

CHEMISTRY OF INDUSTRIAL MATERIALS

Editors

Dr. K. CHENNAKESAVULU

Dr. J. KARTHIKEYAN

Dr. T. KRITHIGA

Dr. S. SUNITHA

Dr. A. SHEIK MIDEEN

Dr. S. SUPRIYA

Dr. V. KAVITHA

Mrs. X. JANET SABINA

DEPARTMENT OF CHEMISTRY

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

PREFACE

Chemistry is the branch of science that deals with matter and its physical and chemical properties. It is important for budding engineers to have an understanding of chemistry as it applies to their needs. Chemistry is considered as one of the essential elements for understanding the nature of various engineering materials. In this context, Chemistry of Industrial Materials is considered as an important subject for engineering students from the branches of Mechanical, Automobile, Aeronautical, Mechanical and Production and Civil Engineering. This book is the concerted effort of various members of the Department of Chemistry. Their qualifications and experience have enabled them to write the book in an easy, interesting and simplified manner.

The book has been divided into five units covering all the aspects of Industrial materials. The content provided is primarily aimed at engineering students and gives sufficiently comprehensive information on all the units discussed. A question bank is also a part of this book and is given at the end of each chapter. This will help students check their understanding and prepare themselves for examination in this subject. The five topics covered in this book are given below.

Unit I – Fuels—Different types of fuels and their classification are discussed here in detail. Various methods of manufacture and analysis of fuels, such as proximate analysis, ultimate analysis, etc are also covered.

Unit II – Phase Equilibria – This unit explains the basics of phase equilibrium studies with pertinent examples. Both one and two component systems are exhaustively discussed with specific examples.

Unit III – Explosives and Rocket Propellants – The classification and assessment of different types of explosives are discussed. The unit also covers the basic principles underlying rockets and rocket propulsion system. Classification of propellants is also covered.

Unit IV –Lubricants – This unit covers the three types of lubrication mechanisms. It also explains the various properties of lubricants in detail along with its classification.

Unit V –Composites and Abrasives—This unit introduces composites and its constituents. The different types of composites are discussed comprehensively with a brief introduction to cermets and its applications. It also covers the properties and manufacture of abrasives.

The faculty of the Department of Chemistry wish to thank the management for giving them the opportunity to write this book.

ACKNOWLEDGEMENT

The faculty members of Department of Chemistry are proud to dedicate this book to our beloved **Founder Chancellor** of **Sathyabama Institute of Science and Technology (Deemed to be University)** **Col. Dr. JEPPIAAR, M.A., B.L., Ph.D.**

The authors are grateful to **Tmt. REMIBAI JEPPIAAR, Chancellor** of Sathyabama Institute of Science and Technology (Deemed to be University), for her support and encouragement.

The authors would like to express sincere thanks to **Dr. Marie Johnson B.E., M.B.A., M. Phil., Ph.D., Vice-President** and **Dr. Mariazeena Johnson B.E., M.B.A., M. Phil., Ph.D., Pro Chancellor** of Sathyabama Institute of Science and Technology (Deemed to be University) for having given us the encouragement and opportunity to bring out this course book.

Special thanks to the **Vice-Chancellor** of Sathyabama Institute of Science and Technology (Deemed to be University), **Dr. K.V. Narayanan** for devoting his precious time, earnest efforts and relentless perseverance for improving the quality of this book.

The authors express their acknowledgement to **Dr. T. Sasipraba, Pro-Vice Chancellor** and **Dr. B. Sheela Rani, Director Research** of Sathyabama Institute of Science and Technology (Deemed to be University) for their moral support.

The **Registrar, Dr. S.S. Rau** deserves special thanks for his valuable suggestions and guidance.

The authors, the faculty of Department of Chemistry, would like to exchange thanks and acknowledge their priceless contributions towards content enrichment.

CONTENTS

UNIT	TITLE	PAGE No.
1	FUELS Dr. J. Karthikeyan & Dr. K. Chennakesavulu	1-24
2	PHASE EQUILIBRIA Dr. T. Krithiga & Dr. S. Sunitha	25-48
3	EXPLOSIVES AND ROCKET PROPELLANTS Dr. A. Sheik Mideen	49-72
4	LUBRICANTS Dr. S. Supriya & Dr. V. Kavitha	73-92
5	COMPOSITES AND ABRASIVES Mrs. X. Janet Sabina	93-110

Introduction - Classification of fuels - Characteristics of a fuel –Calorific value of fuel, GCV, NCV, Determination of calorific value of a fuel by Bomb calorimeter. Problem based on calorific value. Coal: Classification of coals based on energy content. Chemistry and analysis of coal: Proximate analysis and ultimate analysis. Manufacture of metallurgical coke: Otto-Hoffmann's method. Cracking: Fluidized bed catalytic cracking. Knocking in compression ignition and spark ignition engines. Gaseous fuels: CNG - LPG - Producer gas. Ethanol as a fuel.

INTRODUCTION

One of the characteristics of complex society is a high level of energy consumption. The per capita energy consumption is taken to be the measure of living standards of people. Just some 150 years ago, fuels were used primarily for cooking, heating and lighting purposes. Apart from complex cooking and heating, today fuels are used in transportation, communication, illumination, manufacturing and a host of other applications.

Coal, oil and natural gas, which are presently the principal sources of energy, are called fossil fuels (non-renewable energy sources). These fossil fuels are thought to have been formed over millions of years ago. Until the industrial revolution, fire wood was the main source of energy. As the wood sources depleted due to extensive, reckless deforestation, coal (black diamond) took the place of wood as a source of energy in industries and transportation. During the period of 1920 – 1930, the consumption of natural gas and petroleum increased rapidly due to expanding use as fuel for internal combustion engines.

With an enormous rise in world population during the past few decades, the energy requirements have also increased at even larger rate. Our increasing appetite for energy is one of the causes for our energy crisis. According to some projections, we may run out of fossil fuels, by 2025. A considerable interest has been evinced in developing an alternate energy source. Much research has been focused on 'nuclear' and 'solar energy'.

Among alternate energy sources, nuclear fission is slowly replacing fossil fuels as a potential energy source of electric power. It generates enormous amount of energy but at the same time produces highly radioactive materials that must be stored carefully in fail-proof containers for centuries. For these and other reasons, the promise of cleaner, safer more economical and practically inexhaustible energy source though yet to be developed, controlled thermo nuclear fusion cannot be ignored.

CHEMICAL FUELS

A combustible chemical substance containing carbon as the main constituent, which on proper burning liberates large amount of heat, which can be used economically for domestic as well as industrial purpose.

When a chemical fuel undergoes combustion in presence of air, carbon and hydrogen are converted into carbon dioxide and water respectively. Since the heat content of combustion products being lower than that of reactant, so that the energy released during the combustion process is the difference in the energy of the reactants(C, H and O etc.,) and that of the products formed. The examples of chemical fuels include wood, coal, crude oil, natural gas etc.

Chemical fuels are primarily used as a source of heat and power. Apart from this, they are also used as reducing agents in metallurgical applications, to produce electrical power which is the back bone of all chemical and mechanical industries.

CLASSIFICATION OF FUELS

Chemical fuels are broadly classified as solids, liquids and gases based on their physical state in which they are used. These are further classified as primary and secondary fuels. A fuel that occurs in nature is called a “primary fuel” while all others, which are derived from primary fuels are called secondary fuels. Complete classifications of chemical fuels with suitable examples are summarized.

Types	Solid	Liquid	Gaseous
Primary fuel (Natural)	Wood, Coal, Peat, Lignite	Crude oil	Natural gas
Secondary fuel (Derived from primary fuel)	Coke, Charcoal, Coal	Fuel oil, Kerosene, Diesel, Petrol, LPG,	Water gas, Oil gas, Bio gas

CALORIFIC VALUE OF A FUEL

An important parameter of fuels is calorific value. It gives useful information about its heating efficiency. The performance of a fuel is expressed in terms of its calorific value.

Calorific value of the fuel is defined as “the total quantity of heat liberated when a unit mass of the fuel is burnt completely” in presence of air or oxygen.

The calorific value is normally expressed in calorie per gram (Cal / g) or kilocalorie per kg (kcal/kg) for solid fuels and kilocalorie per cubic meter (kcal/m³) for gaseous fuels.

GROSS (GCV) CALORIFIC VALUE OF A FUEL

“The total quantity of heat liberated, when one unit quantity of the fuel is burnt completely and the products of combustion have been cooled to room temperature”.

All fuels invariably contain carbon and hydrogen. Carbon and hydrogen present in fuels are converted into carbon dioxide and steam respectively on combustion. On cooling the combustion products, steam gets condensed to water and liberates its latent heat. The measured gross calorific value includes the latent heat of steam. Therefore called as higher or gross calorific value.

$$\text{GCV} = \frac{1}{100} [8,080 \times C + 34,500 (H - \frac{O}{8}) + 2,240 \times S] \text{ kcal/kg}$$

NET (NCV) CALORIFIC VALUE OF A FUEL

“The net heat evolved when one unit quantity of the fuel is burnt completely in air and the products are allowed to escape as such”.

In actual practice, the combustion products are not cooled to room temperature but simply let off into the atmosphere. Since this calorific value does not include the latent heat of steam, so that net calorific value is always lower than gross calorific value.

Net calorific value (NCV) = Gross calorific value (GCV) – Latent heat of steam

$$\text{NCV} = (\text{GCV} - 0.09 H \times 587) \text{ kcal/kg}$$

DETERMINATION OF CALORIFIC VALUE BY BOMB CALORIMETER

It is used to determine the calorific value of solid and liquid fuels.

Construction: A simple sketch of bomb calorimeter is shown in Fig 1. It consists of a strong cylindrical stainless steel bomb in which the combustion of fuel takes place. The bomb has a lid, to make a gas tight seal. The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrode, small ring is attached. In this ring, a nickel or stainless steel crucible can be supported. The bomb is placed in a copper calorimeter, which is surrounded by an air-jacket and water jacket to prevent heat loss. The calorimeter is provided with a stirrer and Beckmann's thermometer which can read temperature difference of 1/100th degree.

Working: A known mass of the given fuel is taken in clean crucible. The crucible is supported over the ring. A magnesium wire, touching the fuel sample, is then stretched across the electrodes, and then bomb is filled with oxygen to 25 atmospheric pressure. The bomb is then lowered into copper calorimeter, containing a known mass of water and initial temperature of the water is noted. The electrodes are then connected to 6V battery, sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is recorded.

Calculations:

$m(g)$ = mass of the fuel

W = mass of water in the calorimeter

w = water equivalent of calorimeter.

t_1 = Initial temperature of water in calorimeter

t_2 = final temperature of water in calorimeter

By heat balance,

Heat produced by the fuel due to combustion = heat absorbed by water and calorimeter

If x is the calorific value of fuel, then heat produced = $(x \times m)$ cal

Heat absorbed by water and calorimeter = $(W + w) \times (t_2 - t_1)$

Or

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

Or

$$x = \frac{(W + w) \times (t_2 - t_1)}{m}$$

The calorific value (x) calculated by the above equation gives the higher calorific value of the fuel, due to the condensation of water vapour. For calculating more accurate calorific value of a fuel, the following corrections should be considered.

