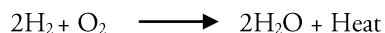
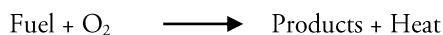


UNIT-2 CHAPTER-1

ENERGY SYSTEM

- **Introduction**

- A fuel is a substance that produces useful energy either through combustion or through nuclear reaction.
- An important property of a fuel is that the energy is released in a controlled manner and can be harnessed economically for domestic and industrial purposes.
- Wood, coal, charcoal, petrol, diesel, kerosene, producer gas and oil gas are some of the common examples of fuels.
- Fuels that produce heat energy by combustion are termed as chemical fuels.
- During combustion, carbon, hydrogen, sulphur and phosphorus that are present in the fuel combine with oxygen and release energy.



- However, combustion is not always necessary for a fuel to produce heat. Energy can also be liberated by fission or fusion of nuclei.
- This energy is much greater than the energy released by chemical fuels, and such fuels are termed as nuclear fuels. For example, plutonium, tritium, uranium, etc.

- **Classification of Fuels**

Fuels can be classified on the basis of their (I) occurrence (II) physical state

(I) On the basis of occurrence, fuels are of two types

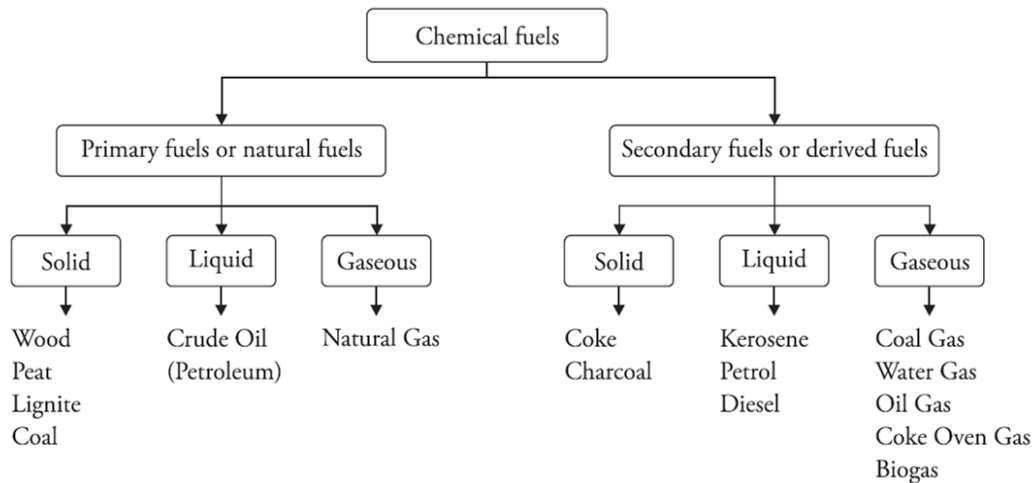
(a) **Primary Fuels or Natural Fuels** These are found to occur in nature and are used as such either without processing or after being processed to a certain extent, which does not alter the chemical constitution of the fuel. These are also known as fossil fuels. Examples include wood, peat, lignite, coal, petroleum, natural gas, etc.

(b) **Secondary Fuels or Derived Fuels** These are the fuels that are derived from primary fuels by further chemical processing, for example, coke, charcoal, kerosene, producer gas, water gas, etc.

(II) On the basis of their physical state, fuels may be classified as follows:

- (a) Solid fuels
- (b) Liquid fuels
- (c) Gaseous fuels

The classification can be summarized as shown in the following diagram.



• Characteristics of a Good Fuel

1. **High Calorific Value:** A good fuel should possess high calorific value because calorific value determines the efficiency of the fuel. Higher the calorific value, greater is the heat liberated per unit mass or volume.
2. **Ignition Temperature:** It is the lowest temperature to which a fuel must be preheated so that it starts burning smoothly. An ideal fuel should have moderate ignition temperature. Low ignition temperature can cause fire hazards, making storage and transportation difficult. Fuel with low ignition temperature can burn spontaneously leading to explosion. High ignition temperature, on the other hand, makes it difficult to kindle (ignite) the fuel.
3. **Moisture Content:** Moisture content should be low because the presence of moisture lowers the calorific value of the fuel.
4. **Non-combustible Matter:** After combustion, the non-combustible matter is left behind as ash or clinkers. Non-combustible matter reduces the calorific value of the fuel and also requires additional money investment for storage, handling and disposal of the waste products produced.

5. **Velocity of Combustion:** If the velocity of combustion is low, then a part of the liberated heat may get radiated instead of raising the temperature; hence, the required high temperature may not be attained. On the other hand, if the velocity of combustion is very high then the rate of combustion might become uncontrollable. For a continuous supply of heat, fuel must burn with a moderate rate.
6. **Combustion Products:** The products obtained during combustion of the fuel should be harmless and non-polluting. Harmful gases such as CO_2 , SO_2 , H_2S , PH_3 and PbBr_2 should not be produced, and also the amount of smoke produced should be less.
7. **Cost of the Fuel:** A good fuel should be readily available at a low cost.
8. **Storage and Transportation:** A good fuel should be easy to handle, store and transport at low cost.
9. **Size:** In case of solid fuels, the size should be uniform so that combustion is regular.
10. **Combustion Should Be Controllable:** The combustion process should be controllable, that is it can be started or stopped when required.

• Calorific Value

- It is defined as the total amount of heat liberated when a unit mass or volume of fuel is burnt completely.

Units of heat

- (i) **Calorie** It is defined as the amount of heat required to raise the temperature of 1 g of water by 1°C (from 15°C to 16°C). $1 \text{ calorie} = 4.185 \text{ Joules} = 4.185 \times 10^7 \text{ ergs}$.
- (ii) **Kilocalorie** It is defined as the amount of heat required to raise the temperature of 1 kg of water by 1°C (from 15°C to 16°C). $1 \text{ kcal} = 1000 \text{ cal}$.
- (iii) **British Thermal Unit (BTU)** It is defined as the amount of heat required to raise the temperature of 1 pound (lb) of water by 1°F (from 60°F to 61°F).
 $1 \text{ BTU} = 252 \text{ cal} = 0.252 \text{ kcal} = 1054.6 \text{ Joule} = 1054.6 \times 10^7 \text{ ergs}$.
- (iv) **Centigrade Heat Unit (CHU)** It is defined as the amount of heat required to raise the temperature of one pound of water by 1°C (from 15°C to 16°C).
 $1 \text{ kcal} = 3.968 \text{ BTU} = 2.2 \text{ CHU}$

- **Gross Calorific Value (GCV):** It is also called higher calorific value (HCV) and is defined as the total amount of heat produced when a unit quantity (mass/volume) of fuel is burnt completely, and the products of combustion are cooled to room temperature.
- Usually all fuels contain hydrogen. During combustion, the hydrogen present in the fuel is converted into steam. When the combustion products are cooled to room temperature, the steam gets condensed into water and heat that equals the latent heat of condensation of steam is evolved.
- This heat gets included in the measured heat, and so its value is high; hence, it is called higher calorific value.
- **Low Calorific Value (LCV):** It is also termed as net calorific value (NCV) and is defined as the heat produced when a unit quantity (mass/volume) of a fuel is burnt completely and the hot combustion products are allowed to escape.
- In actual practice, when a fuel is burnt water vapor escapes along with the hot combustion gases; hence, heat available is lesser than the gross calorific value. Therefore, this is called low calorific value or net calorific value.

Thus $LCV = HCV - \text{Latent heat of water vapour formed.}$

As 1 part by weight of hydrogen gives 9 parts by weight of water,
 $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$LCV = HCV - \text{Weight of hydrogen in unit mass/volume of fuel} \times 9 \times \text{latent heat of steam}$

Solved Examples

1. 2 kg of a coal sample was burnt in a bomb calorimeter. The heat liberated was estimated and found to be 14114 kcal. Calculate the calorific value of the coal sample.

Solution

Heat liberated on burning 2 kg coal = 14,114 kcal.

Therefore, heat liberated on combustion of 1 kg coal = $14114/2 = 7057$ kcal.

[Ans Calorific value of coal = 7057 kcal/kg]

2. The gross calorific value of a fuel containing 8% hydrogen was found to be 9225.9 kcal/kg. Find out its net calorific value if the latent heat of steam is 587 kcal/kg.

Solution

$NCV = GCV - 0.09 H \times \text{Latent heat of steam (H = \% of hydrogen in fuel)}$.

$NCV = 9225.9 - 0.09 \times 8 \times 587$.

$= 9225.9 - 422.64 = 8803.26$ kcal/kg

[Ans LCV/NCV = 8803.26 kcal/kg]

Practice problems

1. Calculate the GCV of a coal sample if its LCV is 6767.45 cal/g and if it contains 5% hydrogen. (Latent heat of steam is 587 cal/g). [Ans GCV = 7031.6 cal/g]
2. The gross calorific value of a fuel containing 6% H was found to be 9804.6 kcal/kg. Find the net calorific value if the latent heat of steam is 587 cal/g. [Ans 9487.62 kcal/kg]

• Determination of Calorific Value

The calorific value of solid and non-volatile liquid fuels is determined by bomb calorimeter, whereas the calorific value of gaseous fuels is determined by Junkers calorimeter.

Bomb calorimeter

Principle A known amount of fuel is burnt in excess of oxygen and the heat liberated is absorbed in a known amount of water. This heat liberated is measured by noting the change in temperature.

Calorific value of the fuel is then calculated by applying the following principle:

Heat liberated by fuel = Heat absorbed by water and the calorimeter.

