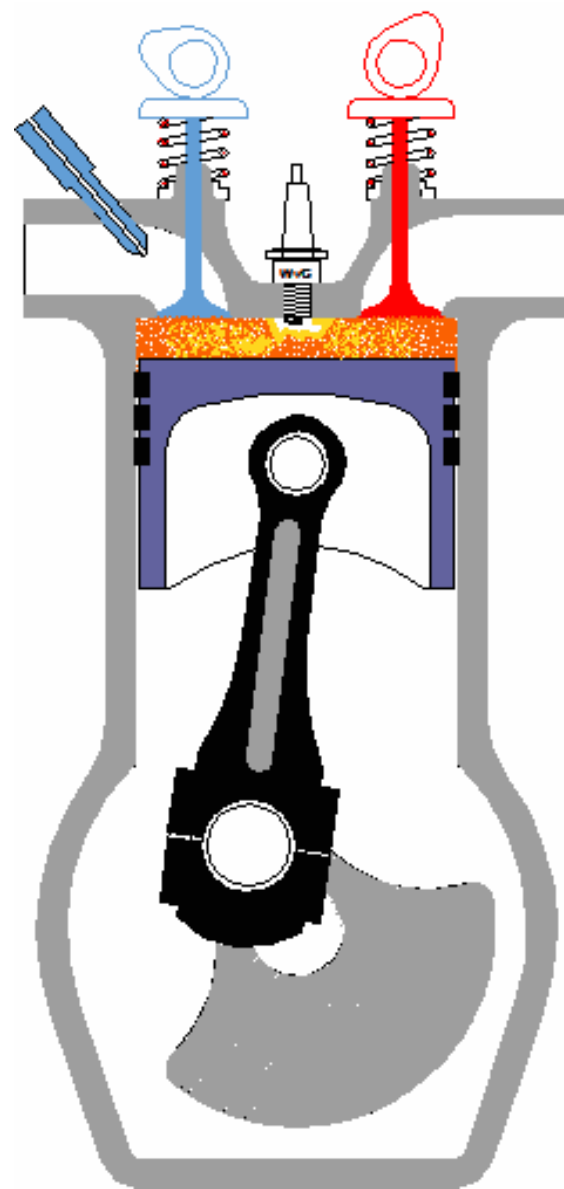
$$HCV = \frac{(W + w)\,(t_2 - t_1)\,*S}{m}$$

$$= \frac{(385 + 3500)\,(29.2 - 26.5)*1}{0.83} = 12638 \text{ cal g}^{-1}$$

$$NCV = (HCV - 0.09\,H \times L) \text{ cal g}^{-1}$$

$$= (12638 - 0.09 \times 0.7 \times 587) \text{ cal g}^{-1} = 12601 \text{ cal g}^{-1}.$$

Knocking

- In an internal combustion engine, combustion of air/fuel mixture is initiated by the spark produced in the cylinder, which pushes the piston out

- The ratio of the gaseous volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke is known as **compression ratio**

- Good fuels give a high compression ratio, where uniform combustion takes place

- However, certain unwanted chemical constituents in the fuel cause non-uniform combustion, causing an explosive violence in side the cylinder which is known as **knocking**

- Compression ratio depends on the nature of constituents of the fuel. Efficiency of IC engine increases with compression ratio

- The reason behind knocking characteristic of fuels are not fully understood

Camshaft

Spark plug

Fuel-air mixture ignited

Fuel injector

Cylinder

Fan

Piston

Exhaust

Oil filter

Alternator (produces electrical power)

Inlet valve

Crankshaft

camshaft

spark plug

valve spring

cam

exhaust valve

mixture in

intake valve

cylinder head

combustion chamber

cooling water

cylinder block

piston

connecting rod

crankcase

crankshaft

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COMBUSTION AND CAUSES OF KNOCKING

In a petrol engine, a mixture of gasoline vapor and air at 1:17 compression ratio is used as the fuel.

This mixture is compressed and ignited by an electric spark.

After the reaction is initiated by a spark, a flame should spread rapidly and smoothly through the gas mixture and the expanding gas drives the piston down the cylinder.

The products of oxidation reaction increases the pressure and pushes the piston down the cylinder.

The rate of oxidation of a hydrocarbon molecule depends on the number of carbon atoms in a molecule, structure and temperature.

If the combustion proceeds in a regular way, there is no problem in knocking.

Compression ratio is defined as the ratio of the cylinder vol at the end of the suction stroke (V_2) to that at the end of the compression stroke (V_1) of the piston.

In some cases, the rate of combustion will not be uniform due to unwanted chemical constituents of gasoline or pockets of air-fuel mixture exploding in an uncontrolled manner during the suction stroke.

The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "Knocking".

Knocking property of the fuel reduce the efficiency of engine.

The tendency to knock depends not only on the fuel but also on the engine design, shape of head, location of plug, etc., and also upon the running conditions.

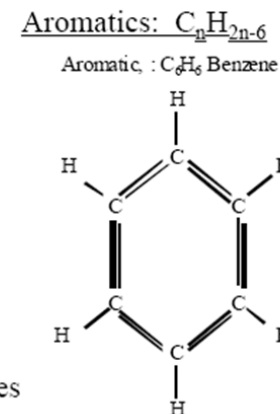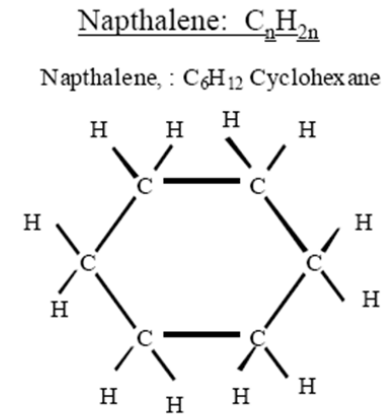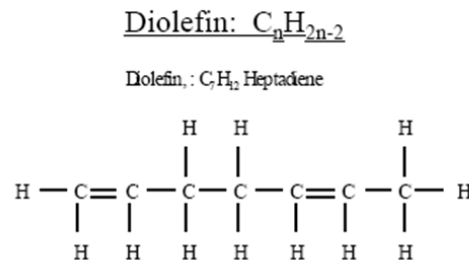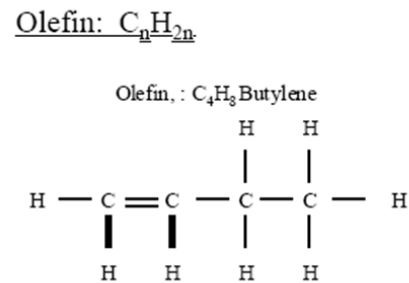A good gasoline should resist knocking.