Corrections:

To get more accurate results, the following corrections are applied

1. **Fuse wire correction (C_1):** the heat liberated, as measured above, includes the heat given out by ignition of the fuse wire used.
2. **Cotton correction (C_2):** if fuel is ignited with the help of cotton, it will give extra heat and that must also be subtracted.
3. **Acid correction (C_a):** Fuels containing S and N are oxidized to H_2SO_4 and HNO_3 respectively. Formations of these acids are exothermic reactions. So, the measured heat also includes the heat given out during the acid formation.

$$S + 2H + 2O_2 \longrightarrow H_2SO_4 + \text{Heat}$$

$$2N + 2H + 3O_2 \longrightarrow 2HNO_3 + \text{Heat}$$
4. **Cooling correction (C_c):** time taken to cool the water in calorimeter from maximum temperature to room temperature is noted. From the rate of cooling

(dt^0/min) and the actual time taken for cooling (t min), the cooling correction of $dt \times t$ is added to the rise in temperature.

By considering all the corrections, the actual calorific value of a fuel can be calculated by using formula.

$$CV = \frac{(W+w)(t_2-t_1+C_c) - (Ca+C1+C2)}{\text{Mass of fuel}(m)} \text{ cal / g}$$

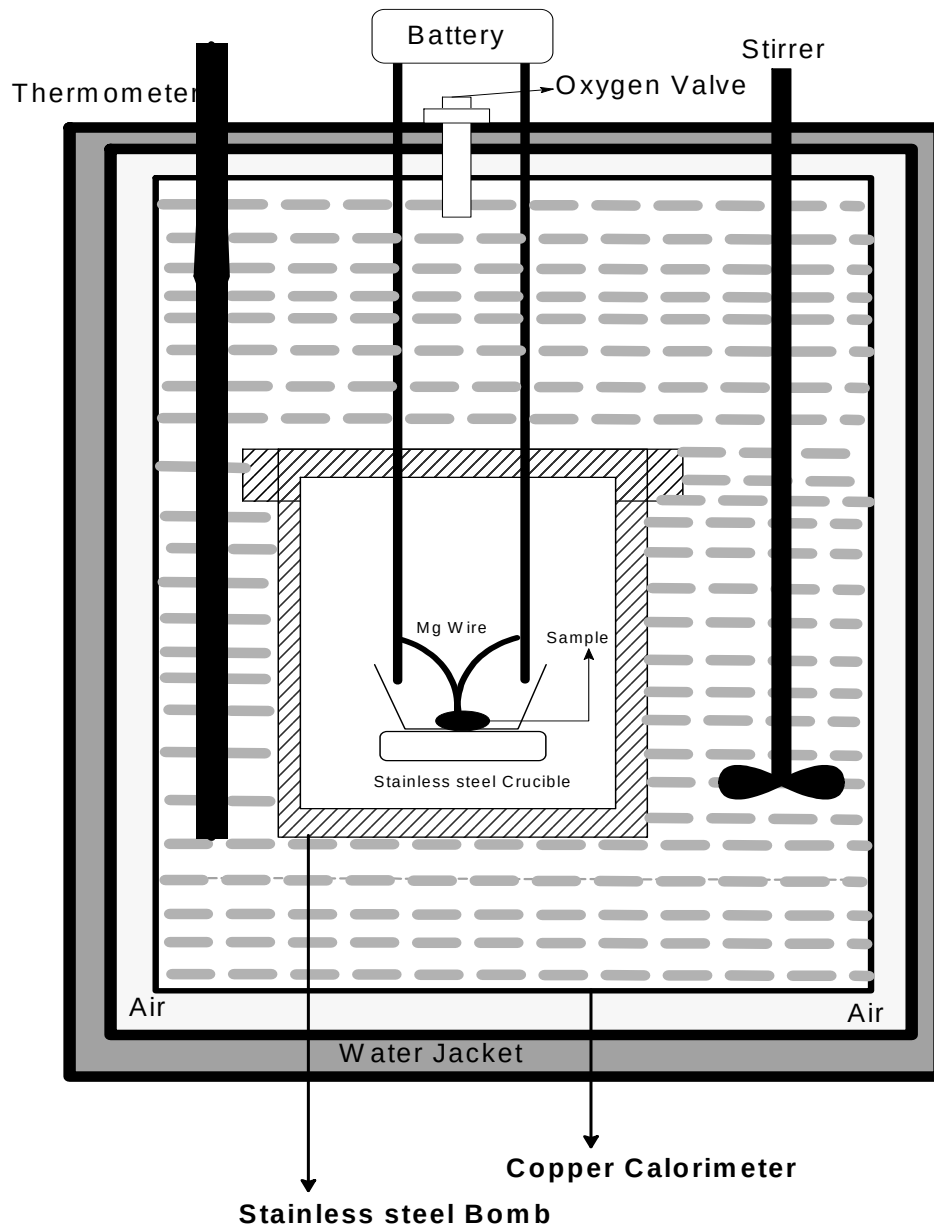


Fig. 1. Bomb Calorimeter

Problems based on determination of calorific value

1. Calculate the gross and net calorific value of coal having the following composition. C = 85%, H = 8%, S = 1%, N = 2%, Ash = 4%, latent heat of steam = 587 cal/g.

Solution:

$$\text{GCV} = \frac{1}{100} [8,080 \times C + 34,500 (H - \frac{O}{8}) + 2,240 \times S] \text{ kcal/kg}$$

$$\text{GCV} = \frac{1}{100} [8,080 \times 85 + 34,500 (8 - \frac{O}{8}) + 2,240 \times 1] \text{ kcal/kg}$$

$$\text{GCV} = \frac{1}{100} [686,800 + 276,000 + 2,240] \text{ kcal/kg}$$

$$\text{GCV} = \frac{1}{100} [965,040] \text{ kcal/kg}$$

$$\text{GCV} = 9,650.4 \text{ kcal/kg}$$

$$\text{NCV} = (\text{GCV} - 0.09 H \times 587) \text{ kcal/kg}$$

$$\text{NCV} = (\text{GCV} - 0.09 \times 8 \times 587) \text{ kcal/kg}$$

$$\text{NCV} = 9,227.8 \text{ kcal/kg}$$

2. 0.72g of a fuel containing 80% C, when burnt in a bomb calorimeter, increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250g of water and its water equivalent is 150g, calculate GCV of the fuel. Give your answer in kJ/kg.

Solution: $x = 0.72\text{g}$, $W = 250\text{g}$, $w = 150\text{g}$, $t_1 = 27.3^\circ \text{C}$ $t_2 = 29.1^\circ \text{C}$

$$\text{GCV} = \frac{(W + w) \times (t_2 - t_1)}{x} \text{ kcal/kg}$$

$$\text{GCV} = \frac{(250 + 150) \times (29.1 - 27.3)}{0.72} \text{ kcal/kg}$$

$$\text{GCV} = 1000 \times 4.2 \text{ kJ/kg} = 4,200 \text{ kJ/kg}$$

3. On burning 0.83g of a solid fuel in a bomb calorimeter, the temperature of 3,500g of water increased from 26.5°C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385 g and 587 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its GCV and NCV.

Solution:

Wt. of Fuel(x) = 0.83g, wt. of water(W) = 3500g, water equivalent of calorimeter(w) = 385g, latent heat of steam = 587 cal/g, $t_2 = 29.2^\circ \text{C}$, $t_1 = 26.5^\circ \text{C}$, $H\% = 0.7\%$.

$$\text{GCV} = \frac{(W + w) \times (t_2 - t_1)}{x} \text{ cal/kg}$$

$$\text{GCV} = \frac{(3500 + 385) \times (29.2 - 26.5)}{0.83} = 12,638 \text{ cal/kg}$$

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

$$\text{NCV} = [12,638 - 0.09 \times 0.7 \times 587] = 12,601 \text{ cal/kg}$$

4. A sample of coal contains C = 93%, H = 6%, and ash = 1%. The following data were obtained when the above coal was tested in bomb calorimeter.

1. Wt.of coal burnt : 0.92g
2. Wt. of water taken:550g
3. Water equivalent of bomb and calorimeter : 2200g
4. Rise in temperature : 2.42 °C
5. Fuse wire correction : 10.0 cal
6. Acid correction : 50.0 cal

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

Solution :

Wt.of coal sample(x) = 0.92g

Wt.of Water(W) = 550g

Water equivalent of calorimeter(w) = 2,200g

Temperature(t₂-t₁) = 2.42 °C

Acid correction = 50 cal

Fuse wire correction = 10 cal

Latent heat of steam = 580 cal/g

Hydrogen percentage = 6%

$$\text{GCV} = \frac{(W + w) \times (t_2 - t_1) - [\text{Acid} + \text{Fuse corrections}]}{x} \text{ cal/kg}$$

$$\text{GCV} = \frac{(550 + 2200) \times (2.42) - [50 + 10]}{0.92} \text{ cal/kg}$$

$$\text{GCV} = 7,168.5 \text{ cal/g}$$

$$\text{NCV} = [\text{GCV} - 0.09\text{H} \times \text{latent heat of steam}]$$

$$\text{NCV} = [7,168.5 - 0.09 \times 6 \times 580] = 6,855.3 \text{ cal/g.}$$

Coal and Classifications of coal by rank

Coal – is a highly carbonaceous matter that has been formed as a results of vegetable matter under certain favorable conditions. It is chiefly composed of C,H,N and O besides Non-combustible inorganic matter.

Coal is classified on the basis of its rank. The rank of coal denotes its degree of maturity. Vegetable matter under the action of pressure, heat and anaerobic conditions, gets converted into different stages of coal namely

Wood → Peat → Lignite → Bituminous coal → Anthracite

Here peat is the most immature coal, hence it is of the lowest rank whereas anthracite is the most matured coal, and hence it is of the highest rank. The process of conversion of lignite to anthracite is called coalification of wood or metamorphism of coal. With the progress of coal forming reaction, moisture content and oxygen content reduces and percentage of carbon increases. Also calorific value increases from peat to bituminous.

Chemistry and analysis of coal: Proximate analysis and ultimate analysis

To assess the quality of coal the two analysis are carried out, these are

Proximate analysis and ultimate analysis

Proximate analysis: It is a approximate analysis in this the determination of percentage of moisture, volatile matter, ash, and fixed carbon are carried out.

1. **Determination of percentage of moisture:** About 1g of powdered coal sample is heated in a crucible at 105 to 110°C for an hour in a hot air oven, the crucible is taken out and kept in a desiccators, cooled and weighed, and the loss in weight is reported on percentage basis.

$$\text{Percentage of moisture} = \frac{\text{LOSS IN WEIGHT}}{\text{WEIGHT OF COAL TAKEN}} \times 100$$

Significance: The moisture decreases the calorific value, increases the cost and combustion becomes difficult, so good sample of coal contains low percentage of moisture.