Construction

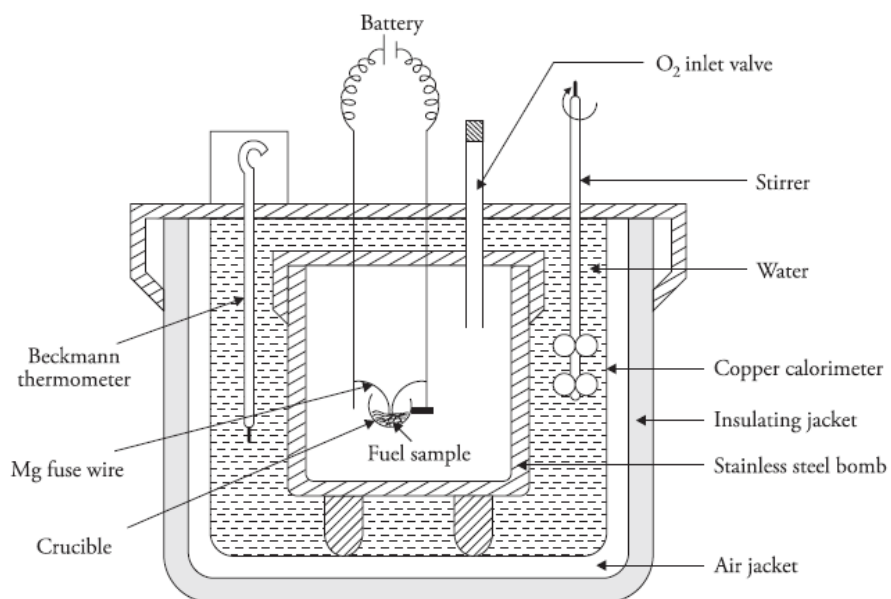


Figure 1: Bomb calorimeter

It consists of the following parts:

- (i) **Stainless Steel Bomb** It consists of a long cylindrical container made up of stainless steel. It has a lid that is made air tight with the help of screws. The lid is provided with two holes for electrodes and has an oxygen inlet valve. A small ring is attached to one of the electrodes. This ring acts as a support for nickel or stainless steel crucible in which the fuel is burnt. Magnesium wire touching the fuel sample extends across the electrodes. The steel bomb is lined inside with platinum to resist corrosive action of HNO_3 and H_2SO_4 vapors formed because of burning of fuel and is designed to withstand high pressure (25–50 atm).
- (ii) **Copper Calorimeter** The bomb is placed in a copper calorimeter containing a known amount of water. The calorimeter is provided with an electrical stirrer and a Beckmann thermometer that can read accurate temperature difference of up to 1/100th of a degree.
- (iii) **Air Jacket and Water Jacket** The copper calorimeter is surrounded by an air jacket and a water jacket to prevent loss of heat owing to radiation.

Working

- A known amount of fuel (0.5–1 g) is taken in a clean crucible supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes.
- About 10 mL of distilled water is introduced into the bomb to absorb vapors of sulphuric acid and nitric acid formed during combustion, and the lid of the bomb is tightly screwed.
- The bomb is filled with oxygen at 25 atmospheric pressure and placed in the copper calorimeter containing a known weight of water. The stirrer is started and the initial temperature of water is noted.
- The electrodes are then connected to a 6-volt battery to complete the circuit. The sample burns and heat is liberated. This heat is absorbed by water.
- Maximum temperature shown by the thermometer is recorded. Time taken to cool the water in the calorimeter from maximum temperature to room temperature is also noted.
- The gross calorific value of the fuel is calculated as follows.

Calculations

Let Weight of fuel sample taken = x g, Weight of water in the calorimeter = W g, Water equivalent* of calorimeter, stirrer, thermometer, bomb etc = w g, Initial temperature of water in the calorimeter = t_1 °C, Final temperature of water in the calorimeter = t_2 °C, Higher calorific value of fuel = H calorie / g, Heat liberated by burning of fuel = $x \times H$, Heat gained by water = $W \times \Delta T \times \text{specific heat of water} = W (t_2 - t_1) \times 1 \text{ cal}$, Heat gained by calorimeter = $w (t_2 - t_1)$

$$\begin{aligned} \text{Total heat gained} &= W (t_2 - t_1) + w (t_2 - t_1) \\ &= (W + w) (t_2 - t_1) \end{aligned}$$

But

Heat liberated by the fuel = Heat absorbed by water and calorimeter.

$$x \times H = (W + w) (t_2 - t_1)$$

$$x = \frac{(W+w)(t_2-t_1)}{H} = \text{cal/g (or kcal/kg)}$$

Net (lower) calorific value

$$\text{LCV} = \text{HCV} - 0.09 H \times 587 \text{ cal/g or kcal/kg}$$

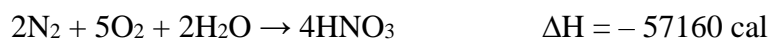
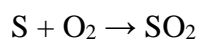
(Latent heat of condensation of steam = 587 kcal/kg).

Corrections

The following corrections are applied to get more accurate results

(a) **Fuse Wire Correction** The gross calorific value calculated above includes the heat liberated by the ignition of Mg fuse wire; 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 get oxidized to H_2SO_4 and HNO_3 , respectively:



Hence, the formation of acids is exothermic and this should be subtracted from the obtained value of GCV.

(c) **Cooling Correction** Heating and cooling are simultaneous processes. As the temperature rises above the room temperature, the loss of heat occurs due to radiation and the highest temperature recorded will be slightly less than that obtained if there was no heat loss. A temperature correction (cooling correction) is therefore necessary to get the correct rise in temperature.

If the time taken for the water in the calorimeter to cool from maximum temperature attained to room temperature is 'x' minutes and the rate of cooling is dt/min, then the cooling correction is $x \times dt$ and this is to be added to the rise in temperature.

$$\text{HCV of fuel (H)} = \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{acid} + \text{fuse wire correction})}{\text{Mass of the fuel (x)}}$$

Solved examples

1. 0.72 g of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3 °C to 29.1 °C. If the calorimeter contains 250 g of water

and its water equivalent is 150 g, calculate the HCV of the fuel. Give your answer in kJ/kg.

Solution

Here $x = 0.72$ g, $W = 250$ g, $w = 150$ g, $t_1 = 27.3$ °C, $t_2 = 29.1$ °C
Therefore, HCV of fuel

$$H = \frac{(W + w)(t_2 - t_1)}{\text{Mass of the fuel } (x)} \text{ cal/gm}$$

$$H = \frac{(250 + 150)(29.1 - 27.3)}{0.72} \text{ cal/gm} = 1000 \times 4.18 \text{ J/gm} = 4180 \text{ J/gm}$$

$$= 4180 \text{ kJ/kg}$$

(1 cal=4.18 Joules)

2. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water increased from 26.5 °C to 29.2 °C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g, respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific values.

Solution

Here, Weight of fuel (x) = 0.83 g; weight of water (W) = 3500 g; water equivalent of calorimeter (w) = 385 g; ($t_2 - t_1$) = (29.2 °C – 26.5 °C) = 2.7 °C; percentage of hydrogen (H) = 0.7%; Latent heat of steam = 587 cal/g.

$$\text{HCV of fuel } (H) = \frac{(W + w)(t_2 - t_1)}{x} \text{ cal/g} = \frac{(3500 + 385) \times 2.7}{0.83} = 12,638 \text{ cal/g}$$

$$\text{Net calorific value} = (\text{HCV} - 0.09 H \times 587) = (12638 - 0.09 \times 0.7 \times 587) \text{ cal/g.}$$

$$= (12,638 - 37) \text{ cal/g} = 12,601 \text{ cal/g}$$

3. A coal sample contains: C = 93%; H = 6% and ash = 1%. The following data were obtained when the above coal was tested in a bomb calorimeter:
- (i) Wt of coal burnt = 0.92 g
 - (ii) Wt of water taken = 550 g
 - (iii) Water equivalent of bomb and calorimeter = 2200 g
 - (iv) Rise in temperature = 2.42 °C
 - (v) Fuse wire correction = 10.0 cal
 - (vi) Acid correction = 50.0 cal

Calculate the gross calorific value of the coal.

SolutionWt of coal (x) = 0.92 g;Wt of water taken (W) = 550 gWater equivalent of bomb and calorimeter (w) = 2200 gRise in temperature ($t_2 - t_1$) = 2.42 °C;

Fuse wire correction = 10.0 cal

Acid correction = 50.0 cal; latent heat of condensation of steam = 580 cal/g;

Percentage of hydrogen = 6%

$$\begin{aligned} \text{GCV} &= \frac{(W + w)(t_2 - t_1) - (\text{Acid} + \text{fuse wire correction})}{x} \\ &= \frac{(550 + 2200) \times 2.42 - (50 + 10)}{0.92} = 7168.5 \text{ cal/g} \end{aligned}$$

4. A coal sample contains C = 92%, H = 5% and ash = 3%. When this coal sample was tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained

Wt of coal burnt = 0.95 g

Wt of water taken = 700 g

Water equivalent of bomb and calorimeter = 2000 g

Rise in temperature = 2.48 °C

Fuse wire correction = 10.0 cal

Acid correction = 60.0 cal

Cooling correction = 0.02 °C

Calculate the gross and net calorific value of the coal sample in cal/g. Assume the latent heat of condensation of steam as 580 cal/g.