Hydrocarbons in different fuels

	B.P	C-atoms	Uses
Uncondensed gases	< 30°C	C_1-C_4	LPG fuels
Gasoline/Petrol	40-120	C_5-C_9	Fuel for IC engines
Naptha/S.Spirit	120-180	C_9-C_{10}	Solvent in paints
Kerosene oil	180-250	C_{10}-C_{16}	Fuel for stove & jet
Diesel oil	250-320	C_{15}-C_{18}	Diesel engine fuels
Heavy oil	320-400	C_{17}-C_{30}	Fuels for ships

- Knocking tendency depends on the chemical structure of fuel, which decreases in the following order.

- Straight chain paraffins > Branched chain paraffins > Cycloparaffins > Olefins > Aromatics

- Knocking results in loss of efficiency of the engine

- Knocking characteristics of a combustion engine fuel (petrol) – octane number or rating

- Antiknock quality of a fuel is expressed as its octane number

Fuel Components

Paraffin: C_nH_{2n+1}

Paraffin, Straight Chain: C_8H_{18} n-Octane

Olefin: C_nH_{2n}

Olefin, : C_4H_8 Butylene

Napthalene: C_nH_{2n}

Napthalene, : C_6H_{12} Cyclohexane

Paraffin, Branched Chain: C_8H_{18} iso-Octane

Diolefin: C_nH_{2n-2}

Diolefin, : C_7H_{12} Heptadiene


Aromatics: C_nH_{2n-6}

Aromatic, : C_6H_6 Benzene
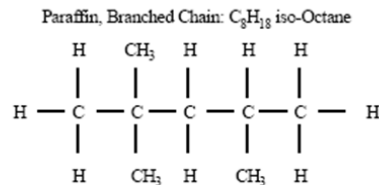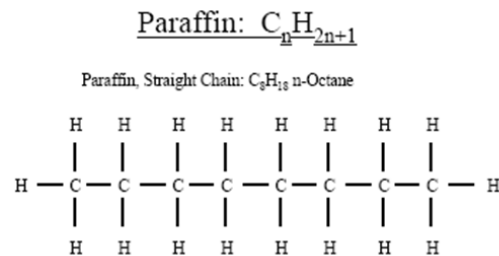
When n≤4   Molecules are gases at normal temperature and pressures
Boiling points of hydrocarbon's increase with molecular weight, i.e., n increases

The knocking tendency decreases with increase in the compactness of the molecules, double bonds and cyclic structure.

imp

Reason: Aromatic fuels such as benzol can be used at higher compression ratios without knocking than normal straight chain paraffinic petrol.
Straight chain HCs possess high vapour pressure (low b.p) than aromatics. Thus, the possibility for spontaneous ignition at higher compression is greater for straight chain hydrocarbons.
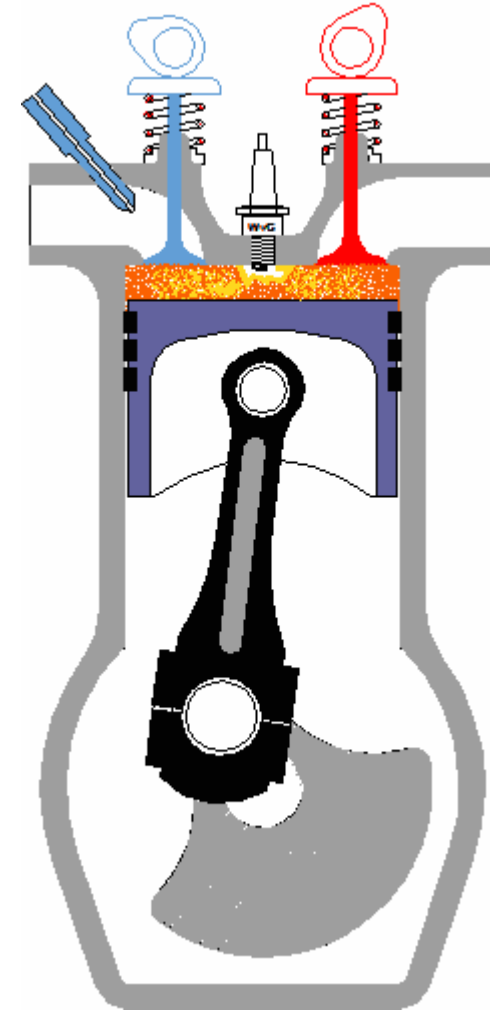
Octane number

- Octane number gives the efficiency of fuel based on its knocking characteristics
- N-heptane was found to knock very badly and has been given an antiknock value of zero
- Iso-octane gives very little knocking and has been given an antiknock value of 100
- Octane number system has been devised between these two extreme numbers
- Octane number of a fuel is the percentage of iso-octane present in a mixture of iso-octane and n-heptane, which gives the same knocking characteristics of the fuel under test.
- E.g gasoline having 75 octane number is one having the same knocking characteristic as that of a 75:25 mixture of iso-octane and n-heptane

imp ✓

Fuel Additives to Reduce Knocking

- Chemical additives are used to raise the octane number of gasoline.

- The most effective antiknock agents are lead alkyls;

- (i) Tetraethyl lead (TEL), $(C_2H_5)_4Pb$ was introduced in 1923

- (ii) Tetramethyl lead (TML), $(CH_3)_4Pb$ was introduced in 1960

- Most effective antiknock agent is tetraethyl lead (TEL) along with ethylene dibromide which prevents deposition of lead by forming volatile lead halides

- Others are tetramethyl lead, tertiary butyl acetate, diethyl telluride

- About 1970 low-lead and unleaded gasoline were introduced over toxicological concerns with lead alkyls (TEL contains 64% by weight lead).

- Alcohols such as ethanol and methanol have high knock resistance.

- Since 1970 another alcohol methyl tertiary butyl ether (MTBE) has been added to gasoline to increase octane number.

Cetane number

- In diesel engines, the combustion of fuel is not by ignition as in petrol engines, but by the application of heat and pressure

- **There is a delay period between the injection of diesel fuel and its ignition. If this delay period is large, too much fuel accumulates in the cylinder and burn very rapidly and causes diesel knock.**

- Increasing delay period occurs in the series :

- n-paraffin < Olefins < naphthenes < isoparaffins < aromatics

- Order is the reverse for gasoline antiknock quality.