2. **Determination of percentage of volatile matter**

The above sample is covered with a lid and heated in a muffle furnace at 925±20°C for exactly 7 min. The crucible is cooled and weighed.

Significance: High volatile matter coals burns with long flame, high smoke and low calorific value and also increases the space required for the combustion and affects the design of the furnace. So good sample of coal

should contain low percentage of volatile matter. (Generally volatile matter consists combustible gases like methane, Hydrogen, CO, Hydrocarbons and Non combustible gases like CO₂ and N₂)

$$\% \text{ of volati. matter} = \frac{\text{LOSS IN WEIGHT DUE TO REMOVAL OF VOLATILE MATTER}}{\text{WEIGHT OF COAL SAMPLE TAKEN}} \times 100$$

3. **Determination of Percentage of Ash:** The above sample without lid is heated in a muffle furnace at 700 to 750° C for half an hour. The crucible is cooled, dried and weighed. This procedure is repeated till the constant weight is obtained.

Significance: The increase of ash decreases the calorific value of coal and also creates atmospheric pollution. The clinker (Fused mass of coal) obstructs the air supply and combustion becomes irregular, so the good sample of coal should contain low percentage of ash.

$$\text{Percentage of ash} = \frac{\text{WEIGHT OF ASH LEFT}}{\text{WEIGHT OF COAL TAKEN}} \times 100$$

4. **Determination of percentage of fixed carbon:** There is no direct method to determine the percentage of fixed carbon. It is determined by subtracting the sum of the percentage of moisture, Volatile matter and ash from 100.

Significance: The percentage of fixed carbon increases the calorific value of coal increases. It also helps in design of furnace and shape of fire box. The fixed carbon means, the carbon which is burning in the solid state during combustion. The percentage of fixed carbon increases from lowest rank coal peat to highest rank coal anthracite.

$$\% \text{ of fixed carbon} = 100 - \% \text{ of (moisture + volatile matter + ash)}$$

Ultimate analysis

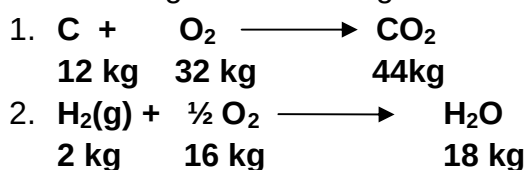
It is an accurate analysis and it helps in

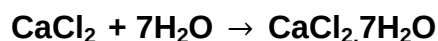
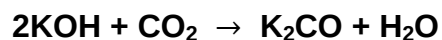
- To determine the calorific value of coal by theoretically using Dulong's formula.
- The amount air required for the complete combustion of coal
- To decide the coal sample can be used to convert coke or not.

The following determination are carried out in this analysis

1. Determination of percentage of carbon and hydrogen

About 1 to 2g of powdered coal is heated in a combustion apparatus in the presence of oxygen. The gases (CO₂ and H₂O) released are absorbed into a tubes containing of known weight of KOH, and CaCl₂.





$$\text{Percentage of C} = \frac{\text{INCREASE IN WEIGHT OF KOH TUBE} \times 12 \times 100}{\text{WEIGHT OF COAL SAMPLE TAKEN} \times 44}$$

$$\text{Percentage of H} = \frac{\text{INCREASE IN WEIGHT OF CaCl}_2 \text{ tube} \times 2 \times 100}{\text{WEIGHT OF COAL SAMPLE TAKEN} \times 18}$$

Significance: the percentage of carbon increases the calorific value of coal also increases. Even though hydrogen has more calorific value than carbon, it increases the tendency of coal to retain moisture and also it is associated with volatile matter and decreases the calorific value, hence a good sample coal should contain high percentage of carbon and low percentage of hydrogen.

Determination of percentage of Nitrogen

About 1g of accurately weighed powdered coal is heated strongly along with con. H_2SO_4 , K_2SO_4 (to rise the Boiling point of solution), CuSO_4 (act as catalyst) in a long necked Kjeldahl's flask. When solution becomes clear it is treated with NaOH or KOH solution. The ammonia liberated is absorbed in a known volume of std. acid solution. The acid left unused is found out by titrating against std. alkali solution. From the volume of acid used, the percentage of nitrogen is determined as follows.

Significance: N_2 has no calorific value and the presence is undesirable, it also creates atmospheric pollution due to the formation of oxide of nitrogen.

$$\text{Percentage of N}_2 = \frac{\text{VOLUME OF ACID USED} \times \text{NORMALITY} \times 1.4}{\text{WEIGHT OF COAL TAKEN}}$$

Determination of percentage of Sulphur

The washings from the bomb are taken after the determination of calorific value of coal. The sulphur is present in the form of sulphate and by treating it with barium chloride. The formed barium sulphate, is filtered, washed, dried and weighed.

Significance: Though sulphur has calorific value, it leads to the formation of SO_2 and SO_3 . These gases are corrosive and cause atmospheric pollution. The sulphur containing coals cannot be used for the formation of coke which is used in iron industry. So good sample of coal should contain low percentage of sulphur.

$$\text{Percentage of S} = \frac{\text{WEIGHT OF BaSO}_4 \text{ OBTAINED} \times 32 \times 100}{\text{WEIGHT OF COAL SAMPLE TAKEN IN BOMB} \times 233}$$

1. **Determination of percentage of Ash:** The above sample without lid is heated in a muffle furnace at 700 to 750° C for half an hour. The crucible is

cooled, dried and weighed. This procedure is repeated till the constant weight is obtained.

Significance: the increase of ash decreases the calorific value of coal and also creates atmospheric pollution. The clinkers (Fused mass of coal) obstructs the air supply and combustion becomes irregular, so the good sample of coal should contain low percentage of ash.

Determination of percentage of oxygen: It is determined by subtracting the sum of the percentages of carbon, hydrogen, Nitrogen, sulphur and ash from 100.

Significance: The oxygen in the coal combine with hydrogen and it is in the form of moisture so it reduces the calorific value of coal and also it affects the coking power. So a good sample of coal should have low percentage of oxygen.

Percentage of O = 100 - Percentage of (C + H + S + N + ash)

Manufacturing of metallurgical coke By Otto Hoffman's by-product oven

This method is developed to (i) increase the thermal efficiency of the carbonization process and (ii) recover valuable by-product (like coal gas, ammonia, benzol oil, tar, etc). In this coke oven, is heated externally by producer gas or by a portion of coal gas produced during process, The heating is done on the basis of "regenerative system of heat economy", i.e.,utilizing the waste flue gases for heating the checker work of bricks.

It consists of number of narrow silica chambers placed side by side with vertical flue in-between them to burn a fuel. Each chamber is provided with a charging hole at the top, a gas off-take and a refractory-lined cast iron door at each ends for discharging coke

The crushed coal is introduced through the charging hole at the top of chambers, which are then closed tightly at both ends to prevent any access of air. The coke oven is heated to 1200°C by burning producer gas. The flue gases produced during combustion, before escaping to chimney, pass on their sensible heat to one of the two sets of checker brick-work, till the temperature raised to 1000°C. The inlet gases are passed through the heated checker-brick work, which thus serves to preheat the inlet gases. The flue gases are then allowed to pass through the second set of checker brick to heat it. This checker work then serves to preheat the inlet gases, when the flow is again reversed. Thus, this cycle goes on. The heating is actually continued, till the evolution of volatile matter ceases completely. Carbonization of a charge of coal takes about between 11 to 18 hours.

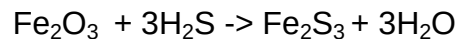
When carbonization is completed, a massive ram pushes the red hot coke into a truck. It is then cooled by dry or wet quenching. The heated gases are then circulated to boilers, where they generate steam. The coke produced by dry

quenching is cheaper, drier and contains lesser dust than wet quenching coke. The yield of the coke is about 65% to 75%. The sketch of Otto Hoffmann's Oven shown in **Fig. 2**.

RECOVERY OF BY-PRODUCTS:

The gas coming out from the oven is known as "coke oven gas" and is mainly composed of tar, ammonia, naphthalene, benzene, H_2S and the gas coal gas.

- i) **Recovery of tar:** The gas is first passed through a tower in which liquor ammonia is sprayed. Here tar is collected in a tank. The ammonia is recovered and used again.
- ii) **Recovery of ammonia:** The gases from the chamber are then passed through a tower in which water is sprayed. Here ammonia goes into solution as NH_4OH .
- iii) **Recovery of naphthalene:** The gases are then passed through another tower in which water at very low temperature is sprayed. Here naphthalene gets condensed.
- iv) **Recovery of benzene:** The gases are then sprayed with petroleum, when benzene and its homologues are removed.
- v) **Recovery of H_2S :** The gases are then passed through a purifier, packed with moist Fe_2O_3 . Here H_2S is retained.



After some time, when all Fe_2O_3 is changed into Fe_2S_3 , the purifier is exposed to atmosphere, when Fe_2O_3 is regenerated.

The gas remained after the recovery these products is coal gas which consists of calorific value 5000 K cal/m^3 and is used as a fuel for the carbonization process.

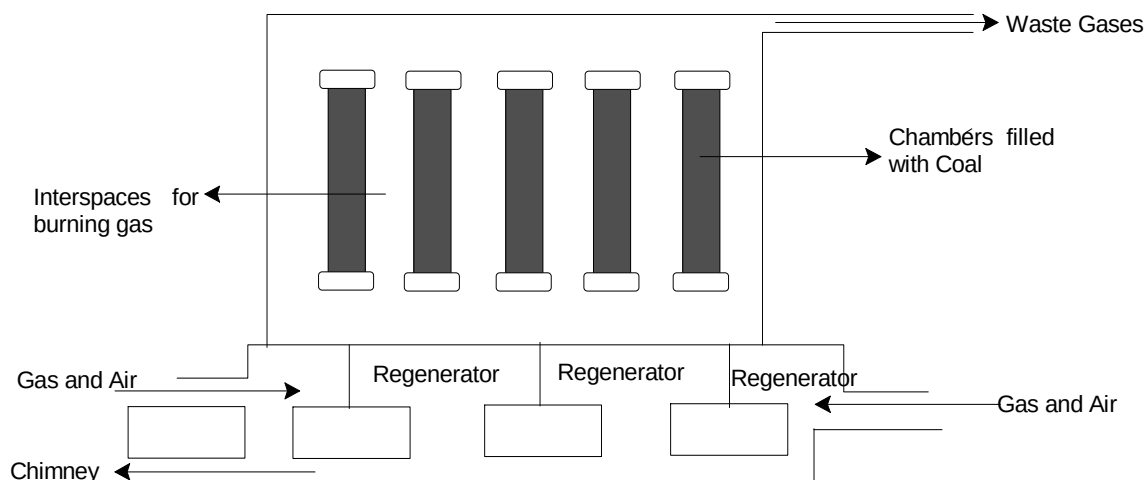


Fig. 2. Otto Hoffmann Oven

Liquid Fuels

Petroleum

Petroleum or crude oil is a brown to black colored viscous liquid found deep in earth's crust. It is composed of various hydrocarbons like straight chain paraffins, cycloparaffins or naphthalenes, olefins, aromatics or more complicated chemicals like asphaltenes while the other organic compounds containing nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The average molecular composition of crude petroleum is

Element	%
Carbon	83 – 85 %
Hydrogen	10 – 14 %
Nitrogen	0.1 – 2 %
Oxygen	0.05 – 1.5%
Sulphur	0.05 – 6.0 %
Metals	< 0.1 %

Classification of petroleum

Petroleum is classified on the basis of the types of hydrocarbon involved or with the part of the world in which it is found.