Solution

$$\begin{aligned} \text{GCV} &= \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{acid correction} + \text{fuse wire correction})}{\text{weight of coal sample taken}} \\ &= \frac{(2000 + 700)(2.48 + 0.02) - (10 + 60)}{0.95} = \frac{(2700)(2.50) - (70)}{0.95} \\ &= \frac{6750 - 70}{0.95} = \frac{6680}{0.95} = 7031.57 \text{ cal/g} \end{aligned}$$

$$\text{LCV or NCV} = \text{HCV} - 0.09 \text{ H} \times 580 \text{ cal/g}$$

$$= 7031.57 - 0.09 \times 5 \times 580$$

$$= 7031.57 - 261 = 6770.57 \text{ cal/g}$$

$$[\text{Ans } \text{HCV/GCV} = 7031.57 \text{ cal/g}]$$

$$\text{LCV/NCV} = 6770.57 \text{ cal/g}]$$

Practice problems

- The temperature of 950 g of water was increased from 25.5 °C to 28.5 °C on burning 0.75 g of a solid fuel in a bomb calorimeter. Water equivalent of calorimeter and latent heat of steam are 400 g and 587 cal/g, respectively. If the fuel contains 0.65% of hydrogen, calculate its net calorific value.

$$[\text{Ans } 5365.66 \text{ cal/g}]$$

- Liquid fuel weighing 0.98 g and containing 90.1% C, 8% H and having the following results in bomb calorimeter experiment

Amount of water taken in calorimeter = 1450 g

Water equivalent of calorimeter = 450 g

Rise in temperature of water = 1.8 °C

If the latent heat of steam is 587 cal/g, calculate gross and net calorific value of fuel.

$$[\text{Ans } \text{GCV} = 3489.79 \text{ cal/g; LCV} = 3067.15 \text{ cal/g}]$$

❖ Power Alcohol

- ❖ Alcohol is an excellent alternative motor fuel for gasoline engines. The alcohols are fuels of the family of the ‘oxygenates’ having one or more oxygen, which contributes to the combustion.
- ❖ Only two of the alcohols are technically and economically suitable as fuels for internal combustion engines that is Methanol and Ethanol.
- ❖ If about 20-25% ethyl alcohol is blended with petrol and used as a fuel, it is known as power alcohol for internal combustion engine.
- ❖ Gasohol is a mixture of 90% unleaded gasoline and 10% ethyl alcohol. Its performance as a motor vehicle fuel is comparable to that of 100% unleaded gasoline, with the added benefit of superior antiknock properties (no premature fuel ignition).
- ❖ No engine modifications are need for the use of gasohol, which has in recent years gained some acceptance as an alternative to pure gasoline.

- ❖ Methanol is produced by a variety of process, the most common are as follows: distillation of wood; distillation of coal; natural gas and petroleum gas.
- ❖ Ethanol is produced mainly from biomass transformation, or bioconversion. It can also be produced by synthesis from petroleum or mineral coal.

❖ **Unleaded petrol:**

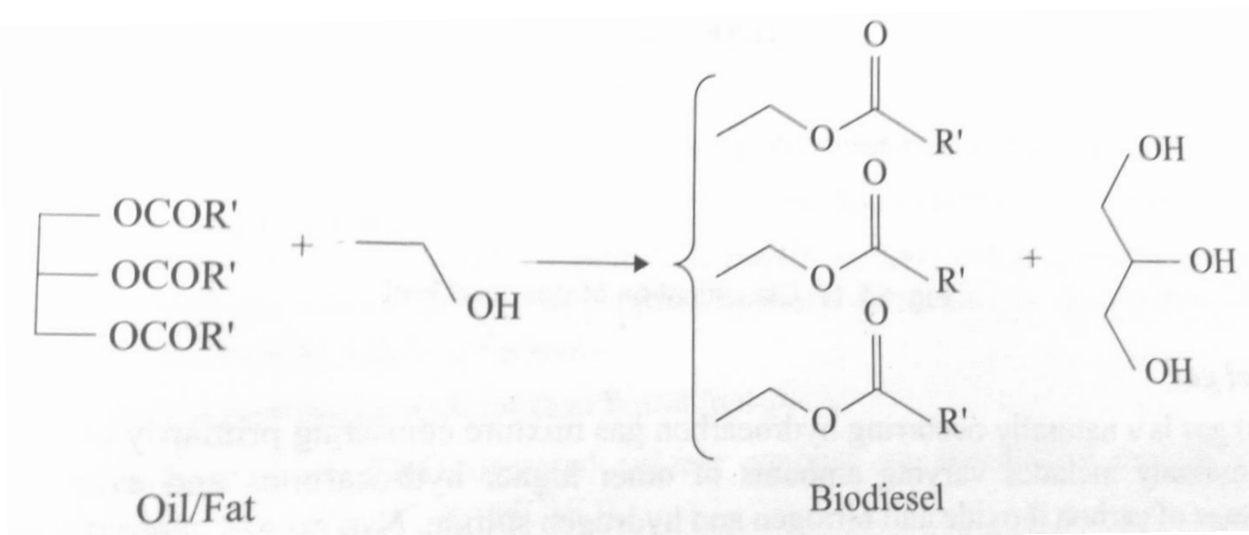
- ❖ Octane rating of petrol in leaded petrol is increased by adding tetra ethyl lead or tetramethyl lead. However, combustion of lead petrol leads to formation of litharge (PbO), which deposition the inner wall of cylinder and jams the piston. Also leaded petrol cannot be used in automobiles equipped cost catalytic converter, because lead present in exhaust gas poisons the catalyst, thereby destroying the active sites.
- ❖ Alternative method of increasing octane number of petrol is to add high octane compounds like isopentane, isooctane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE). Out of these MTBE is preferred, because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing the extent of peroxy compound formation.
- ❖ "Unleaded petrol" is one where in the enhancement of octane rating is accomplished without the addition of lead compounds.
- ❖ It may be pointed here that a major advantage of unleaded petrol is that it permits the use of catalytic converter attached to the exhaust in automobiles. A catalytic converter contains a catalyst (rhodium), which converts the toxic gases (CO and NO) to harmless gases (CO₂ and N₂ respectively).
- ❖ Moreover, it oxidises unburnt hydrocarbon into CO₂ and H₂O.

❖ **Biodiesel**

- ❖ Biodiesel refers to a vegetable oil or animal fat based diesel fuels consisting of alkyl esters.
- ❖ It is used in standard diesel engines. It can be used alone or blended with petrodiesel in any proportions. For identification of blends of biodiesel and conventional hydrocarbon based diesel, system known as the "B" factor is often used. 100% biodiesel is referred to as "B100"; 20% biodiesel, 80% petrodiesel is labeled "B20"; 5% biodiesel, 95% petrodiesel is labeled "B5"; and so on. Blends of 20% or less can be used in diesel equipment with no or only minor modifications. Blends of 20% biodiesel and lower can be used in diesel equipment with no, or only minor modifications.
- ❖ The pure form "B100" can be used only after engine modifications to avoid maintenance and performance problems.
- ❖ Biodiesel can also be used as a low carbon alternative to heating oil.

Production

- ❖ Biodiesel is produced through the base catalyzed trans-esterification of vegetable oil or animal fat with short-chain alcohols such as methanol or ethanol. Alcohol reacts with the fatty acids to form the mono-alkyl ester (biodiesel) and crude glycerol. The reaction is reversible for which excess alcohol must be added to ensure complete conversion. The basic reaction is as follows:



❖ Battery Technology-Introduction

❖ Introduction:

- ❖ With all the new applications, which have developed over the past few decades, the market for consumer batteries has grown correspondingly. Nowadays, the average family may have many batteries at any one time in and around the home.
- ❖ Many of these batteries are of advanced design and construction, giving greatly improved performance as a result of developments in materials science and technology.
- ❖ Although most small consumer batteries are still of the primary variety, there is growing trend to adopt secondary(rechargeable) batteries as being more economical.
- ❖ A cell has only two electrodes (or half cells) that generate electrical energy and the EMF thus, generated depend on the magnitude of the electrode potentials of the two electrodes.
- ❖ Depending on the specific purpose, higher voltage can be achieved by coupling a number of cells in series. The arrangement of two or more cells coupled in series is called a battery.
- ❖ The working principle of a battery is the transformation of free energy change of redox reactions of the electrode active materials of cells into electrical energy.
- ❖ Batteries are the indispensable source of portable energy.

- ❖ Nowadays, wide varieties of batteries are available in the market; and these find extensive applications in modern technology.
- ❖ The batteries are constructed as per the desired requirements and also to suit specific applications.
- ❖ Depending on the type of battery, they are used in electronic gadgets, pacemakers, calculators, power supplies, telecommunication equipment, and so on.
- ❖ High power batteries are also being tested and used in small cars, to minimize the air pollution problem.
- ❖ Nowadays, batteries of long shelf life, power, recharging capacity, tolerance to extreme conditions and reliability are desirable, and have wide applications too.

❖ **Classification of Batteries:**

- Electrochemical cells or batteries are identified as primary (non-rechargeable) or
- Secondary (rechargeable), depending on their capability of being electrically recharged.
- The batteries are classified as (i)primary, (ii)secondary, and (iii)reserve batteries.

(i) Primary batteries

- The working principle of a primary battery is the conversion of the free energy change of the active materials during electrode processes into the electrical energy.
- A battery which is not intended to be recharged and discarded when the battery has delivered all its electrical energy is known as a primary battery.
- The net cell reaction of a primary battery is irreversible and as long as the active materials are present in a battery, the cell generates electrical energy. In other words, primary batteries cannot be recharged.
- Example: Zn-MnO₂ dry cell.

(ii) Secondary or rechargeable batteries

- A secondary battery is known as a galvanic battery, which after discharge, may be restored to the fully charged state by the passage of an electric current through the cell in the opposite direction to that of the discharge.
- In other words, the net cell reactions of battery can be reversed. They are storage devices for electrical energy and are known as 'storage batteries'.
Examples: Lead-acid battery and Ni-Cd battery.
- The secondary batteries have advantages over the other primary batteries that the net cell reactions can be reversed during the charging process and the current can be drawn during the discharge process.
- The secondary batteries have better cycle life and capacity, so that it can be used over and over again.
- The secondary batteries are classified into two types:
 1. Acid storage battery-lead-acid battery.