- **n-hexadecane ; Cetane number = 100**

- **α – methyl naphthalene ; Cetane number = 0**

- A given fuel matches in quality with the blend having 40/60 blend of cetane and methyl naphthalene, it is assigned a cetane number 40

- Cetane number of diesel can be improved by adding pre-ignition dopes such as amyl/butyl nitrite, carbamates, ditertiary butyl peroxide and metal organic compounds.
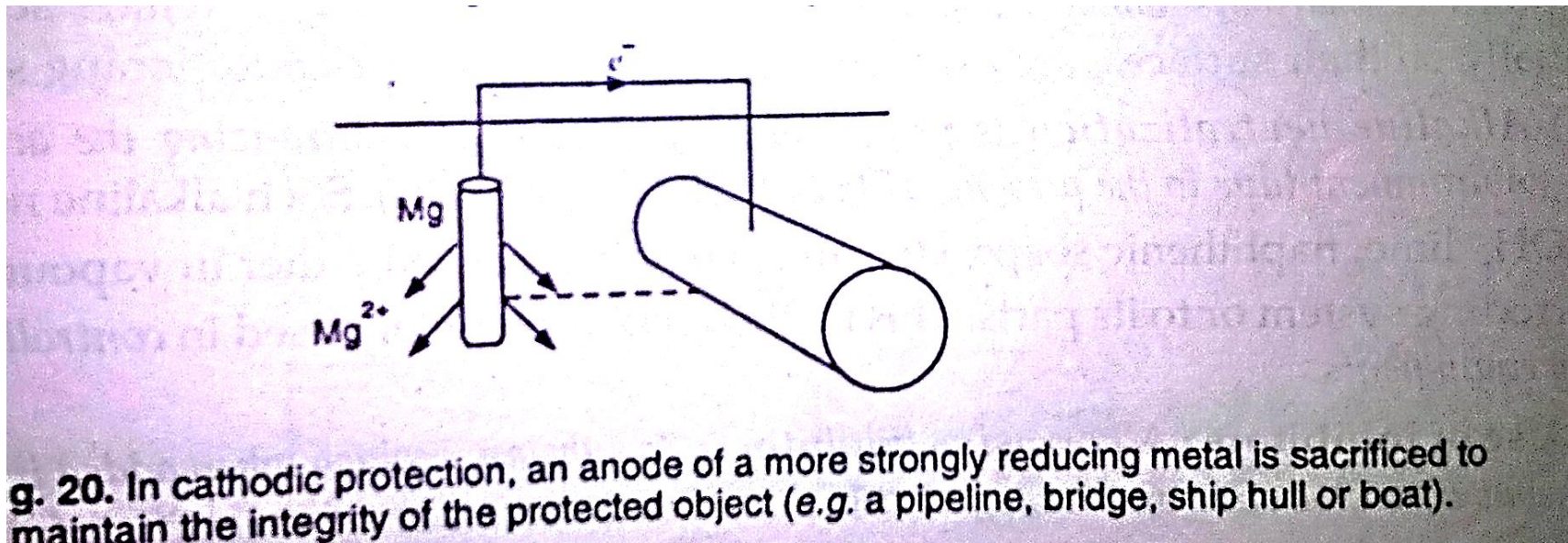

α – methyl naphthalene
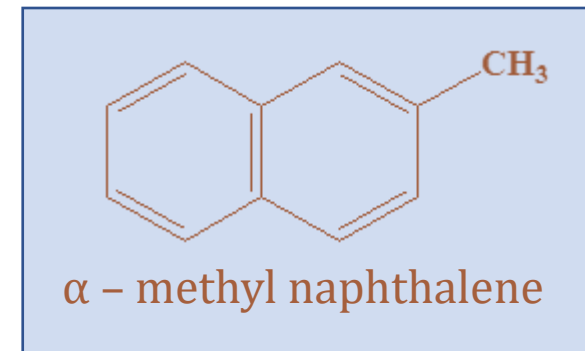
Corrosion protection

Cathodic protection

- Principle is to force the metal to be protected to behave as a cathode (only anode gets corroded!)
- Two types – sacrificial anodic protection and impressed current cathodic protection

Sacrificial anodic protection

- Metallic structure to be protected is connected by wire to a more anodic metal. This way, all the corrosion is concentrated at the anodic metal, which itself may get corroded slowly.
- The more active metal is the sacrificial anode
- The corroded metal can be periodically replaced
- Commonly used sacrifical anode metals are magnesium, Zinc, aluminium and its alloys
- Metal components that are protected this way include buried piplines, underground cables, marine structures, ship hulls, water tanks, piers

g. 20. In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (e.g. a pipeline, bridge, ship hull or boat).

The white patches visible on the ship's hull are zinc block sacrificial anodes.