1. **Paraffinic base type or Pennsylvanian oil:** It is mainly composed of the saturated hydrocarbon from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amount of naphthalenes and aromatics.
2. **Asphaltic base type or Californian oil:** it is mainly composed of cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.
3. **Mixed base type or Mexican oil:** It mainly contains both paraffinic and asphaltic hydrocarbons.

Refining of crude oil

The crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The process is called 'refining of crude oil'.

The process of refining involves the following steps

Step – 1: Separation of water (Cottrell's process)

The crude oil from the oil well is a stable emulsion of oil and salt water. The water from the crude oil is separated by allowing oil to flow between highly charged electrodes where the colloidal water droplets break up to form large drops; this is then separated from the oil.

Step – 2: Removal of harmful sulphur compounds

The sulphur is removed by adding copper oxide, the precipitated copper sulphide is removed by filtration.

Step – 3: Fractional distillation

The crude oil after the removal of various impurities is heated in an iron retort at 400°C, whereby all the volatile constituents of oil are converted into vapor. The hot vapors are sent to a fractionating column which is a tall cylindrical tower consisting of horizontal stainless steel trays provided with long chimneys covered with loose caps as shown in fig 1.2. As the vapors go up, fractional condensation takes place at different heights of the column. The higher boiling (high mol.wt.) fraction condenses first and then the lower boiling (low mol.wt.) fractions settle step by step. The main important fractions obtained are given in the table.

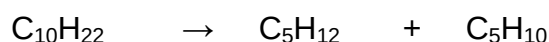
Name of fraction	Boiling range	Composition	Uses
Uncondensed gas	Below 30°C	C ₁ – C ₄	Domestic or industrial fuel (LPG)
Petroleum ether	30 – 70°C	C ₅ – C ₇	As a Solvent
Gasoline or petrol	40 – 120°C	C ₅ – C ₉	As motor fuel, solvent and in dry cleaning
Naptha or solvent spirit	120 – 180°C	C ₉ – C ₁₀	As a solvent and in dry cleaning
Kerosene oil	180 – 250°C	C ₁₀ – C ₁₆	As an illuminant, jet engine fuel
Diesel oil	250 – 320°C	C ₁₀ – C ₁₈	Diesel engine fuel
Heavy oil	320 – 400°C	C ₁₇ – C ₃₀	For getting gasoline by cracking process.

Cracking

Primary distillation of crude oil by fractional distillation yields only 16-20% gasoline. The petrol produced by the distillation process is known as straight run petrol. The

quality of straight run petrol is not very good. The demand for gasoline on the other hand, is increasing steeply. Accordingly the straight run gasoline is found to be inadequate to meet the market demand. So as to increase the yield and quality of petrol, cracking of heavy oil is carried out to meet the present day gasoline demand.

The process of decomposition of bigger hydrocarbon molecules having high boiling points into highly volatile lower hydrocarbon molecules is known as cracking.



(Decane) (n-pentane) (pentene)

B.p =174 °C

B.p= 36 °C

Cracking process aims at

- To convert low demand, high boiling fractions into low boiling fractions suitable for automobiles.
- To produce raw materials for petrochemical industries.

Types of cracking

There are two methods of cracking in use

1. Thermal cracking and, 2. Catalytic cracking

1. Thermal cracking

When cracking is carried out by the application of high temperature and pressure, known as thermal cracking. This process may be carried out either in “liquid phase or vapour phase”.

- a) **Liquid phase cracking:** In this process, the heavy oil is cracked at a temperature of 475 - 530°C and under pressure of 100 kg/cm². The cracked products are then separated by fractionating column. The yield of petrol is 50 - 60 % and the octane rating of the petrol produced is 65 – 70.
- b) **Vapor phase cracking:** In this process, the heavy oil is converted into vapor at about 600 - 650°C and under a low pressure of 10 – 20 kg/cm² for cracking. The yield of petrol is 70 % and the octane rating of the petrol produced is 70.

2. Catalytic cracking

When cracking of heavy oil is carried out in the presence of suitable catalyst like aluminium silicate or alumina, is known as catalytic cracking.

Fluidized bed catalytic cracking or Moving bed catalytic cracking**Optimum conditions:**

Fuel stocks	Gas oil, Heavy oil fractions
Catalyst	$\text{Al}_2\text{O}_3 + \text{SiO}_2$ (Fluidised)
Temperature	550 ⁰ C
Pressure	Little above normal pressure
Production yield	10 ⁶ gallon per day

Process

The solid catalyst is very finely powdered, so that it behaves like a fluid, which can be circulated in gas stream. The hot vapors of heavy oil are mixed with finely powdered catalyst and sent to a reactor at 500⁰C where cracking of the heavy oil takes place. Near the top of the reactor, there is a centrifugal separator called as cyclone, which allows only the cracked oil vapors to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. Here the heavy oil is condensed at the bottom while the gasoline vapor and other gaseous fractions are recovered from the top (see fig 3). The vapors are then admitted into a cooler where gasoline and other dissolved gases are condensed. The two can be separated by a stabilizer. It separates gasoline from other dissolved gases. The other dissolved gases are used to produce superior petrol by polymerization. During the cracking process there is a formation of carbon which is coated over the catalyst particles. Hence catalyst becomes heavier and settles at the bottom of the reactor. The catalyst particle coated with the carbon is sent to a catalyst regenerator at 600⁰C, where the carbon is burnt off and regenerated catalyst is mixed with a fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator, which permits only CO₂ gas to pass out, but holds back catalyst particles.

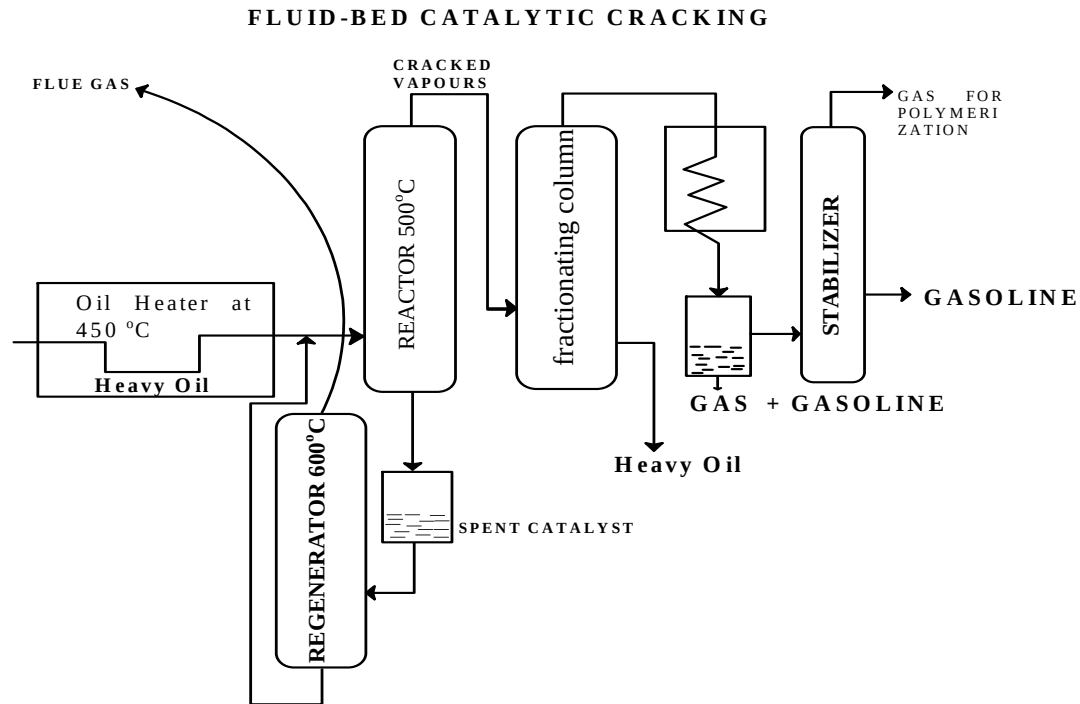


Fig. 3. Fluidised Bed Catalytic Cracking

Advantages of catalytic cracking over thermal cracking

- The yield of gasoline is high because of high percentage of isoparaffins and aromatics.
- A much lower pressure is needed in catalytic cracking.
- Since the cracked petrol contains less amount of alkenes, so that the percentage of gum forming material is low.
- It possess high octane number (70 – 80)
- The harmful sulphur content is low because it escapes out as H_2S gas during cracking.

Knocking in Internal Combustion engines

“Premature instantaneous ignition of fuel – air mixture in an I.C.engine, leading to production of an explosive violence” is known as knocking.

In a four stroke spark ignition engine, petrol vapor is mixed with air in the carburetor then it is sucked into the cylinder during the suction stroke. The mixture is compressed by the piston in the compression stroke, and then the compressed

mixture is ignited by an electric spark. The product of combustion increases pressure and pushes the piston out, providing an output power. 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 of the piston is known as compression ratio. The efficiency of an internal combustion engine increases with the increase in compression ratio, which is dependent on the nature of the constituent present in the gasoline used.

Knocking in spark ignition engine (Petrol engine)

Normally the fuel – air mixture should burn smoothly and rapidly by sparking. In some cases, as a result of compression, the fuel-air mixture may get heated to a temperature greater than its ignition temperature and spontaneous combustion occurs even before sparking. This is called pre-ignition. Further, the spark is also emitted which makes the combustion of the rest of the mixture faster and explosive. So, we have a sudden, badly uncontrolled burning and explosion, which results a characteristic metallic or rattling sound from the engine. This is called knocking or pinking. Knocking lowers the efficiency of engine, which results in loss of energy.

Chemical structure and knocking:

The tendency of fuel constituents to knock is in the following order:

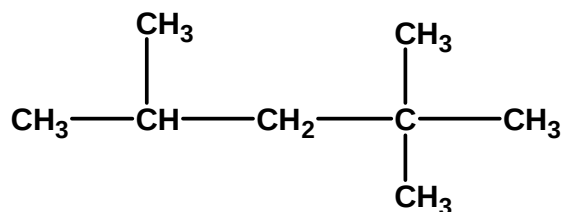
Straight – chain paraffins (n-alkanes) > branched – chain paraffins (iso-paraffins) > olefins > cyclo paraffins(naphthalene) > aromatics.

The chemical structure and knocking study reveals that, the knocking tendency generally decreases with increase of compactness of the molecules, double and triple bonds and ring structure, So that the presence of maximum quantity of aromatics with highest antiknock value are desirable for petrol.