2. Alkaline storage battery-Ni-Cd battery.

(iii) Reserve batteries

- In these reserve types of batteries, vital component is separated from the rest of the battery prior to activation.
- Under this condition, chemical deterioration or self-discharge is essentially eliminated, and the battery is capable of long-term storage.
- Usually, an electrolyte is the component that is isolated.
- These batteries are used, for example, to deliver high power for relatively short periods of time, in missiles, torpedoes and other weapon systems.

Example: LiV_2O_5 cell.

❖ Lithium ion cells

- Nowadays, successfully developed battery system is lithium ion battery (LIB) which has high volumetric and energy densities and is derived from lithium secondary batteries (LSBs) with metallic lithium anodes.
- Lithium secondary batteries have several drawbacks.
- The cell reaction in LIB is merely the migration of lithium ions between +ve and -ve electrodes. No chemical changes were observed in the two electrodes or in the electrolytes.
- This results in chemical transformation of active electrode materials and electrolytes, and thus LIBs can overcome the weakness of LSBs.
- Graphite has layered structure that, as well known, can be intercalated or doped with lithium between the layers to form so-called graphite intercalation compound(GIC).
- It was confirmed that the electrochemical intercalation of lithium in an aprotic organic electrolyte containing complex lithium salts, such as LiPF_6 , LiBF_4 , LiAsF_6 and LiClO_4 , reduces graphite to form Li-GIC and that Li-GIC can electrochemically oxidized by lithium deintercalation (undoping).

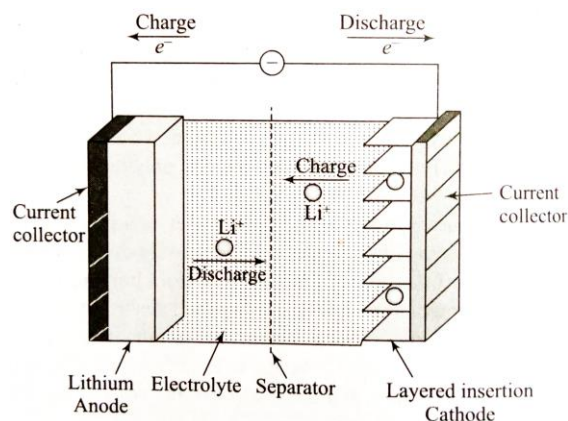


Figure 2: A typical lithium ion cell working

- This means that Li-GIC can be charged and discharged reversibly as rechargeable anodes for nonaqueous electrolyte cells.
- Lithium doping is 'charging' reaction and undoping reaction is discharging one.
- The principle of LiB is shown in Fig. 2. During charging of an LIB cell, lithium ions are extracted by electrochemical oxidation from LiMnO_2 , cathode, and the extracted lithium ions are doped by electrochemical reduction into the carbon anode to form Li-GIC.
- Conversely, during discharging, lithium ions are extracted from the anode by electrochemical oxidation, and they are inserted into the cathode by electrochemical reduction.
- The basic cell structure is then of the type

$$\text{Li}_{(x)}\text{C}_6/\text{LiX in PC-PC}/\text{Li}_{(1-x)}\text{MO}_2$$
- Where LiX is a lithium salt (such as LiClO_4), PC-EC is a mixed propylene carbonate-ethylene carbonate solvent and M is a transition metal.

❖ Cell structure of lithium ion battery:

- (iv) Copper and aluminium foils are used as the anode and cathode current collectors, respectively.
- (v) LiCoO_2 powder was mixed with a polyvinylidene fluoride (PVDF) binder in an appropriate solvent to formulate paint for cathode active matrices and the paint was applied to both.
- (vi) The anodes were prepared in a similar way to the cathodes, namely, by mixing carbon powder and PVDF in a solvent to make a paste and then coating the paste on both surfaces of the copper foil (Fig.3).

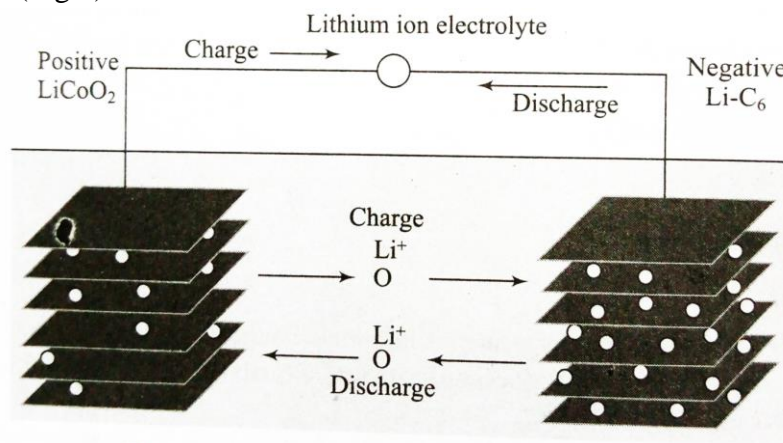
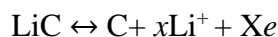


Figure 3: Showing the typical structure of LIB

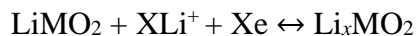
- (vii) Microporous polythene film is used as a separator containing the electrolyte, lithium salts (LiX) in PC-Ec, which is a mixed propylene carbonate-ethylene carbonate solvent. The chemistry of LIB is described below:

- (viii) The advantage of lithium ion cell is that it uses a lithiated carbon intercalation(LiC)material for the –ve electrode instead of metallic lithium.
- (ix) A lithiated transition metal intercalation compound is used for the +ve active material, and the electrolyte is aprotic organic (LiX in PC-EC solvent) solution.
- (x) The reactions at the electrodes and the overall cell reaction are

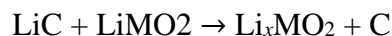
At anode,



At cathode,



Overall reaction,



- (xi) Where Li_xMO_2 represents Li_xCoO_2 , Li_xNiO_2 , and Li_xMnO_2 , the lithiated metal oxide compound.
- (xii) The lithium ions move back and forth between the +ve and -ve electrodes during the charge and discharge.
- (xiii) The electro-chemical process is the uptake of lithium ions at the -ve electrode during the charge and their release during the discharge, rather than lithium plating and stripping. The voltage of LIB is about 3.6-3.7V.

❖ Overview of Oil and lubricants

- The animal and vegetable products were used by man as lubricants for all purpose and were used in large quantities.
- These lubricants were rejected because they lack chemical inertness and later, there conventional lubricants were substituted by petroleum products and synthetic materials.
- Petroleum lubricants are the predominantly occurring hydrocarbon products which are extracted from fluids that occur naturally within the Earth.
- They are used widely as lubricants because they possess a combination of the following desirable properties:
 - available in suitable viscosities,
 - low volatility,
 - inertness (resistance to deterioration of the lubricant),
 - corrosion protection (resistance to deterioration of the sliding surfaces), and
 - low cost.
- Lubricants obtained from synthetic procedures are generally characterized as oily, neutral liquid materials having some properties similar to petroleum lubricants.
- The synthetic lubricants have better properties than the conventional vegetable oils lubricants.
- Synthetic lubricants exhibit greater stability of viscosity with temperature changes, resistance to scuffing and oxidation and fir resistance.

- Since the properties of synthetics vary considerably, each synthetic lubricant tends to find special applications.
- There is a wide scope to exploit lubricants of desired qualities for they are extensively needed for working of all types of engines and machineries in daily life.

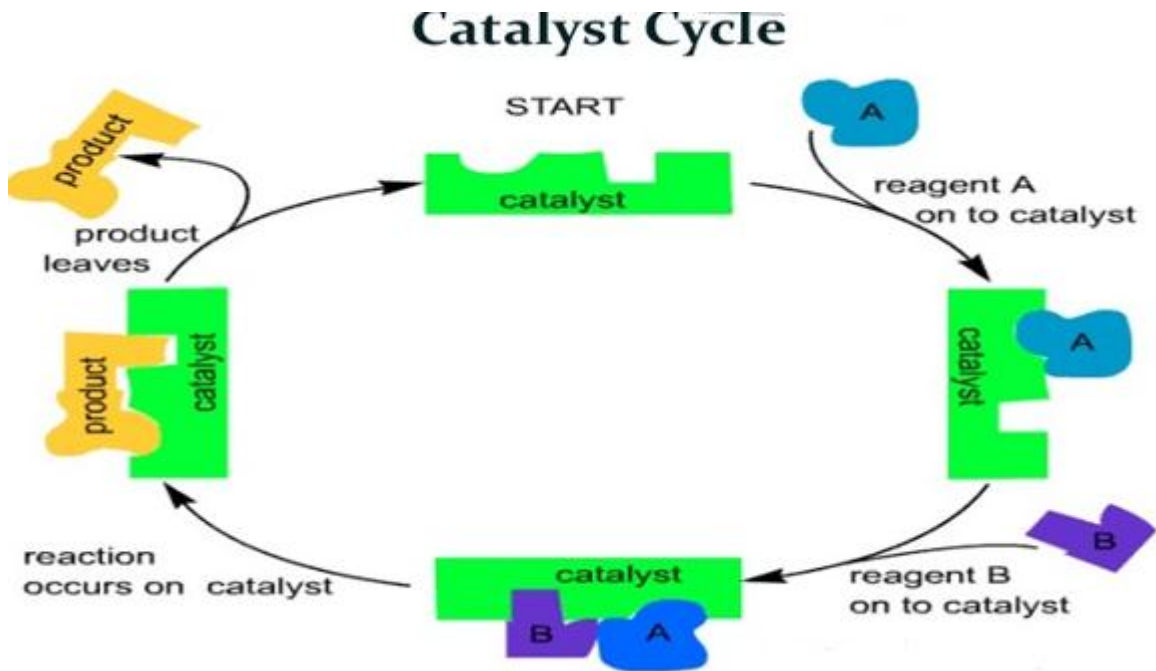
Unit-2

Chapter-2 Catalyst and Surface Chemistry

❖ Catalyst

Catalysts are substances that speed up reactions by providing an alternative pathway for the breaking and making of bonds.