Sacrificial anodes

Impressed current cathodic protection

- An impressed current is applied opposite in direction to the corrosion current, thus converting the corroding metal from anode to cathode
- The current is drawn from a D.C source (battery or rectifier) with an insoluble anode like graphite, high silica iron, scrap iron, stainless steel or platinum.
- A sufficient current is applied to the insoluble anode, buried in soil ad connected to the metallic structure to be protected.
- The anode is in a backfill composed of coke breeze or gypsum, to increase electrical contact with the surrounding soil
- This type of protection is applied to open water-box coolers, water tanks, buried water or oil pipes, condensors, transmission line towers, marine piers, laid-up ships
- Particularly useful to protect large structures
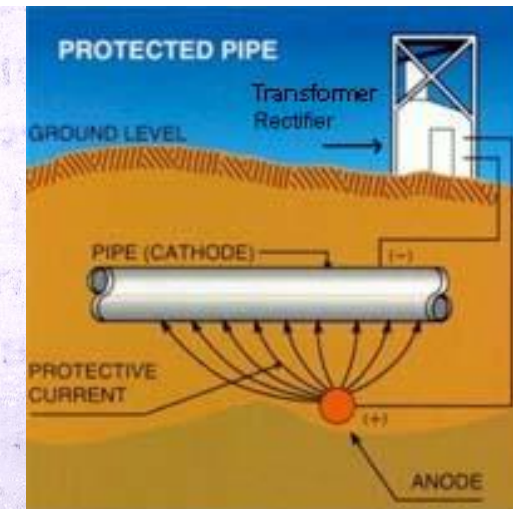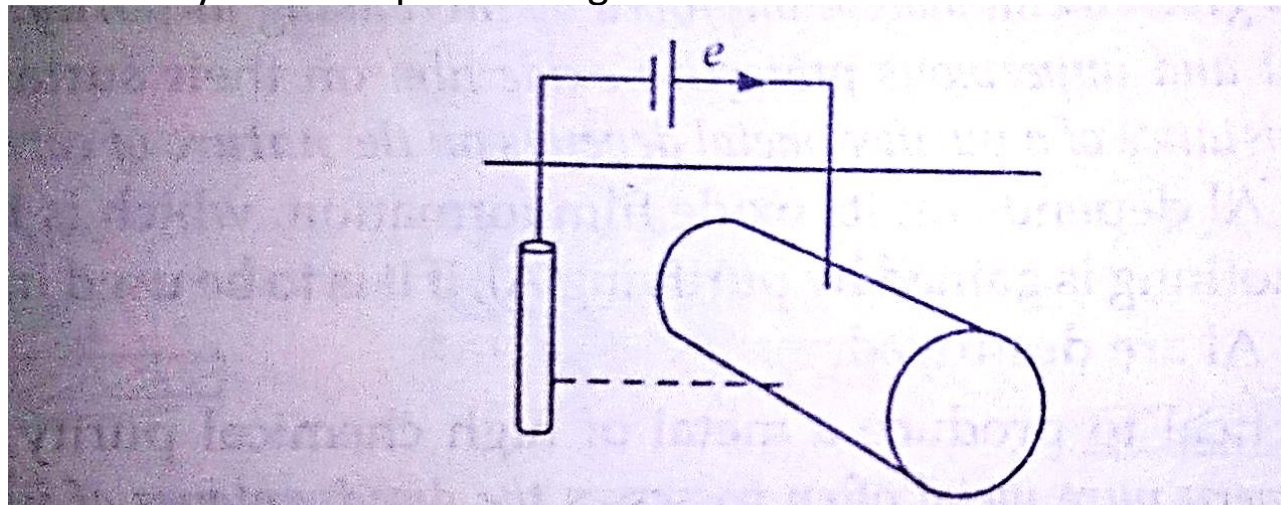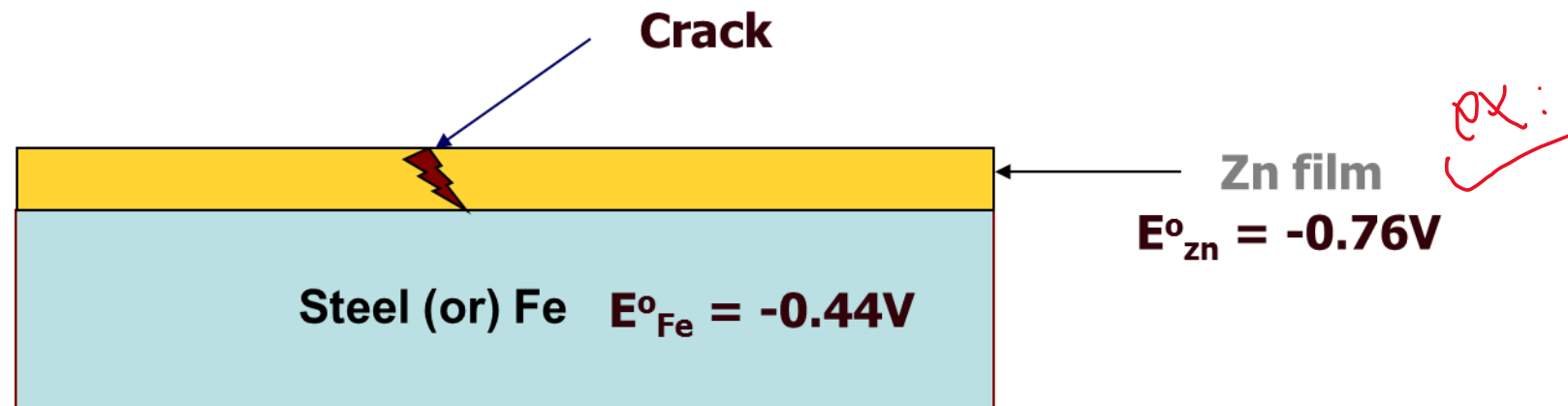

Fig. 21. In impressed-current cathodic protection, electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized.

Protective coatings

- Age old method to protect metal from getting corroded
- The protective coating applied
    - Must be chemically inert to the environment which attacks the metal
    - Must prevent the penetration of the environment to the metal that they protect
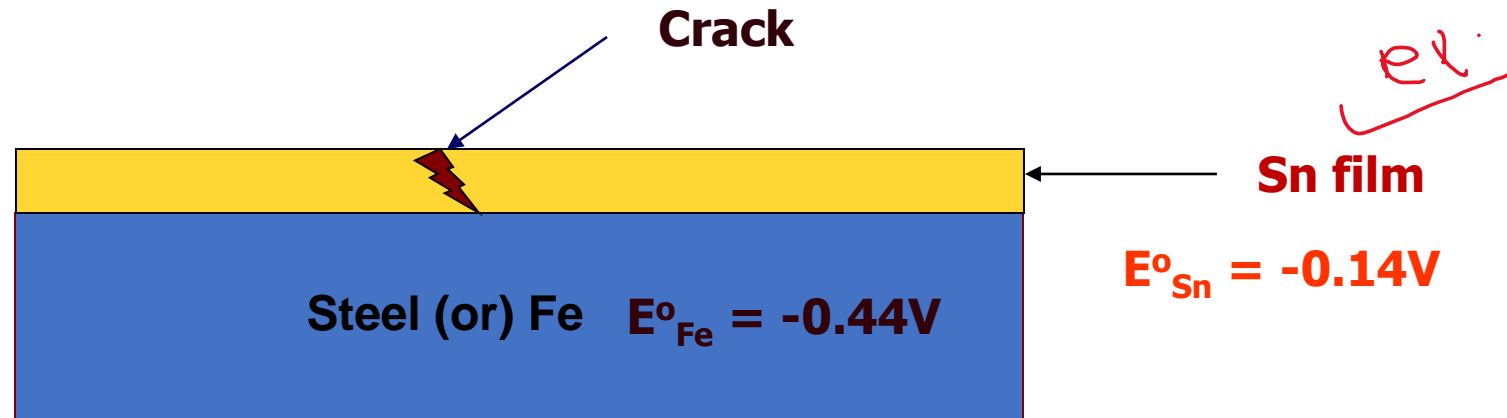
Anodic coatings

- The metal coating chosen , should be anodic to the base metal to be protected
- E.g to protect steel, Zn, Al or Cd are chosen as the coating metals based on the e-chem series
- If any discontinuity or pores in the coating develops, a galvanic corrosion cell develops with the coating metal anodic and the protected metal as cathodic area
- Thus the coating undergoes corrosion and sacrifically (anodically) protects the cathodic metal

Crack

Zn film

E^o_{zn} = **-0.76V**

Steel (or) Fe E^o_{Fe} = **-0.44V**

Graphic courtesy: Dr. Arockiasamy

Cathodic coatings

- Coating of a noble metal (higher electrode potential) with higher corrosion resistance than the base metal
- Base metal is protected only if the coating is continuous without any pores or discontinuities
- Punctures or pores in the coating can accelarate the corrosion of the base metal
- E.g tin coating of iron sheet is protective only as long as the coating is perfect
- Small pores can lead to corrosion of exposed iron (small anodic area) and severe local corrosion can occur leading to pitting and perforation of the base metal