Measurement of knocking in spark ignition engines

Octane number:

The knocking characteristic of the IC engines is normally expressed in terms of octane number. It has been found that, n-heptane knocks very badly and hence its anti-knock value has been given zero. On the other hand, isooctane gives very little knocking, so its antiknock value has been given as '100'. Thus the octane number of the gasoline is define as **“percentage of iso-octane in a mixture of iso-octane and n-heptane, which matches the fuel under test in knocking characteristics”**



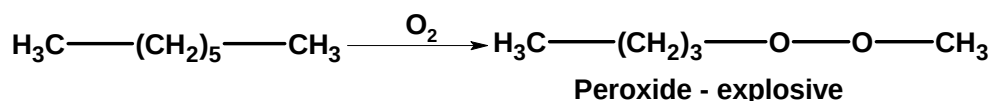
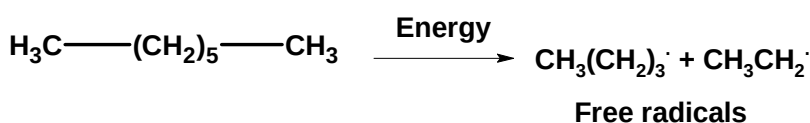
Iso-octane (Octane number = 100)



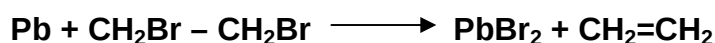
n-Heptane (Octane number = 0)

Mechanism of knocking & Improvement of antiknock value:

Knocking is a free radical chain reaction brought about by a straight chain compound like n-heptane to form the free radical of the type $\text{CH}_3(\text{CH}_2)_3^*$, which is the highly reactive species react with other fractions of the petrol leading to knocking. During knocking peroxy compounds are formed that contribute to the free radical reaction



The knocking in I.C. engine prevented by adding tetra ethyl lead, $(\text{C}_2\text{H}_5)_4\text{Pb}$ (TEL), where TEL is converted into finely divided lead oxide, which readily reacts with free radicals that is formed during the combustion thereby slowing down the chain oxidation reaction and dibromide is added to remove the lead in the form of volatile lead bromide.



Oxygenates

Oxygenates are oxygen containing compounds that are added to fuels, to make them burn more efficiently.

Example: Methyl tertiary butyl ether (MTBE), Ethyl tertiary butyl ether (ETBE), ethyl benzene, isooctane, isopentane etc.

Out of these, MTBE or ETBE 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.

Knocking in compression ignition engines (Diesel engine)

“Delayed ignition or ignition lag, leading to production of an explosive violence”

The diesel engine is a compression ignition engine which uses long straight chain hydrocarbon fuels having boiling range 180 – 360⁰C. In the case of diesel engine, air is passed into the cylinder and compressed to about 500 psi (upstroke). As a result of compression, the temperature of air raises to about 500⁰C. The diesel oil is injected towards the end of the compression stroke in the form of fine droplets into the compressed air in the cylinder heated to 500⁰C by compression. The injected oil droplets absorb the heat from hot air, get vaporized, and attain self ignition temperature and burn spontaneously during downward stroke. However, the combustion of fuel in diesel engines is not instantaneous but there exists an interval of time between fuel injection and start of ignition. This interval of time is called “ignition delay” or “ignition lag”. This is an important parameter of diesel fuels and diesel knock. If the fuel has a short ignition delay, the fuel injected into the burning mixture continues to burn at the rate at which it is injected. On the other hand, if the fuel has a long ignition delay, then the fuel accumulation occurs in the engine even before ignition. So, more and more fuel is injected automatically and sudden ignition may occur that burn the whole of the oil with sudden increase in pressure. This is called “diesel knock”. Longer the ignition delay, larger is the diesel knock.

Chemical structure and Knocking

The tendency of fuel constituents to knock is increases in the following order

n-alkanes < naphthalenes < alkenes < branched alkenes < aromatics.

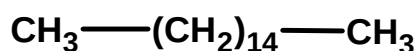
The chemical structure and knocking study reveals that, the presences of maximum quantity of n-alkanes (poor gasoline) with highest antiknock value are desirable for diesel.

Measurement of knocking in compression ignition engines

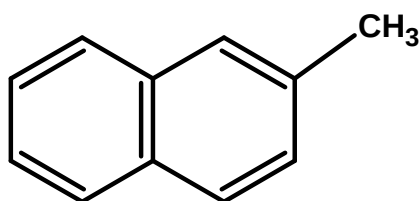
Cetane Number:

The antiknocking properties of diesel fuels are expressed in term of cetane rating or cetane number

“Cetane number is defined as the percentage of cetane in cetane - α - methyl naphthalene mixture, which has the same ignition delay as the diesel oil when burnt in a standard test engine under standard conditions”



n-cetane (Cetane Number = 100)



α - methyl naphthalene (Cetane Number = 0)

Improvement of cetane number:

Cetane number of diesel oil can be improved by adding certain additives called “pre-ignition dopes”. Examples: Isoamyl nitrite, Ethyl nitrate, Acetone peroxide.

Gaseous fuels

Natural gas

Natural gas is obtained from oil wells. Natural gas when available with petroleum oil it is called wet gas. On the other hand, when the gas is associated with crude oil itself then it is called dry gas. The natural gas is purified to remove objectionable materials like water, H_2S , Na_2CO_3 etc, before use. The approximate composition of natural gas is $\text{CH}_4 = 70 - 90 \%$, $\text{C}_2\text{H}_6 = 5 - 10 \%$, $\text{H}_2 = 3\%$, rest CO & CO_2 . The calorific value of natural gas = $13,000 \text{ K. Cal/m}^3$.

Uses:

1. It is used as a domestic fuel and can be conveyed over very large distances in pipelines.
2. It is used as a raw material for manufacturing carbon black and hydrogen.
3. Synthetic proteins are obtained by microbiological fermentation of methane.

Compressed natural gas (CNG)

CNG is natural gas compressed to a high pressure of about 1,000 atm. It is now being used as a substitute for petrol and diesel, since it is comparatively much less pollution causing fuel. During its combustion, no sulphur and nitrogen gas evolved. Moreover, no carbon particles are ejected. Hence, it is better fuel than petrol or diesel for automobiles.

Why CNG is preferred over LPG

- CNG is a much safe fuel, since it ignites at a higher temperature than gasoline.
- The operating cost of CNG fuel is much lower compared to gasoline.
- Combustion of CNG leads to lesser CO emission than gasoline.
- The conversion of gasoline operated automobiles into CNG operated vehicle is easy.
- CNG mixes better with air than liquid fuels

Producer gas

It is essentially a mixture of combustible gases, carbon monoxide and Hydrogen, associated with large percent of non-combustible gases, N_2 , CO_2 etc.

Composition: CO = 22-30%, H_2 = 8-12%, N_2 = 52-55% and CO_2 = 3% its calorific value is about 1,300kcal/m³.

Uses: It is cheap, clean and easily preparable gas and is used

- For heating open-hearth furnaces, Muffle furnaces, retorts
- As a reducing agent in metallurgical operations.

Ethanol as a fuel

When ethyl alcohol is used as a fuel for internal combustion engine, it is called power alcohol. Ethyl alcohol is not used as a prime fuel, but it is only used as an additive to motor fuel. Blends containing upto 25% of alcohols with petrol are used.

Advantage:

- Alcohol has an octane value of about 90. While petrol has octane value of 60 – 70. Consequently, addition of alcohol to petrol increases its octane number. Hence alcohol blended petrol possess better anti-knock properties.
- Alcohol is capable of absorbing any traces of moisture present, so it increases the efficiency of fuel.

Relative advantages of solid, liquid and gaseous fuels

Solid fuels

- Cheap and easily available
- Handling and transportation easy
- Combustion is a slow process and not easy to control it
- Forms large of amount of ash, whose disposal is a big problem
- Calorific value is low.

Liquid fuels

- Higher calorific value than solid fuels
- Combustion takes place immediately and controllable when needed.
- More costly than solid fuels
- After combustion, do not form any ash or residue
- Care must be taken to store them.

Gaseous fuels

- Higher calorific value than solid fuels
- Smokeless, easy to ignite and do not produce ash or residue after combustion.
- Highly inflammable and hence care must be taken during transportation.
- Require large tank for storing.
- Costly compared to solid and liquid fuels.

Test your understanding

1. Define Calorific value? How to determine the calorific value of the fuel by using Bomb Calorimeter?
2. What is meant by cracking of petroleum? Explain fluidized bed catalytic method of obtaining gasoline.
3. What is meant by knocking in petrol engines? How is it expressed? How is it related to chemical constitution? How octane number can be improved?
4. What is meant by knocking in diesel engines? How is it expressed? How is it related to chemical constitution? How cetane number can be improved?
5. How to assess the quality of coal by proximate and ultimate analysis.
6. Explain in detail about the manufacture of metallurgical coke by Otto-Hoffman's method.
7. Write the short notes on Gaseous fuels.

Exercise Problems

1. Calculate the higher and lower calorific values of a coal sample containing 84% C, 1.5% S, 0.6% N, 5.5% H and 8.4 % O. [Ans: HCV=8356 kcal/kg, LCV=8,066kcal/kg]
2. Calculate the gross and net calorific value of a sample of coal having following composition: C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and Ash = 4.4%.

3. Liquid fuel weighing 0.98g and containing 90.1% C, 8%H have 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 latent heat of steam is 587 cal/g, calculate gross and net calorific value of fuel. [Ans: GCV=3490 cal/g and LCV=3097 cal/g]
4. A sample of coal contains C = 92%, H = 5%, and ash = 3%. The following data were obtained when the above coal was tested in bomb calorimeter.
Wt.of coal burnt : 0.95 g
Wt. of water taken: 700 g
Water equivalent of bomb and calorimeter: 2000g
Rise in temperature : 2.48 °C
Cooling correction :0.02 °C
Fuse wire correction : 10.0 cal
Acid correction : 60.0 cal
Calculate gross and net calorific value of the coal assuming the latent heat of condensation of steam as 580cal/g.[Ans: GCV = 7,031.6 cal/g, LCV = 6,770.6 cal/g]
5. The temperature of 950g of water increased from 25.5 to 28.5 on burning 0.75g of solid fuel in a bomb calorimeter. Water equivalent of calorimeter and latent heat of steam are 400g and 587 cal/g respectively. If the fuel contains 0.65% of hydrogen calculate its NCV[Ans: NCV = 5366 cal/g]

Phase diagram - Information from phase diagram - Terminology used in phase diagram. Problems based on phase rule: Gibb's phase rule - Derivation. One component system: Water system. Two component alloy systems: Classification - Reduced phase rule - Thermal analysis. Numerical problems based on eutectic composition: Simple eutectic system: Lead-silver system. Congruent System: Zinc-magnesium system. Incongruent system: Sodium-potassium system. Phase diagram of simple three component system.

Introduction

The phase rule deals with any set of homogeneous bodies having one or more ingredients in common. When such bodies are placed in contact these ingredients may pass spontaneously from one body into another. In the end, a condition of equilibrium is reached, in which the rate of transfer of any ingredient, from one body into other, is exactly balanced by a transfer in the opposite direction. The rule indicates the general nature of the conditions that must be fulfilled for such equilibrium to be possible. Phase rule explains heterogeneous equilibria and it predicts qualitatively the effect of pressure, temperature and concentration on heterogeneous equilibria. That is, it gives information about the behavior of heterogeneous equilibrium systems when they are subjected to changes in variables such as temperature, pressure and concentration.