❖ Catalyst Cycle



- ✓ Catalysts are substances which, when added to a reaction, increase the rate of reaction by providing an alternate reaction pathway with a lower activation energy (E_a).
- ✓ They do this by promoting proper orientation between reacting particles. In biochemistry,
- ✓ Taking Part In The Reaction it will change itself during the process by interacting with other reactant/product molecules.
- ✓ Altering The Rates Of Reactions In most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed
- ✓ Returning to its original form after reaction cycles a catalyst with exactly the same nature is 'reborn. In practice a catalyst has its lifespan - it deactivates gradually during use

TYPES OF CATALYSIS

There are two main types of catalysis :

(a) Homogeneous catalysis

(b) Heterogeneous catalysis

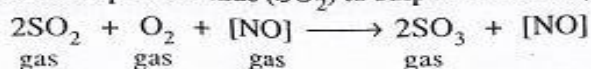
Also, there is a third types of catalysis known as **Enzyme catalysis** which is largely of biological interest. This will be discussed separately at a later stage.

HOMOGENEOUS CATALYSIS

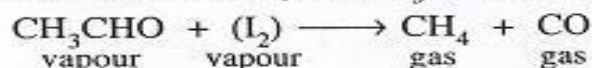
In homogeneous catalysis, **the catalyst is in the same phase as the reactants and is evenly distributed throughout.** This type of catalysis can occur in gas phase or the liquid (solution) phase.

Examples of Homogeneous Catalysis in Gas Phase

(a) Oxidation of sulphur dioxide (SO₂) to sulphur trioxide (SO₃) with nitric oxide (NO) as catalyst,



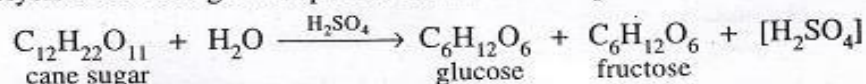
(b) Decomposition of acetaldehyde (CH₃CHO) with iodine (I₂) as catalyst,



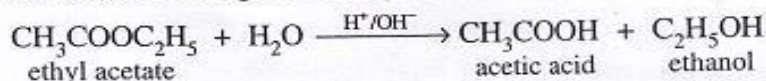
Examples of Homogeneous Catalysis in Solution Phase

Many reactions in solutions are catalysed by acids (H⁺) and bases (OH⁻).

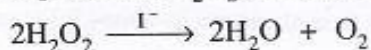
(a) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,



(b) Hydrolysis of an ester in the presence of acid or alkali,



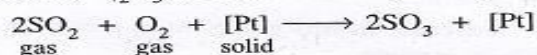
(c) Decomposition of hydrogen peroxide (H₂O₂) in the presence of iodide ion (I⁻) as catalyst,



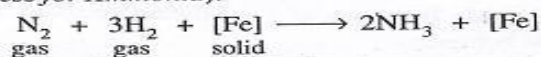
HETEROGENEOUS CATALYSIS

The catalysis in which the catalyst is in a different physical phase from the reactants is termed **Heterogeneous catalysis**. The most important of such reactions are those in which the reactants are in the gas phase while the catalyst is a solid. The process is also called **Contact catalysis** since the reaction occurs by contact of reactants with the catalyst surface. In contact catalysis, usually the catalyst is a finely divided metal or a gauze. This form of catalysis has great industrial importance.

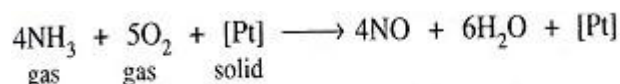
(a) Combination of sulphur dioxide (SO₂) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V₂O₅, (*Contact Process for Sulphuric acid*).



(b) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron, (*Haber Process for Ammonia*).



(c) Oxidation of ammonia to nitric oxide (NO) in the presence of platinum gauze (a stage in manufacture of Nitric acid).



CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them.

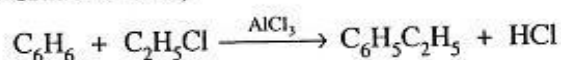
(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction

Qualitative and quantitative analysis show that a catalyst undergoes no change in mass or chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide (MnO_2) used as a catalyst in the thermal decomposing of potassium chlorate is left as a fine powder at the end of the reaction.

(2) A small quantity of catalyst is generally needed to produce almost unlimited reaction

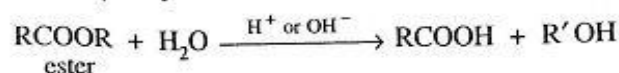
Sometimes a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,



anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene.

For the acid and alkaline hydrolysis of an ester,



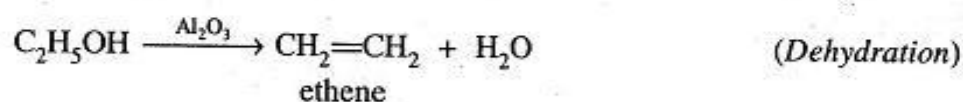
the rate of reaction is proportional to the concentration of the catalyst (H^+ or OH^-).

(3) A catalyst is more effective when finely divided

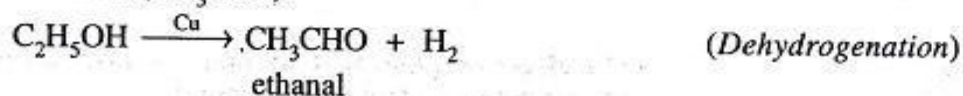
In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

(4) A catalyst is specific in its action

While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol (C_2H_5OH) gives ethene (C_2H_4) when passed over hot aluminium oxide,



but with hot copper it gives ethanal (CH_3CHO).



(5) A catalyst cannot, in general, initiate a reaction

(6) A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium

(7) Change of temperature alters the rate of a catalytic reaction

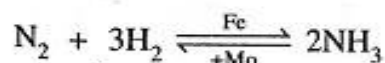
PROMOTERS

The activity of a catalyst can often be increased by addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst.

A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter.

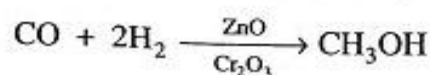
Example of Promoters

Molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.



In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency.

For example, in the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.



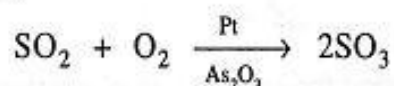
CATALYTIC POISONING

Very often a heterogeneous catalyst is rendered ineffective by the presence of small amounts of impurities in the reactants.

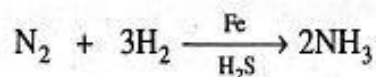
A substance which destroys the activity of the catalyst to accelerate a reaction, is called a poison and the process is called Catalytic poisoning.

Examples of Catalytic Poisoning

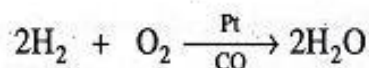
(1) The platinum catalyst used in the oxidation of sulphur dioxide (Contact Process), is poisoned by arsenic oxide (As_2O_3)



(2) The iron catalyst used in the synthesis of ammonia (Haber Process) is poisoned by H_2S .



(3) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide.



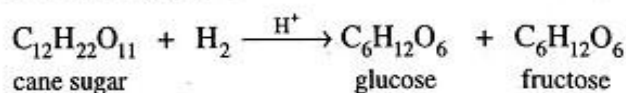
ACID-BASE CATALYSIS

A number of homogeneous catalytic reactions are known which are catalysed by acids or bases, or both acids and bases. These are often referred to as **Acid-Base catalysts**.

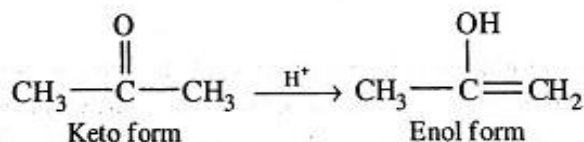
Arrhenius pointed out that acid catalysis was, in fact, brought about by H^+ ions supplied by strong acids, while base catalysis was caused by OH^- ions supplied by strong bases.

Examples of Acid-Base catalysis

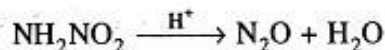
(1) Inversion of Cane sugar :



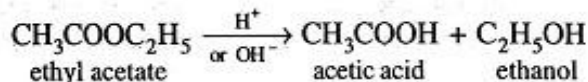
(2) Keto-Enol tautomerism of Acetone :



(3) Decomposition of Nitramide :



(4) Hydrolysis of an Ester :



General Acid-Base catalysis

More recently it has been found that :

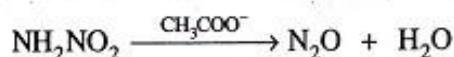
(a) **Not only H^+ ions but all Bronsted bases (proton donors) cause acid catalysis.** Thus the general acid catalysts are :

H^+ , undissociated acids (CH_3COOH), cations of weak bases (NH_4^+), and water (H_2O).

(b) **Not only OH^- ions but all Bronsted bases (proton acceptors) act as base catalyst.** Thus the general base catalysts are :

OH^- , undissociated bases, anions of weak acids (CH_3COO^-) and water (H_2O).