Crack

Sn film

$E^o{}_{Sn} = -0.14V$

Steel (or) Fe $E^o{}_{Fe} = -0.44V$

Graphic courtesy: Dr. Arockiasamy

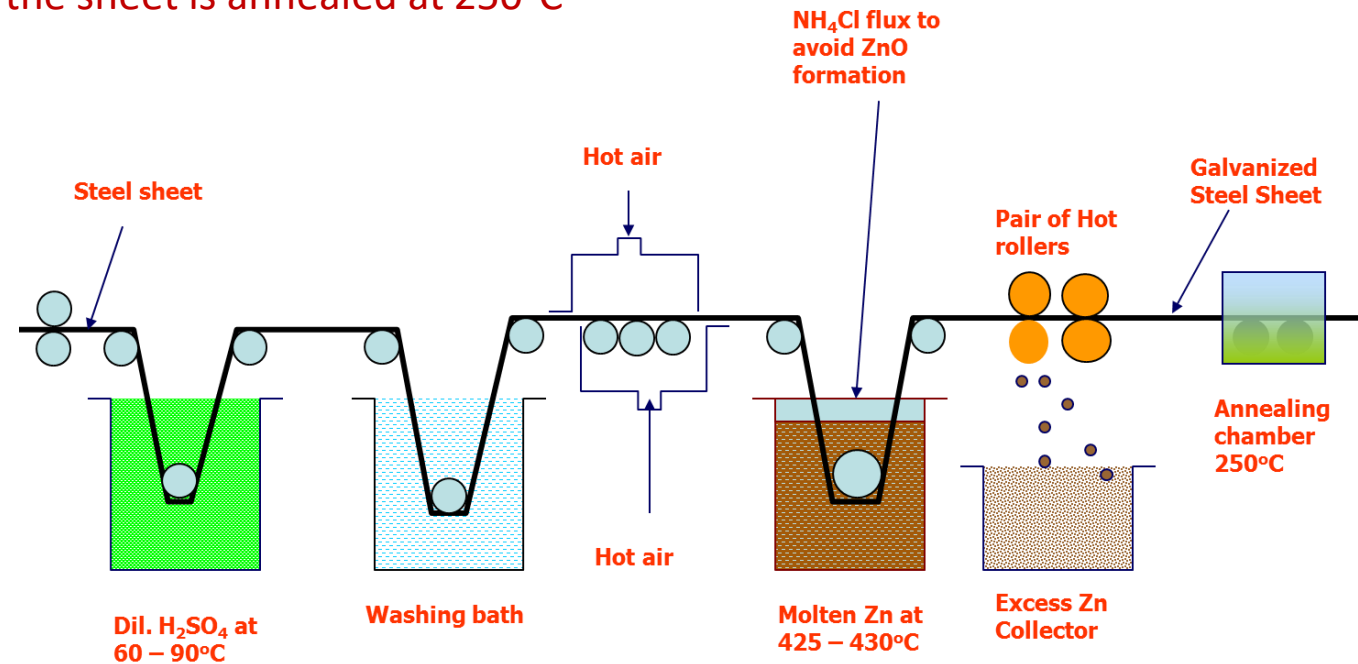| Anodic coating	Cathodic coating
Protects the underlying base metal "sacrificially"	Protects the base metal due to its noble character and higher corrosion resistance
Electrode potential of coating metal is lower than that of base metal	Electrode potential of coating metal is higher than the base metal
If pores or discontinuity breaks out, the base metal is not corroded, until all the coating metal is consumed	If pores break out, the corrosion of base metal is accelerated greatly
Coating of Zn on iron is an example	Coating of tin on iron is an example

Metal Coating methods

Hot dipping

- Used for coating low-melting metals like Zn, Sn, Pb, Al etc on iron, steel and copper which have very high melting points
- Metal to be coated is first covered by a molten flux (zinc chloride) layer, which cleans the base metal surface and prevents the oxidation of the molten coating metal.
- Then the base metal is dipped in a bath of molten coating-metal
- For good adhesion, the base metal surface has to be very clean. Else it cannot be wetted properly

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        Hot dipping
       /           \
 Galvanization    Tinning
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Galvanization

- It is the process of coating iron/steel sheets with a thin coating of Zinc to prevent rusting
- The process involves:
  - ➤ The iron/steel article (sheet, pipe, wire etc) is cleaned by *pickling* with dil. H_2SO_4 for 15 – 20 minutes at 60 -90°C to remove any scale, oxides or other impurities
  - ➤ After washing and drying, the article is dipped in a bath of molten zinc (425 - 435°C)
  - ➤ The surface of the bath is kept covered with a flux (ammonium chloride) to prevent oxidation
  - ➤ The coated sheet is passed through hot rollers to remove excess zinc
  - ➤ Finally the sheet is annealed at 250°C