The Phase Rule

The phase rule is an important tool used for the qualitative treatment of systems in equilibrium. It enables us to predict the conditions that must be specified for a system to exhibit equilibrium. J.W. Gibbs stated the phase rule in 1876. According to the Gibbs phase rule for systems in complete internal equilibrium the mathematical statement is given as

$$F = C - P + 2$$

where,

P = number of phases present in equilibrium

C = number of components in the system

F = number of degrees of freedom for the equilibrium

2 indicate the variables temperature and pressure

Advantages

- It is applicable to both chemical and physical equilibria.
- It is applicable to macroscopic systems and hence no information is required regarding molecular and micro structure.
- It classifies equilibrium states in terms of phases, components and degree of freedom.
- The behaviour of system can be predicted under different conditions.

Limitations

- It is applicable only for the systems which are in equilibrium.
- Only three degrees of freedom viz., temperature, pressure and composition are allowed to influence the equilibrium systems.

Terms involved in Phase Rule

Phase: A phase is defined as any homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of system.

Examples

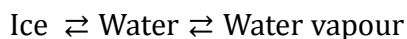
1. A mixture of gases consists of single phase since all gases are completely miscible.
2. Immiscible liquids consist of different phases. Thus kerosene and water do not mix with each other therefore forms two phases.
3. Completely miscible liquids such as benzene and chloroform and water and alcohol exist in single phase.
4. The decomposition of CaCO_3 is an example for three phase system

**Components**

The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by which composition of each phase can be expressed.

Examples

1. Water system exist in three phases



The composition of all the phases is expressed in terms of H₂O and thus it is a one component system.

2. Sulphur exists in four phases, i.e rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour sulphur. Since the composition of each phase is expressed in terms of sulphur. Therefore it is a one component system.
3. In case of sugar solution the composition of solution phase is expressed using sugar and water. Therefore it is a two component system.
4. Consider the decomposition of CaCO₃ into CaO & CO₂.



The composition of any phase can be expressed in terms of at least any two of the independently variable constituents, CaCO₃, CaO & CO₂. Thus it is a two component system.

5. Consider the system



It is an example for three phase and two component system.

Degree of Freedom (or) Variance of a System

The degree of freedom of a system is defined as the number of independent variables such as temperature, pressure and concentration (composition) which must be specified in order to define the system completely.

Examples

1. If $F = 1$, the system is called Univariant.

Example: Water $\rightleftharpoons$ Water vapour

$$P = 2, C = 1$$

$$\text{Then, } F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

2. If $F = 2$, the system is called Bivariant.

Example: Eg. Water vapour

$$P = 1, C = 1$$

$$\text{Then, } F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

3. If $F = 0$, the system is called Invariant.

Example: Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Water vapour

$$P = 3, C = 1$$

$$\text{Then, } F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

Derivation of the Phase Rule

Consider a heterogeneous system containing C components ($C_1, C_2, C_3, \dots$) in which P phases ($\alpha, \beta, \gamma, \dots, P$) are present. We have to determine the degrees of freedom of this system i.e., the number of variables which must be arbitrarily fixed in order to define the system completely. Since the state of the system will depend upon the pressure and temperature, these two variables are always present. The concentration variable, however, depend upon the number of phases. In order to define the composition of each phase it is necessary to specify the concentration of $(C - 1)$ constituents of each phase, the concentration of the remaining component being determined by difference. For P phases, therefore, the total number of concentration variables will be $P(C - 1)$ and these along with the two variables mentioned above viz., temperature and pressure, make the total number of the variables of the system equal to $[P(C - 1) + 2]$.

According to thermodynamics when a system is in equilibrium, the partial molal free energy of each constituent of a phase is equal to the partial molal free energy of the

same constituent in every other phase. The partial molal free energy of the constituents of a phase is a function of the temperature, pressure and $(C - 1)$ concentration variables. Therefore if there is one component in two phases, it is possible to write one equation and if there is one component in three phases, it is possible to write two equations. In general, when P phases are present, $(P - 1)$ equations are available for each component and for C components, the total number of equations or variables are $C(P - 1)$.

Since the number of equations is equal to the number of variables, the number of unknown variables or degrees of freedom (F) will be given as

$$F = \text{Number of variables} - \text{Number of equations}$$

$$F = [P(C - 1) + 2] - [C(P - 1)]$$

$$F = PC - P + 2 - PC + C$$

$$F = C - P + 2$$

Phase Diagram

The graphical representation expressing the conditions of pressure and temperature in which the various phases exist and transfer from one phase to another phase is called the phase diagram of a system.

Application

1. One Component System

Example: Water System

It is a one component system which consists of three phases, namely solid, liquid and vapour. The phase diagram for the water system is shown in Figure 1.

Phase Diagram of Water System:

The phase diagram consists of three curves namely OA, OB and OC. Each curve separates two phases and hence the system is “univariant” along the curve.

$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

The Curve OA represents the equilibrium between ice and vapour phases. It is called the vapour pressure curve or sublimation curve of ice. Its lower end A extends to absolute zero.

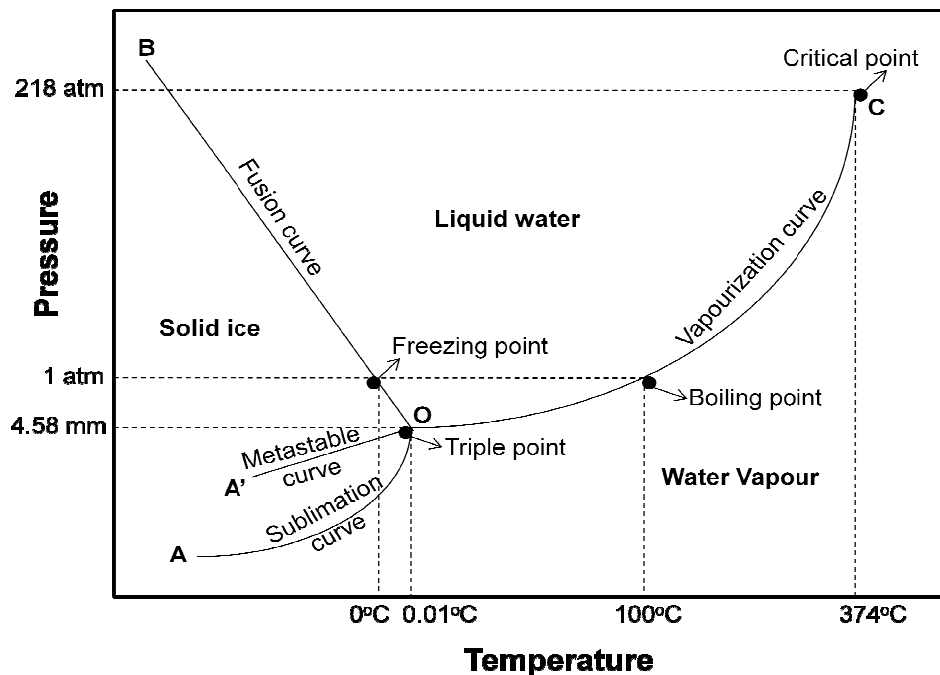
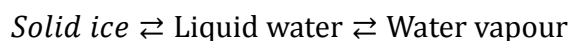


Fig. 1. Phase Diagram of Water System

The Curve OB represents the equilibrium between ice and water. It is called the fusion curve of ice and indicates the temperatures and pressures at which the ice and water can coexist in equilibrium. It is inclined towards pressure axis which indicates that the melting point of ice is lowered by increase of pressure.

The Curve OC represents the equilibrium between water and vapour at different temperatures. It is called the vapour pressure curve of water as it gives the vapour pressure of water at different temperatures. The curve OC extends till the critical temperature (374°C) and critical pressure (218 atm) of water since above this temperature liquid water cannot exist.

Along OA, OB and OC the two phases namely ice and vapour, ice and water and water and vapour meet at the point “O” where all the three phases ice, water and vapour coexist. This is known as triple point.



The temperature and pressure of triple point of water are 0.01°C and 4.58mm of mercury.

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Therefore “O” is an invariant point.

The water system consists of three areas AOB, BOC and COA. Each area represents a single phase and hence the system is ‘bivariant’.

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

S.No	Area	Phase	Component
1.	AOB	Ice	H_2O
2.	BOC	Water	H_2O
3.	COA	vapour	H_2O

The water can be cooled below its freezing temperature without the separation of ice then the water is said to be supercooled. The vapour pressure curve of water OC continues below the point “O” as shown in the figure OA’. The water and vapour phase is in equilibrium along the curve OA’ is known as metastable equilibrium.

2. Two Component Systems

When the two independent components present in a heterogeneous system, the system is called a two component system.

Classification

The two component system is classified into the following types:

a. Simple Eutectic System

The two components are miscible in the liquid state and are not miscible in the solid state and form a eutectic mixture.

Examples

- i. Lead – Silver system
- ii. Bismuth – Cadmium system

Uses of eutectic system

- i. De-silverisation of lead.
- ii. Preparation of solders (Eg: Pb – Sn solder).

b. Systems having,**(1) Congruent Melting Point**

The two component system possesses a congruent melting point when it melts at a constant temperature to give liquid melt of the same composition as that of solid.

Examples

- i. Zinc – Magnesium system
- ii. Ferric chloride – water system
- iii. Mercury – Thallium system

(2) Incongruent Melting Point

The system possesses an incongruent melting point if on heating it decomposes below its melting point and forms a new compound and a solution having different composition from the corresponding solid state.

Examples

- i. Sodium – Potassium system
- ii. Gold – Antimony system
- iii. Sodium – Bismuth system

c. Solid Solution Formation

When two different metals dissolve in liquid and or in solid state, the resulting phase is called solid solution. Solid solution is formed when the solvent and solute atoms have similar sizes.

Examples

- i. Copper – Nickel system
- ii. Copper – Gold system

Reduced Phase Rule

Definition

For a two component system, the minimum number of phases is one and maximum number of degrees of freedom is 3. Therefore three variables is necessary to describe a system. Since three variables are difficult to plot, the pressure variable is neglected. This reduces the degree of freedom of the system by one and the phase rule equation is written as

$$F = C - P + 1.$$

This equation is known as “**reduced phase rule**”.

Thermal Analysis

Thermal analysis is a method involving the study of cooling curves of various compositions of a system during solidification. The shapes of freezing point curves for any system involving metal can be determined by thermal analysis. The plot of change in temperature with time indicates the composition of the solid.

Cooling Curve of Pure Metal

A pure substance in the fused state is allowed to cool slowly and the temperature is noted at definite time intervals. The graph is plotted between temperature and time. Initially the rate of cooling is continuous, when it reaches the point ‘b’ solid begins to appear, now the temperature remains constant until the liquid melt is completely solidified at the point ‘c’. The horizontal line ‘bc’ represents the equilibrium between the solid and liquid melt. After the point ‘c’ temperature of the solid begins to decrease along the curve ‘cd’.