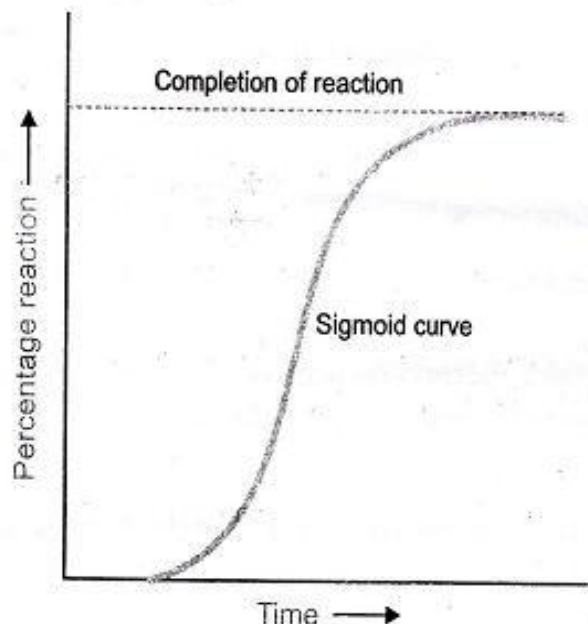
The catalysis brought about by general acids and bases is termed **General Acid-Base catalysis**. For elucidation, decomposition of nitramide is also catalysed by acetate ions (CH_3COO^-).



AUTOCATALYSIS

When one of the products of reaction itself acts as a catalyst for that reaction the phenomenon is called Autocatalysis.

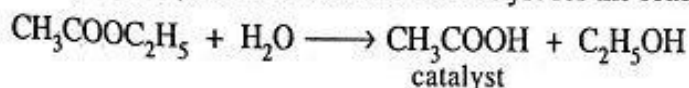
In autocatalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (Fig. 21.4). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.



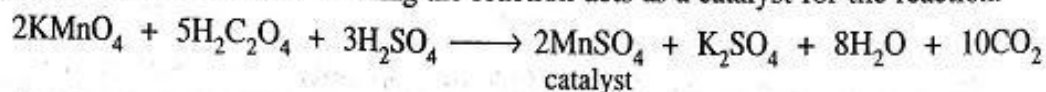
■ Figure 21.4
 Curve showing the rise of rate of reaction with time.

Examples of Autocatalysis

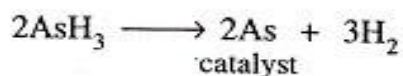
(1) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate forms acetic acid (CH_3COOH) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.



(2) **Oxidation of Oxalic acid.** When oxalic acid is oxidised by acidified potassium permanganate, manganous sulphate produced during the reaction acts as a catalyst for the reaction.



(3) **Decomposition of Arsine.** The free arsenic produced by the decomposition of arsine (AsH_3) autocatalyses the reaction.



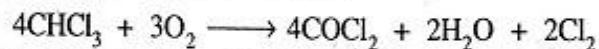
NEGATIVE CATALYSIS

When a catalyst reduces the rate of a reaction, it is called a Negative catalyst or Inhibitor. This phenomenon is called Negative catalysis or Inhibition. Negative catalysis is useful to slow down or stop altogether an unwanted reaction.

Examples of Negative Catalysis

(1) **Oxidation of Trichloromethane (CHCl₃)**

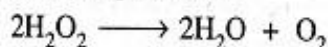
Trichloromethane (or chloroform) is used as anaesthetic. Upon oxidation by air it forms carbonyl chloride (COCl₂) which is a poisonous substance.



2 per cent of ethanol (C₂H₅OH) when added to chloroform acts as a negative catalyst and suppresses the formation of carbonyl chloride.

(2) **Decomposition of Hydrogen peroxide**

The decomposition of hydrogen peroxide,



is retarded by the presence of *dilute acids* or *glycerol*.

(3) **Tetraethyllead as Antiknock**

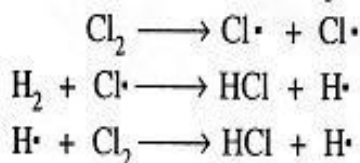
When tetraethyllead, Pb(C₂H₅)₄, is added to petrol, it retards the too rapid or explosive combustion of the fuel which is responsible for knocking of the engine.

Explanation of Negative Catalysis

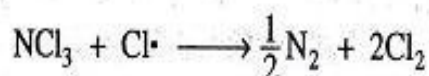
The mechanism of negative catalysis could be different for different reactions.

(1) **By poisoning a catalyst.** A negative catalyst may function by poisoning a catalyst which already happens to be present in the reaction mixture. For example, the traces of alkali dissolved from the glass of the container, catalyse the decomposition of hydrogen peroxide (H₂O₂). But the addition of an acid would destroy the alkali catalyst and thus prevent decomposition.

(2) **By breaking a chain reaction.** In some cases negative catalysts are believed to operate by breaking the chain of reactions. For example, the combination of H₂ and Cl₂, which is a chain reaction, is negatively catalysed by nitrogen trichloride (NCl₃).





NCl₃ breaks the chain of reactions by absorbing the propagating species (Cl), and the reaction stops.

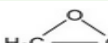
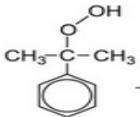


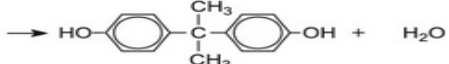


➤ Catalysis of metal salts Criteria for choosing the catalyst for industrial process.

✓ **Heterogeneous catalysis**

Process	Catalyst	Equation
Making ammonia	Iron	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Making synthesis gas (carbon monoxide and hydrogen)	Nickel	$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g. petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on alumina	$CH_3CH_2CH_2CH_2CH_2CH_3(g) \rightarrow$  $(g) + H_2(g)$
Making epoxyethane	Silver on alumina	$C_2H_4(g) + \frac{1}{2}O_2(g) \rightarrow$  (g)
Making sulfuric acid	Vanadium(V) oxide on silica	$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$
Making nitric acid	Platinum and rhodium	$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

✓ **Homogeneous catalysis**

Manufacture	Catalyst	Equation
Ethane-1,2-diol	Sulfuric acid	 + $H_2O \rightarrow HOCH_2CH_2OH$
2,2,4-Trimethylpentane (iso-octane)	Hydrogen fluoride	$H_3C-\overset{\overset{CH_3}{ }}{C}=CH_2 + H-\overset{\overset{CH_3}{ }}{C}-CH_3 \rightarrow H_3C-\overset{\overset{CH_3}{ }}{C}-CH_2-\overset{\overset{CH_3}{ }}{C}-CH_3$
Phenol and propanone	Sulfuric acid	 \rightarrow  + $CH_3-CO-CH_3$
Bisphenol A	Sulfuric acid	$CH_3-CO-CH_3 + 2$  \rightarrow  + H_2O

Applications of Catalysis

Industrial applications

Almost all chemical industries have one or more steps employing catalysts

1. Petroleum, energy sector, fertiliser, pharmaceutical, fine chemicals

Environmental applications

– Pollution controls in combination with industrial processes

- ❖ Pre-treatment - reduce the amount waste/change the composition of emissions
- ❖ Post-treatments - once formed, reduce and convert emissions
- ❖ Using alternative materials

– Pollution reduction

- ❖ gas - converting harmful gases to non-harmful ones
- ❖ liquid - de-pollution, de-odour, de-colour etc
- ❖ solid - landfill, factory wastes

Advantages of catalytic processes

– Achieving better process economics and productivity

- ❖ Increase reaction rates - fast
- ❖ Simplify the reaction steps - low investment cost
- ❖ Carry out reaction under mild conditions (e.g. low T, P)
- low energy consumption

– Reducing wastes

- ❖ Improving selectivity toward desired products - less raw materials required, less unwanted wastes
- ❖ Replacing harmful/toxic materials with readily available ones

- Producing certain products that may not be possible without catalysts
- Having better control of process (safety, flexible etc.)
- Encouraging application and advancement of new technologies and materials

Surface Chemistry

Adsorption: Adsorption is the phenomenon of higher concentration of any molecular species at the surface than in the bulk.

Adsorbent: The substance on the surface of which adsorption takes place is called adsorbent.

Adsorbate: The substance which is being adsorbed on the surface of another substance.

Desorption: The process of removal of an adsorbed substance from the surface on which it is adsorbed.

Adsorption is the process in which matter is extracted from one phase and concentrated at the surface of a second phase. (Interface accumulation). This is a surface phenomenon as opposed to absorption where matter changes solution phase, e.g. gas transfer.

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or (dissolved) solid to a surface. This process creates a film of the *adsorbate* on the surface of the *adsorbent*.

This process differs from absorption, in which a fluid (the *adsorbate*) permeates or is dissolved by a liquid or solid (the *adsorbent*).

Note that adsorption is a surface-based process while absorption involves the whole volume of the material.