NH_4Cl flux to avoid ZnO formation

Hot air

Steel sheet

Galvanized Steel Sheet

Pair of Hot rollers

Annealing chamber 250°C

Hot air

Dil. H_2SO_4 at 60 – 90°C

Washing bath

Molten Zn at 425 – 430°C

Excess Zn Collector

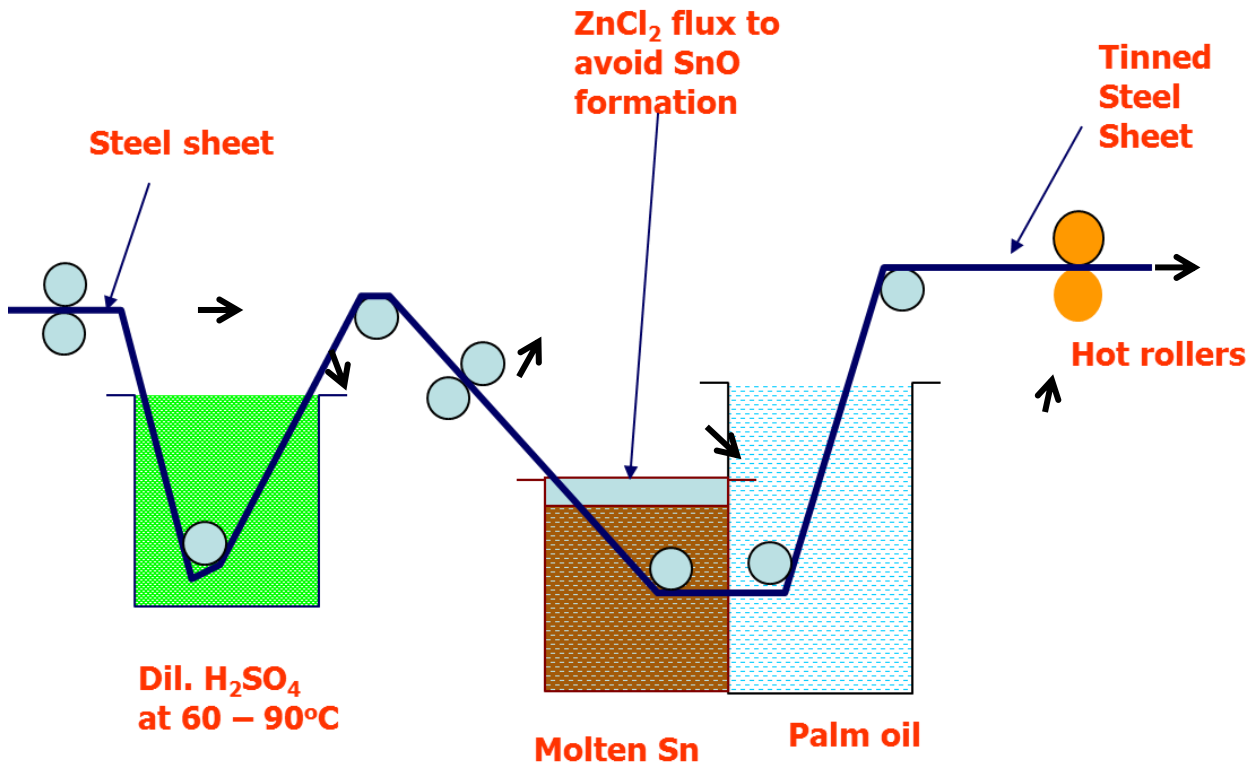**m.p of Zn = 419°C**

Graphic courtesy: Dr. Arockiasamy

- Iron used in roofing sheets, wires, nails, bolts, screws, buckets, tubes etc are protected from corrosion by the process of galvanization
- The Zn coating may get dissolved on contact with dilute acids, forming toxic compounds. For this reason, galvanised utensils are not suitable for preparing and storing foodstuff, especially the acidic ones

Tinning

- The process involves:
  - ➢ The iron/steel sheet is cleaned by *pickling* with dil. H_2SO_4 to remove any oxide films
  - ➢ Then dipped in a bath of molten zinc chloride flux, to aid in better adhesion of tin
  - ➢ The sheet then passes through molten tin an then through palm oil which protects the freshly coated hot tin from getting oxidised
  - ➢ the sheet is passed through rollers to attain uniform thickness

ZnCl$_2$ flux to avoid SnO formation

Tinned Steel Sheet

Steel sheet

Hot rollers

Dil. H$_2$SO$_4$ at 60 − 90°C

Acid Pickling

Molten Sn

Palm oil

m.p of Sn = 232°C

Graphic courtesy: Dr. Arockiasamy

- Tin has considerable resistance against atmospheric corrosion
- It is also non-toxic and so widely used in coating steel, copper and brass sheets that are used in making containers for foodstuff
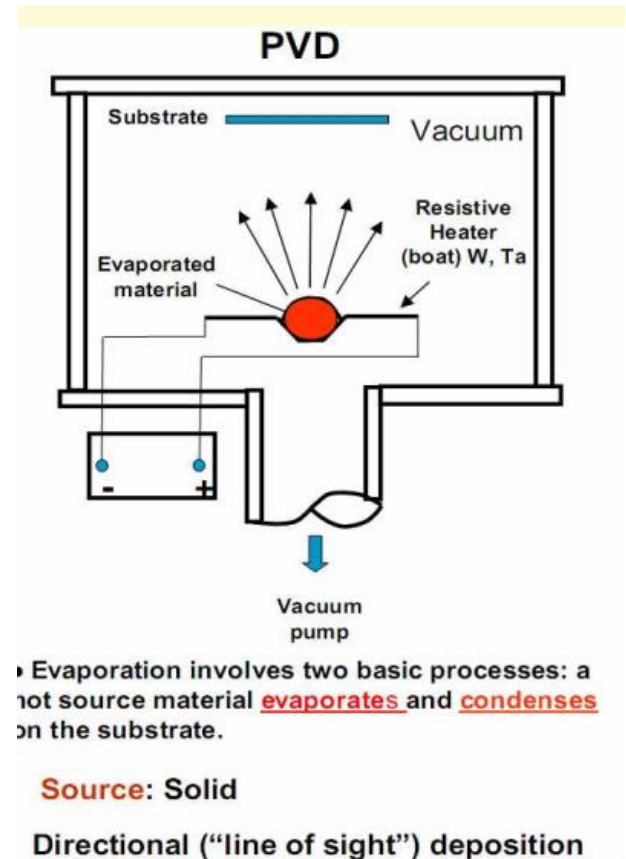- Tinned copper sheets are used for making utensils and refrigeration equipment

Galvanization	Tinning
Coating of iron /steel with a thin coat of zinc to protect it from rusting	Coating iron/steel with a coat of tin to prevent rusting
Zn protects iron sacrificially, since it has lower electrode potential than iron	Tin protects iron due to its noble character and its high corrosion resistance
In galvanised articles, zinc continues to protect the iron sacrificial galvanic cell action even when the coating is broken in places	Tin protects iron inly as long as the coating is perfect without any discontinuities by pores or punctures
Galvanised iron cannot be used for making food storage containers because zinc may react with food acids forming highly toxic compounds	Tin coated containers can be used for storing foodstuff due to non-toxic nature of tin

Vapour deposition techniques

- **Physical vapor deposition (PVD)**
- **Chemical vapour deposition (CVD)**

Physical vapour deposition (PVD)

- The processes of depositing materials directly from the vapour phase
- *Physical vapour deposition* (PVD) involves the generation of a vapour flux and its subsequent condensation in the form of a thin film on a substrate in a vacuum chamber
- Many methods such as *thermal and electron-beam evaporation, sputtering, and laser ablation* to generate the vapour flux from a target made of a specific material
- PVD techniques are used to fabricate a wide variety of thin films ranging from decorative optical coatings to high-temperature superconducting films
- The thickness of the deposits can vary from a few angstroms to several millimeters
- A very large number of inorganic materials (metals, alloys, compounds, and mixtures) as well as some organic materials can be deposited using PVD techniques

PVD

Substrate ▬▬▬▬▬ Vacuum

Resistive Heater (boat) W, Ta

Evaporated material

Vacuum pump

- Evaporation involves two basic processes: a hot source material evaporates and condenses on the substrate.