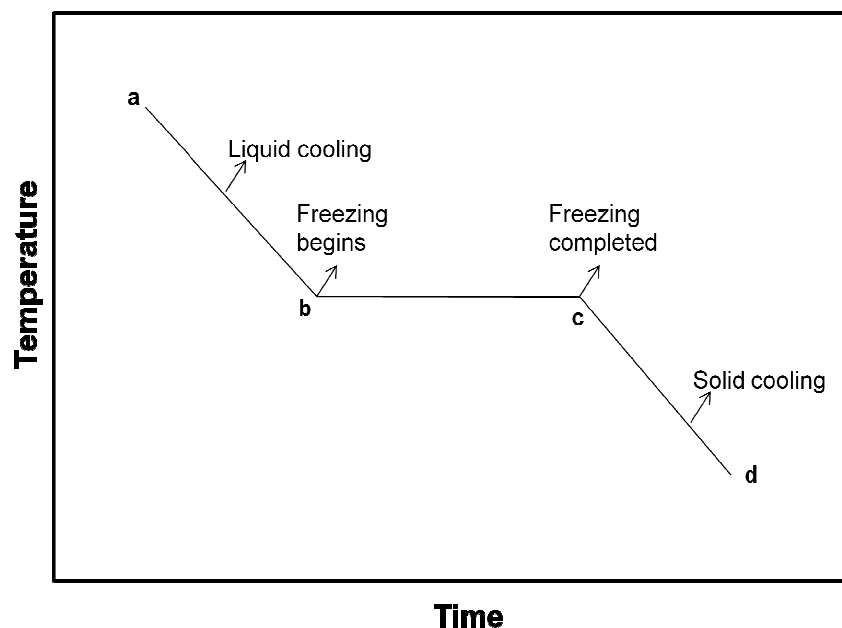


Figure 2: Cooling Curve of Pure Metal

Cooling Curve of Mixture of two Solid Substances

Consider a mixture of two substances (A and B) in the fused state is allowed to cool slowly, the temperature at different time intervals is noted, the same cooling curve is obtained. Initially the rate of cooling is continuous, when it reaches the point 'b', one substance (either A or B) begins to solidify out from the liquid, which is indicated by a break and the rate of cooling is different. The decreasing temperature with different time at different rate can be noted. On further cooling, at the break point 'c' the second compound also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture (line 'cd'). After the break point 'd' cooling of solid mass begins. The temperature of horizontal line 'cd' gives the eutectic temperature. The experiment is repeated for different compositions of A and B, and the various cooling curves are recorded. From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X– axis and the temperature in Y– axis.

Uses of cooling curve

1. Melting point and eutectic temperature of various compounds can be obtained.
2. The percentage purity of the compounds can be calculated.
3. The behavior of the compounds can be studied.

4. The composition corresponding to its freezing point gives the composition of the alloy.

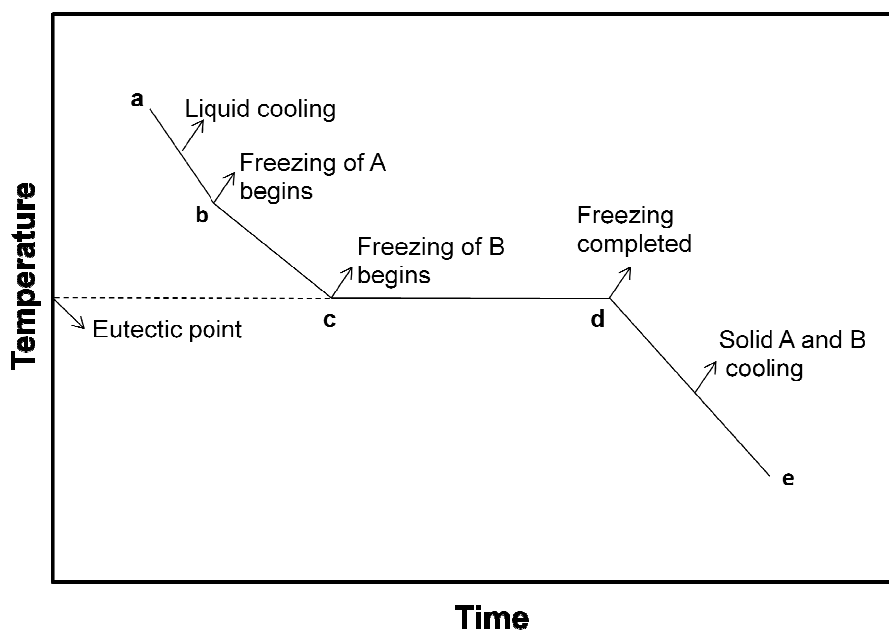


Figure 3: Cooling Curve of a Mixture of Two Solids A and B

Eutectic system:

Consider a binary system in which two components are miscible in all proportions in the liquid (molten) state. They do not react chemically and each component has the property of lowering each other's freezing point. Such a binary system is called Eutectic system. (Eutectic – Easy to melt).

Eutectic mixture: A solid solution of two component system which has the lowest freezing point of all the possible mixtures of the components is called eutectic mixture.

Eutectic point: Minimum freezing point attainable corresponding to the eutectic mixture is called eutectic point. The eutectic mixture has a definite composition and a sharp melting point. However, it is not a compound for the components are not present in stoichiometric proportions.

Construction of Simple Eutectic Diagram

From the cooling curve of any mixture of a definite composition it is possible to obtain its freezing point and eutectic temperature. It involves the study of temperature – time curves of the various compositions of alloy systems during solidification.

Consider a number of mixtures of metals A and B of different compositions lying between 100% A and 100% B are prepared. These are heated above the respective melting points therefore there exist only one phase (liquid phase) in each case. Each liquid is then allowed to cool slowly and the temperature is recorded after regular interval of time and several cooling curves (1, 2, 3, 4, 5, 6, 7) are obtained as shown in the figure. The first break in each curve (a, b, c, d, e, f, g, h) occurs at the freezing point of the mixture of that particular composition. As the mixtures differ in the compositions, their freezing point will be obtained at different temperatures. The second break occurs at the point at which the temperature remains constant and that is the eutectic temperature of the mixture. The freezing point of pure A and pure B are determined in a similar manner. The equilibrium diagram for the system of two metals is determined as shown in the figure 4.

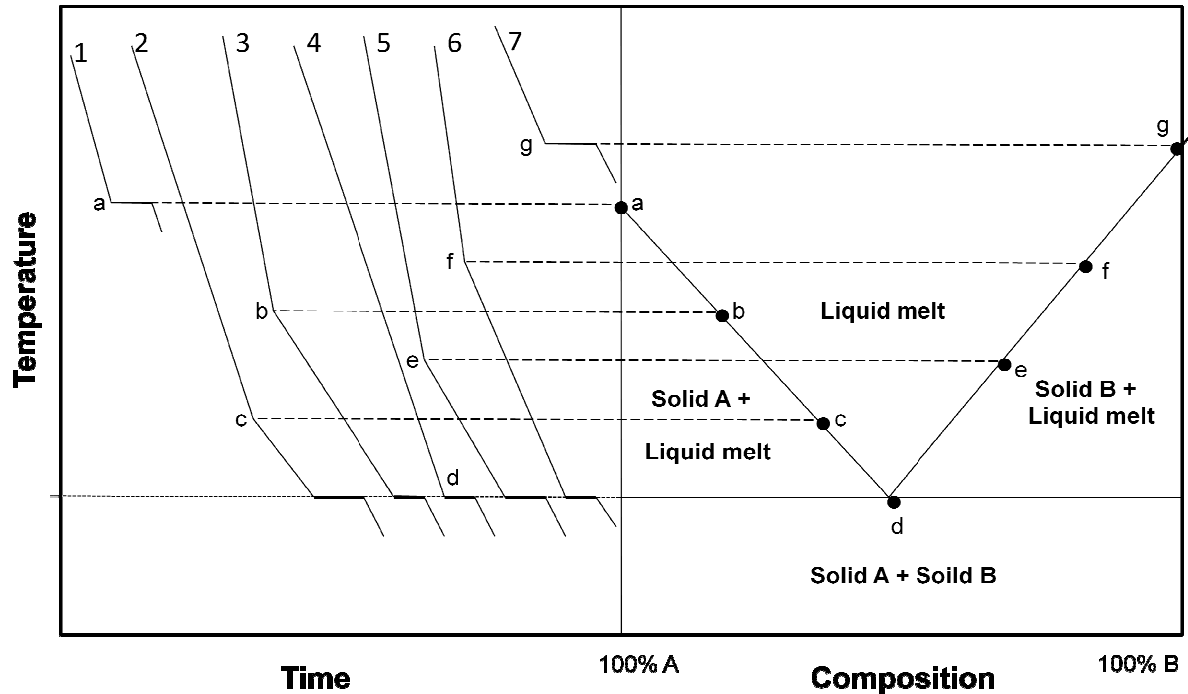


Fig. 4. Construction of Phase diagram of two solids A and B

The Lead-Silver System

It is a two – component system with four possible phases – solid Ag, solid Pb, solution of Ag + Pb and its vapour. The two metals are completely miscible with each other in liquid state and do not form any chemical compound. There is almost no effect of pressure on equilibrium, the temperature and composition are considered to construct the phase diagram at constant atmospheric pressure. It consists of

(1) Curves AO and BO.

(2) Eutectic point “O”.

(3) Areas: Above AOB / Below AO / Below BO.

Curve AO	Curve BO
It is the freezing point curve of Ag (961°C)	It is the freezing point curve of Pb (327°C)
It shows decrease in freezing point / melting point of Ag due to the addition of Pb to Ag	It shows decrease in freezing point / melting point of Pb due to the addition of Ag to Pb

Here $C = 2$ and $P = 2$, then according to the reduced phase rule $F = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant. The curves AO & BO meet at the point “O”, which is called eutectic point. Here, Solid Ag, Solid Pb and solution of Ag & Pb are in equilibrium. Thus, $C = 2$ and $P = 3$. Hence according to the reduced phase rule $F = C - P + 1 = 2 - 3 + 1 = 0$ and the system is invariant. The point O (303°C) represents a fixed composition of 97.4 % Pb and 2.6 % Ag, and is called eutectic composition. The components Ag and Pb exist as solution. Thus, $C = 2$ and $P = 1$. Hence $F = C - P + 1 = 2 - 1 + 1 = 2$ and the system is bivariant. The system will exist when the temperature $T > 303^{\circ}\text{C}$, $\text{Pb} < 97.4\%$ and $\text{Ag} > 2.6\%$.