The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

Adsorbent Materials

- Activated Carbon
- Activated Alumina
- Silica Gel
- Molecular Sieves (Zeolites)
- Polar and Non-polar adsorbents



Zeolite

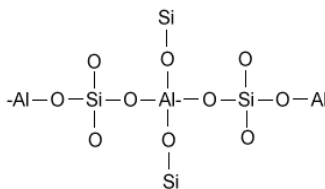


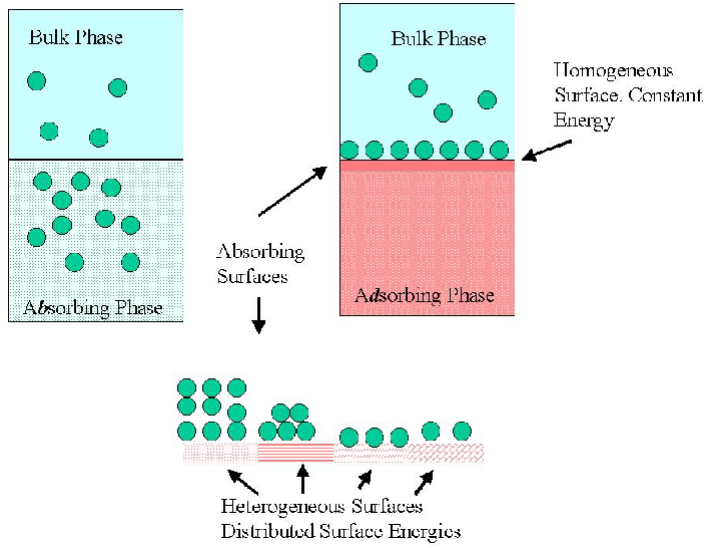
Figure 1: Basic Zeolite Structure



Activated Alumina

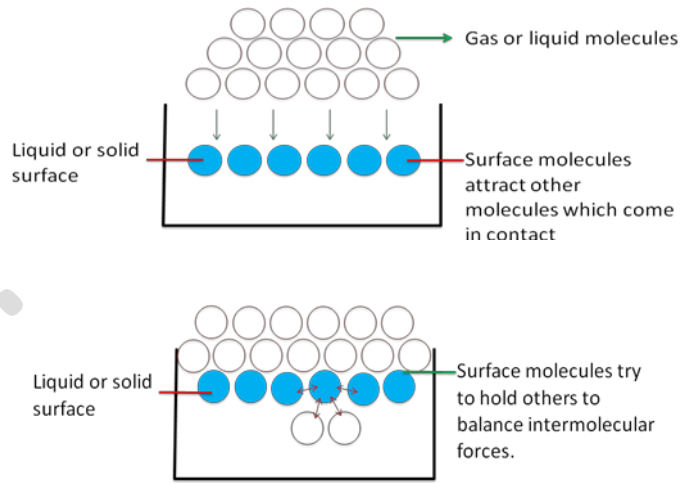
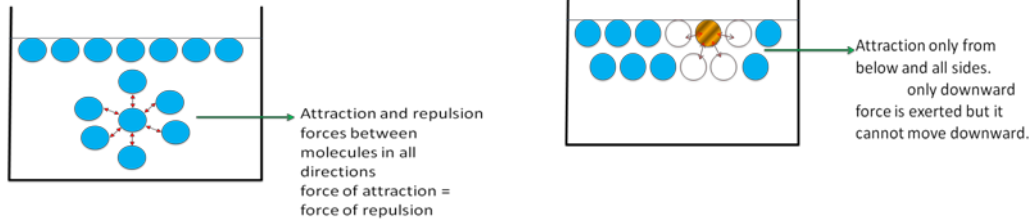
Activated carbon

- Made from nutshells, wood, and petroleum, bituminous coal by heating in the absence of oxygen to dehydrate and carbonize (remove volatile components).
- "Activation" is the process that produces the porous structure essential for effective adsorption by oxidation of carbon with water vapor or CO₂.
- Activated carbon attracts non-polar molecules such as hydrocarbons

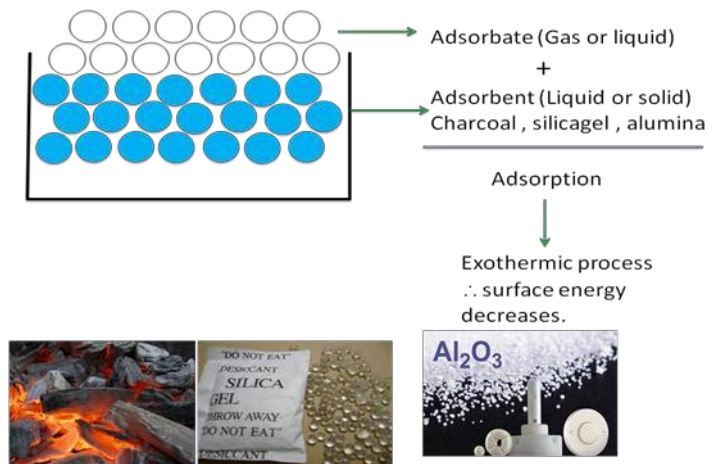


Adsorption

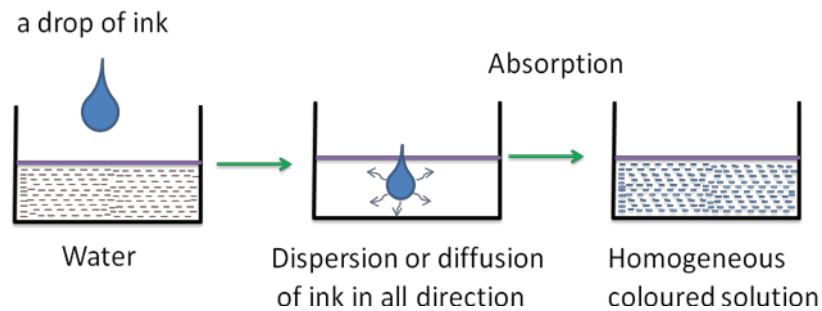
Surface tension



Conc. of other molecules at the surface will be higher and they do not penetrate into the surface of liquid or solid. → Adsorption



Absorption



Difference between absorption & adsorption

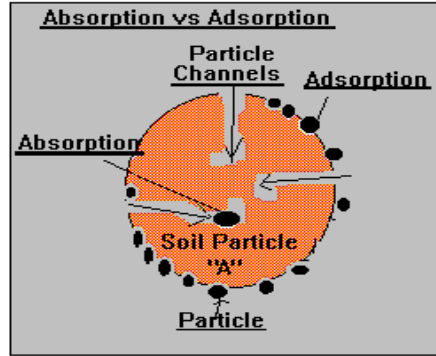
Absorption

- The molecules of the sub. get diffused in the whole of the solid or liquid.
- It forms homogeneous mixture.
- It is not surface phenomena.
- eg. Addition of dye in to water and form colored solution.

Adsorption

- The molecules get attracted on the surface of solid or liquid and remain there.
- It forms heterogeneous mixture.
- It is surface phenomena.
- eg. Addition of charcoal to the colored solution which removes color.

Adsorption vs absorption



Difference between Physical adsorption VS Chemisorption

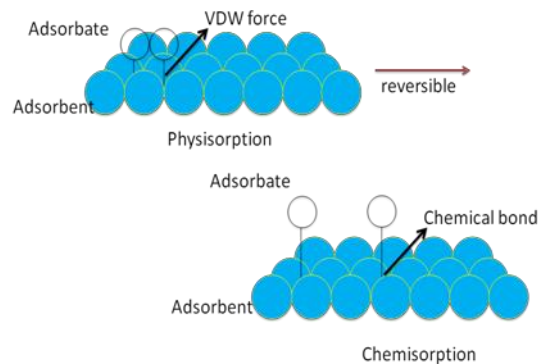
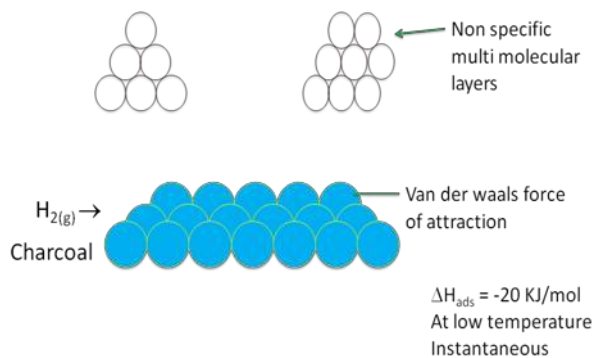
Physical Adsorption

- Caused by intermolecular van der Waal’s forces.
- Depends on nature of gas. Easily liquefiable gases are adsorbed readily.
- Heat of adsorption is small (about 5 kcal/mol)
- It is reversible process.
- Occurs rapidly at low temperature; decreases with increasing temperature.
- Increase of pressure increases adsorption; decrease of pressure causes desorption.
- Forms multimolecular layers on adsorbent.

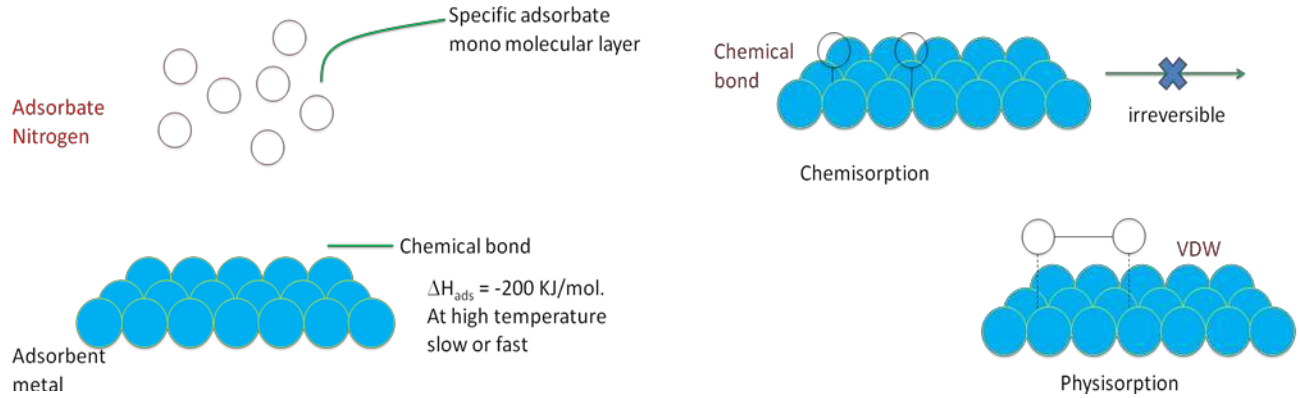
Chemical Adsorption

- Caused by chemical bond formation.
- Much more specific than physical adsorption.
- Heat of adsorption is large (20-100 kcal/mol)
- It is irreversible process.
- Increases with increase of temperature.
- Change of pressure has no such effects.
- Forms unimolecular layer.