Source: Solid

Directional ("line of sight") deposition

Thermal evaporation method

- During this process, atoms and clusters of atoms or molecules are removed in the form of a vapour flux from a metal crucible, containing some bulk material (target) by heater the crucible, either by passing a current through it or by a heater filament.
- Alternatively, during electron-beam (e-beam) evaporation, a beam of electrons bombards the bulk material in the crucible to generate the vapour flux

- The crucible and its contents are placed in a vacuum chamber, with pressure typically below 10^{-4} Torr. The vapour flux condenses on a substrate.
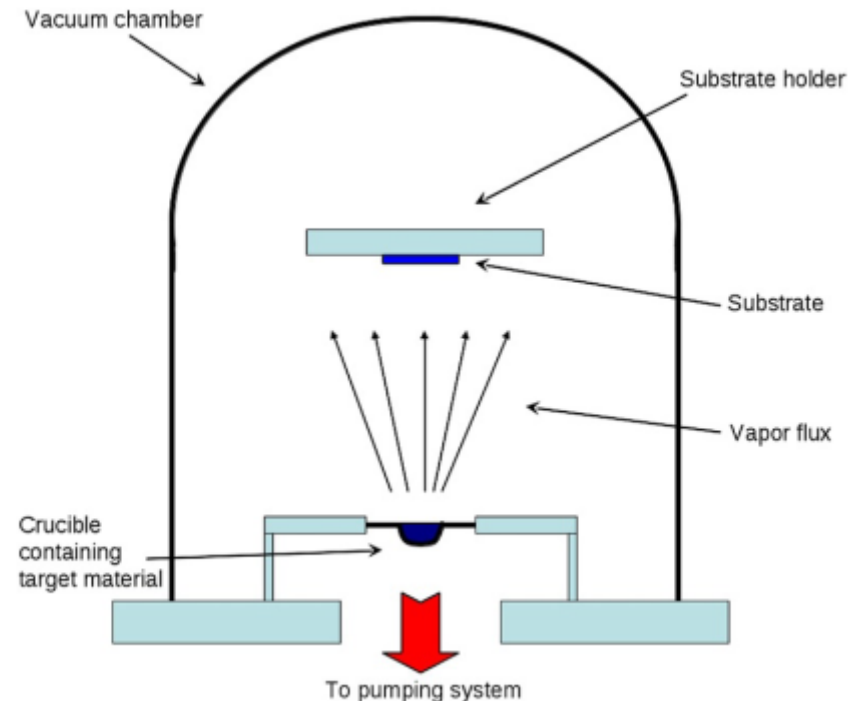
- For most materials that vaporize below a temperature around 1,500°C, evaporation can be achieved simply by putting the source material in contact with a hot surface that is resistively heated by passing a current through it

aluminized PET film for food packaging

Sputtering method

- A cathode made of the target material is bombarded by energetic ions generated in a glow-discharge plasma situated in front of the target
- The bombardment process causes the removal, i.e., sputtering, of target atoms by momentum transfer from the bombarding energetic gas ions (such as argon ions) accelerated in an electric field.
- The sputtered atoms form a vapour flux, which may then condense on a substrate as a thin film
- In **DC mode**, a cathode (target), an anode (on which the substrate is placed), and a DC power source are placed in a vacuum chamber. Argon is widely used to establish a discharge.
- The **RF configuration** is generally used for the deposition of electrically insulating materials such as oxides and polymers.
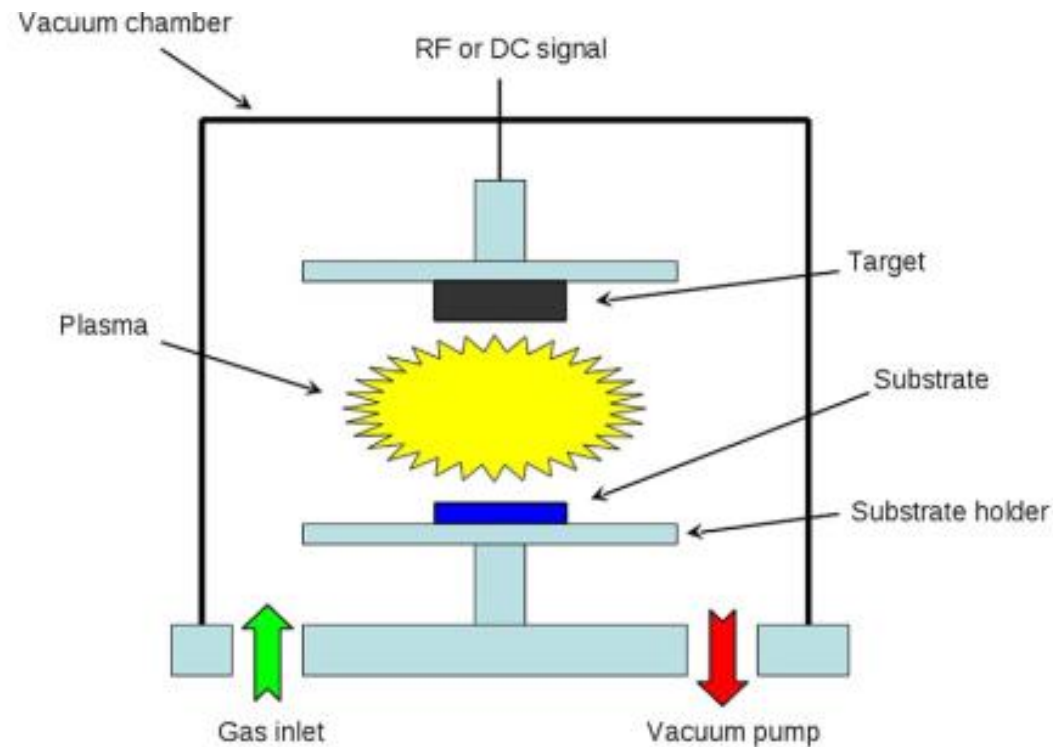
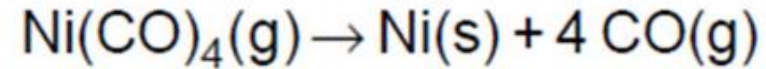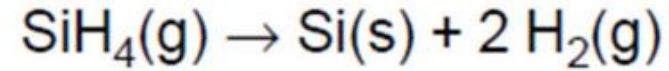Schematic of a typical sputtering system in either the DC or the RF configuration.

- In the **magnetron-assisted** configuration, a magnetic field is imposed to increase the plasma density as well as the current density at the cathode (target), thereby effectively increasing the sputtering rate.

- The magnetic field is tangential to the cathode surface.