Physical Adsorption



Chemical Adsorption (Chemisorption)



Factors affecting adsorption:

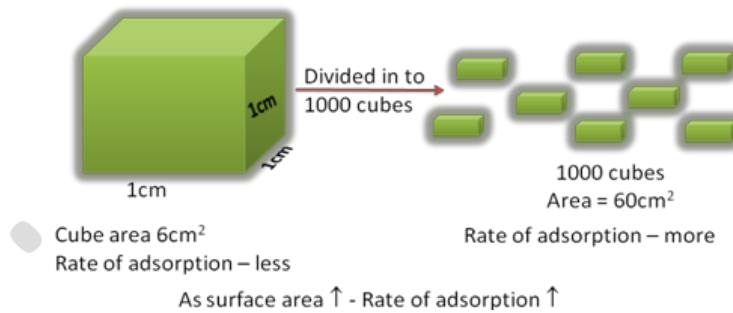
Effect of adsorbate: The easily liquifiable gases like NH_3 , HCl , CO_2 etc. are adsorbed to a greater extent than the permanent gases such as H_2 , O_2 , N_2 , etc.

Effect of specific area of the adsorbent: The greater the specific area of the solid, the greater would be its adsorbing capacity.

Effect of temperature: Adsorption decreases with increase in temperature.

Effect of pressure: An increase in pressure causes an increase in the magnitude of adsorption of an adsorbent.

Specific area of adsorbent



Freundlich adsorption Isotherm

Freundlich proposed an empirical relation in the form of a mathematical equation:

$$W/m \propto P^{1/n}$$

Where $n > 1$

$$\therefore P^{1/n} \text{ is between } P^1 \text{ and } P^0$$

$$W/m = K P^{1/n}$$

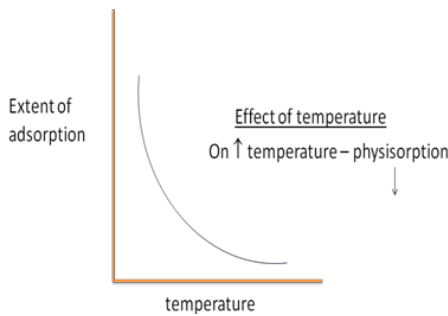
K = proportionality constant

Freundlich adsorption isotherm

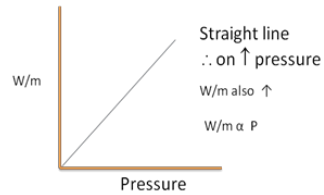
$$\log W/m = \log K + 1/n \log P$$

$$Y \text{ (axis)} = C \text{ (intercept)} + m \text{ (slope)} \cdot X \text{ (axis)}$$

This equation is a straight line at low pressure. But at higher pressure, they showed a slight curve, especially at low temperature.



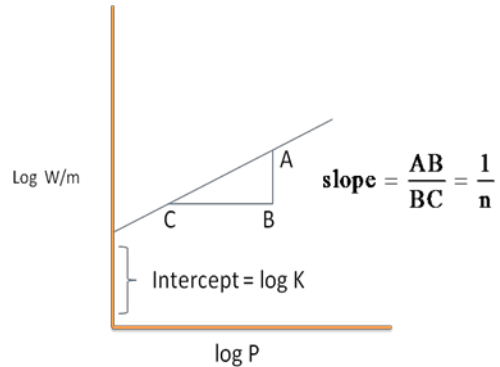
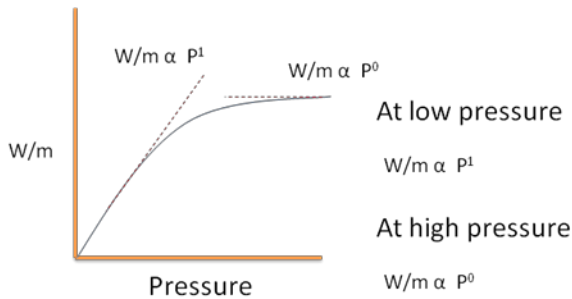
W = concentration or moles of the adsorbate
 m = weight or conc. of the adsorbent
 W/m = extent of adsorption



Adsorption Isotherm (plot at constant temperature)
 Relation between W/m and pressure can be established from experimental results

Effect of Temperature

Effect of Pressure



Where,

W = Adsorbate

m = Adsorbent

P = Pressure which lies between P^1 to P^0

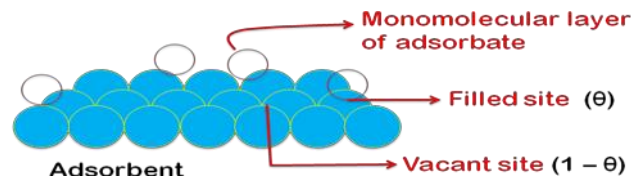
If graph is a straight line then Freundlich adsorption isotherm is satisfied.

Limitations of Freundlich adsorption isotherms

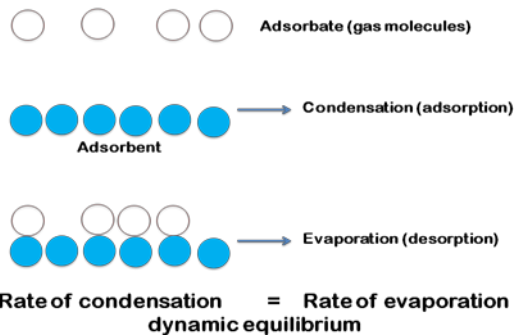
1. Applicable at low pressure
2. Constants K and n changes with change in temperature.
3. Isotherm is empirical one – based on experimental with certain gases. No theoretical relevance.

Langmuir adsorption isotherm

- Langmuir considered that when the gas molecules strikes a solid surface, the surface adsorbs some of this gas molecules and some are evaporated (or are desorbed rapidly).
- A dynamic equilibrium is eventually established between the two opposing process, adsorption and desorption.
- Based on kinetic theory of gases, the assumptions are:



Process



- If θ is the fraction of total surface covered by the adsorbed molecules, the fraction of the empty surface area is $(1 - \theta)$.
- The rate of adsorption (R_a) is proportional to available empty surface $(1 - \theta)$ and pressure (P) of the gas.

$$R_a \propto (1 - \theta) P$$

$$R_a = K_1 (1 - \theta) P$$

(K_1 = Rate constant for desorption process)

- The rate of desorption (R_d) is proportional to the covered surface (θ).

Therefore, $R_d \propto \theta$
 $R_d = K_2 \theta$

(K_2 = Rate constant of adsorption process)

At dynamic equilibrium, the rate of desorption is equal to the rate of adsorption.

$$\begin{aligned}
 K_2 \theta &= K_1 (1 - \theta) P \\
 K_2 \theta &= K_1 P - K_1 P \theta \\
 K_2 \theta + K_1 P \theta &= K_1 P \\
 \theta (K_2 + K_1 P) &= K_1 P
 \end{aligned}$$

Therefore,

$$\theta = \frac{K_1 P}{(K_2 + K_1 P)} \dots\dots\dots(1)$$

- The mass of the gas (W) adsorbed per unit mass of adsorbent is directly proportional to the fraction of surface covered (θ).

$$\begin{aligned}
 W &\propto \theta \\
 W &= K_3 \theta \dots\dots\dots(2)
 \end{aligned}$$

Putting the value of eq. (1) in eq. (2),

$$W = \frac{K_3 \cdot K_1 P}{(K_2 + K_1 P)} \dots\dots\dots(3)$$

Now dividing equation (3) with K_2 ,

Therefore,

$$W = \frac{K_3 \cdot K_1}{K_2} \frac{P}{K_2 + K_1 P}$$

Where, $\frac{K_3 \cdot K_1}{K_2} = A = \text{Proportionality Constant}$

$\frac{K_1}{K_2} = B = \text{Proportionality Constant}$

$$W = \frac{AP}{1 + BP}$$

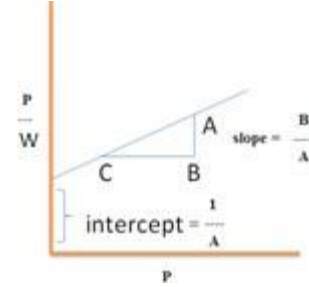
$$W \cdot (1 + BP) = AP$$

$$\frac{P}{W} = \frac{BP + 1}{A}$$

$$\frac{P}{W} = \frac{B}{A} P + \frac{1}{A}$$

$$Y = m \cdot X + C$$

Slope Intercept



- The pressure (P) is very low, the factor [(B/A) P] may be ignored and isotherm becomes:

$$\frac{P}{W} = \frac{1}{A}$$

Therefore, $W = A \cdot P$ (at low pressure)

- If the pressure (P) is very high, the factor 1/A may be ignored and isotherm becomes :

$$\frac{P}{W} = \frac{B}{A} P$$

$$\frac{1}{W} = \frac{B}{A}$$

Therefore, $W = A/B$ (at high pressure)

Conclusion:

- At low pressure, the amount of gas adsorbed (W) is directly proportional to pressure (P).
- At high pressure, the mass adsorbed reaches a constant value (A/B) when the adsorbent surface is completely covered with uni-molecular layer of gas.
- At this stage, adsorption is independent of pressure.

Applications of Adsorption

- In gas masks
- In catalysis
- In adsorption indicators
- In chromatographic analysis
- In softening of hard water
- In paint industry
- In removing moisture from air in the storage of delicate instruments