- This configuration enables sputtering at low pressure with a high deposition rate
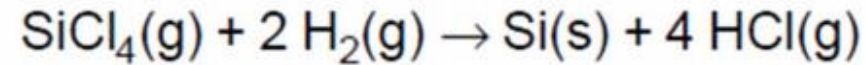
Chemical vapour deposition (CVD)

- *Chemical vapour deposition* (CVD) involves either the dissociation of a gaseous chemical and/or chemical reactions between gaseous reactants when heated, irradiated by photons, or subjected to a plasma.
- Depending on the activation sources for the chemical reactions, the deposition process can be categorized into thermally activated, laser assisted, or plasma-assisted CVD
- As a product, a thin film is deposited on a surface.
- This technique is used to produce very pure high-performance solid materials.
- Depending on the activation sources for the chemical reactions, the deposition process can be categorized into **thermally activated**, **laser assisted**, or **plasma-assisted CVD**
- The CVD process occurs in a vacuum chamber, with pressures ranging from the atmospheric pressure (atmospheric-pressure CVD) to below 10^{-8} Torr (ultrahigh-vacuum CVD)
- The main steps are
    1. transport of reacting gaseous species to the surface of a substrate
    2. adsorption of the species on that surface
    3. heterogeneous surface reaction catalysed by the surface of the substrate
    4. surface diffusion of the species to growth sites
    5. nucleation and growth of the film on the substrate
    6. desorption of gaseous reaction products and transport of reaction products away from the surface
- The chemical reactions include pyrolysis, oxidation, reduction, hydrolysis, or a combination of these and may be catalysed by the substrate
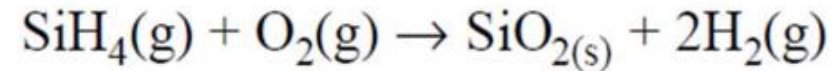
Some important reactions for CVD process

pyrolysis
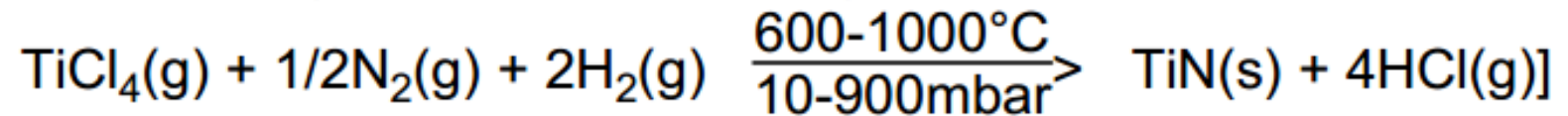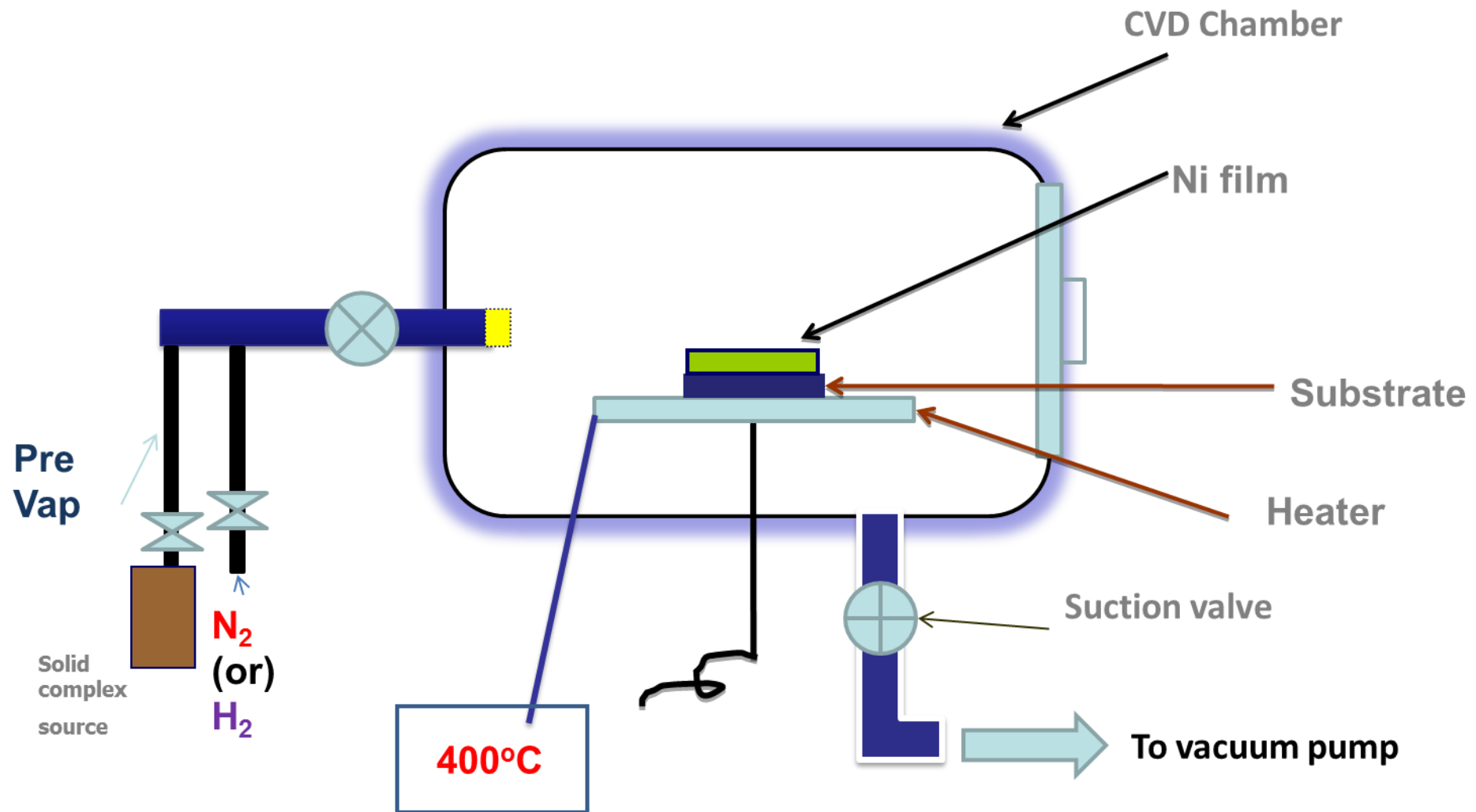
$$SiH_4(g) \rightarrow Si(s) + 2\,H_2(g)$$

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4\,CO(g)$$

Reduction

$$SiCl_4(g) + 2\,H_2(g) \rightarrow Si(s) + 4\,HCl(g)$$

Oxidation

$$SiH_4(g) + O_2(g) \rightarrow SiO_{2(s)} + 2H_2(g)$$

Nitridation

$$TiCl_4(g) + 1/2\,N_2(g) + 2H_2(g) \xrightarrow[\text{10-900mbar}]{\text{600-1000°C}} TiN(s) + 4HCl(g)]$$

CVD Chamber

Ni film

Substrate

Heater

Pre Vap

Solid complex source

N₂ (or) H₂

400°C

Suction valve

To vacuum pump

	CVD	PVD
Deposition	• T = 800 - 1000 ℃	• T = 70 - 500 ℃
Cycle Time	• 8 – 24 hours	• 3-4 hours for cutting tools
Properties	• excellent adherence • coating thickness up to 20 μm	• excellent adherence • uniform coating thickness • typical coating thickness 3-5 μm
Applications	• cutting tools, forming tools	• cutting tools, forming tools, components, medical devices, decorative