Area	Existence	P	C	F
Below AO	Ag + Solution of Pb/Ag	2	2	1
Below BO	Pb + Solution of Ag/Pb	2	2	1
Below Eutectic Temperature	Solid Ag + Solid Pb	2	2	1

Application of Pb-Ag System

Pattinson's Process (Desilverisation of Lead)

The argentiferous lead containing small amount of silver is melted well above the melting temperature of pure lead (327°C). Let the point 'a' represent the system molten lead on the diagram. It is then allowed to cool when the temperature of the melt falls along the dashed line ab. As the temperature corresponding to b on the curve AO is reached, solid lead begins to separate and the solution would contain relatively larger amount of silver. On further cooling, more of lead separates along the curve AO until the eutectic point O is reached. Lead is continuously removed and the percentage of silver in the melt goes on increasing. At O, and the alloy containing 2.6% Ag and 97.4% Pb is obtained.

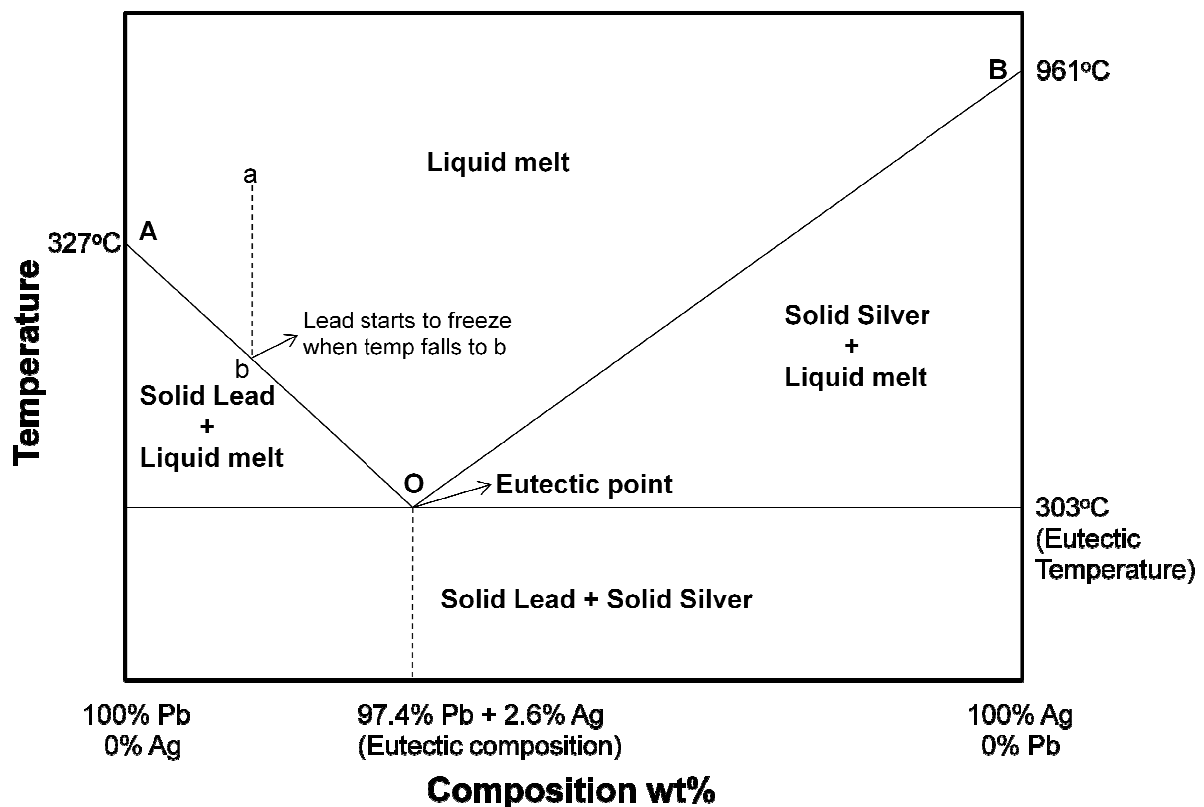


Fig. 5. The Lead-Silver System

Phase Diagram of System Having Congruent Melting Point

When two components combine in a definite proportion, one or more stable compounds are formed. These compounds melt at constant temperature to give liquid melt of the same composition. The temperature at which a compound melts to give its liquid phase is known as congruent melting point.

Examples: Zinc – Magnesium system; Tin – Magnesium system.

Let us consider a general system and let A and B be the two components and AB is the stable compound formed by them (Figure 6).

In this system, there are three different solid phases namely solid A, solid B and solid compound AB. Accordingly, there will be three freezing point curves AC, BE and CDE. Along the curves, the system is univariant as they separate two phases each ($F = C - P + 1 = 2 - 2 + 1 = 1$).

Curve AC: Along AC, solid A and liquid melt are in equilibrium.

Curve BE: Along BE, solid B and liquid melt are in equilibrium.

Curve ACDEB: Along ACDEB, compound AB and its liquid melt are in equilibrium.

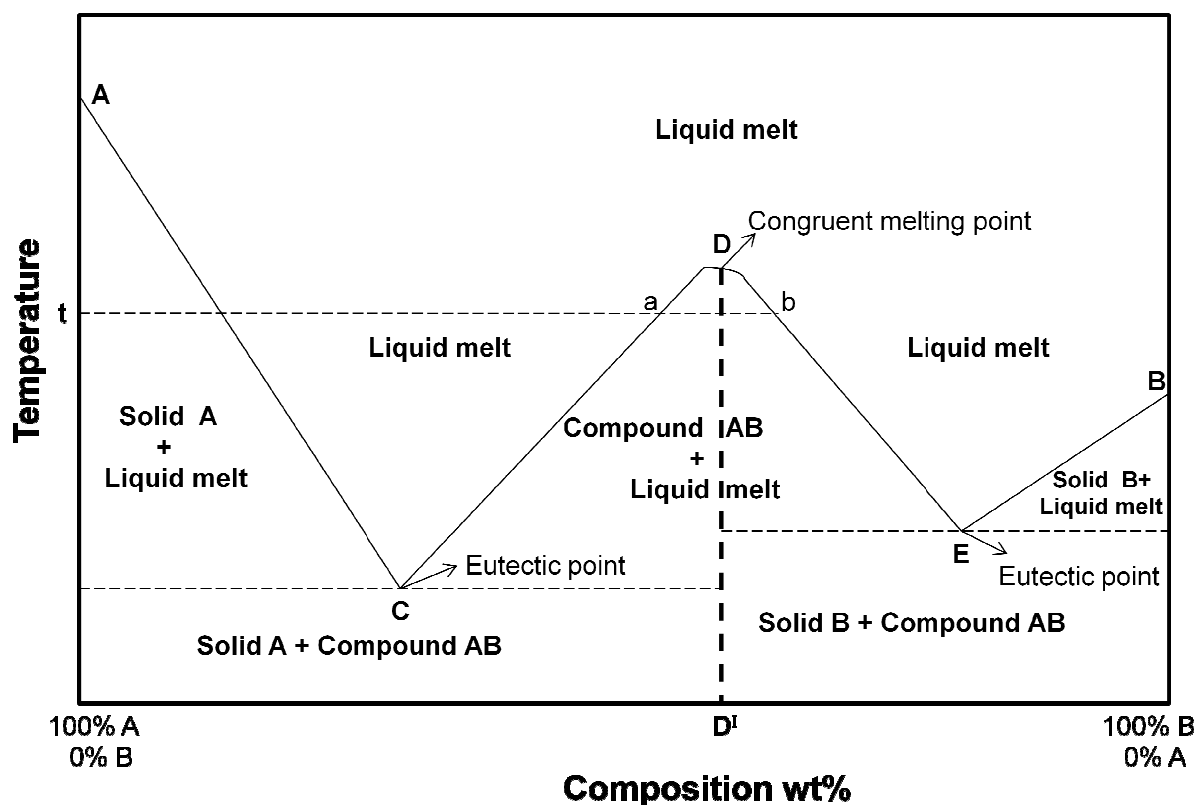


Figure 6: Phase diagram of system with Congruent Melting Point

Congruent Melting Point

The maximum point D of the curve is the congruent melting point of the compound because the solid and liquid phases have the same composition.

Evidently, at this temperature the two component system has become one component because both these phases can be represented by one component AB. Therefore, according to phase rule, D is a non-variant point [$F = C - P + 1 = 1 - 2 + 1 = 0$].

The shape of the curve CDE depends upon the stability of the compound AB.

- a. If the compound is very stable and does not dissociate on melting, a sharp apex results.
- b. If the compound partially dissociates during melting, the maximum becomes broader.

Eutectic Points C and E

- i. The phase diagram of congruent system may be considered as equivalent to two simple eutectic phase diagrams. There are two eutectic points C and E.
- ii. At C, the solid A and compound AB are in equilibrium with liquid melt while at E, the solid B and compound AB are in equilibrium with liquid melt.
- iii. At the eutectic point, the system is non-variant [$F = C - P + 1 = 2 - 3 + 1 = 0$].
- iv. It will be seen in the diagram that at a certain temperature say t , the liquid phase can have two compositions 'a' and 'b'. In other words, the compound AB can have two solubilities at the same temperatures.
- v. This can readily be explained if the diagram is made up of two parts, DD' as the dividing line.
- vi. The left half of the diagram shows two component systems A and AB while the right half shows two component systems B and AB.
- vii. On the left hand side, the curve CD represents the usual depression in freezing point of the compound AB on the addition of A while on the right hand side, the curve DE represents the usual depression in freezing point of the compound AB on the addition of B.

Areas

The area above the curves AC, CDE, and BE represents the solution of A and B (the liquid melt).

The single phase system at any point in this area is bivariant [$F = C - P + 1 = 2 - 1 + 1 = 2$]. All other areas represented in the diagram have two phases each and hence the system is univariant [$F = C - P + 1 = 2 - 2 + 1 = 1$].

Zinc-Magnesium System

In Zn-Mg binary alloys system, the components form one or more compounds in some stoichiometric proportions. These compounds melt into the liquid state having the same composition as the solid. Such compounds are called compounds with congruent melting points. Thus, a compound is said to possess congruent melting point, if it melts sharply at a constant temperature into a liquid, having the same composition as that of the solid.

Zinc and magnesium melt at 420°C and 650°C respectively and they form a compound $MgZn_2$ in which the ratio of Mg and Zn is 1:2. This compound melts at D (590°C). In the phase diagram the right consists of Zn and $MgZn_2$ system and the left consists of $MgZn_2$ and Mg. The curve BE and AC represent the compositions of liquids in equilibrium with solid Zn and solid Mg respectively. The central portion of curve CDE has maxima at D (590°C). This gives the conditions of equilibrium of liquid with solid compound, $MgZn_2$. At D, the liquid has the same composition as the solid in equilibrium. Thus, the temperature at D represents the melting point of the compound $MgZn_2$. As $MgZn_2$ can co-exist in solid and liquid of same composition, $MgZn_2$ is said to have congruent melting point. The composition corresponding to point D is 33.3% Mg and 66.7% Zn in the ratio of 1:2. The sharpness of maxima (point D) gives the information about the stability of the compound formed. A sharp maxima indicates that the compound does not dissociate appreciably whereas a flat maxima indicates an appreciable dissociation of the system. There are two eutectic points, C and E. At E the solid Zn and $MgZn_2$ deposits; while at C, Mg and $MgZn_2$ are the two phases.

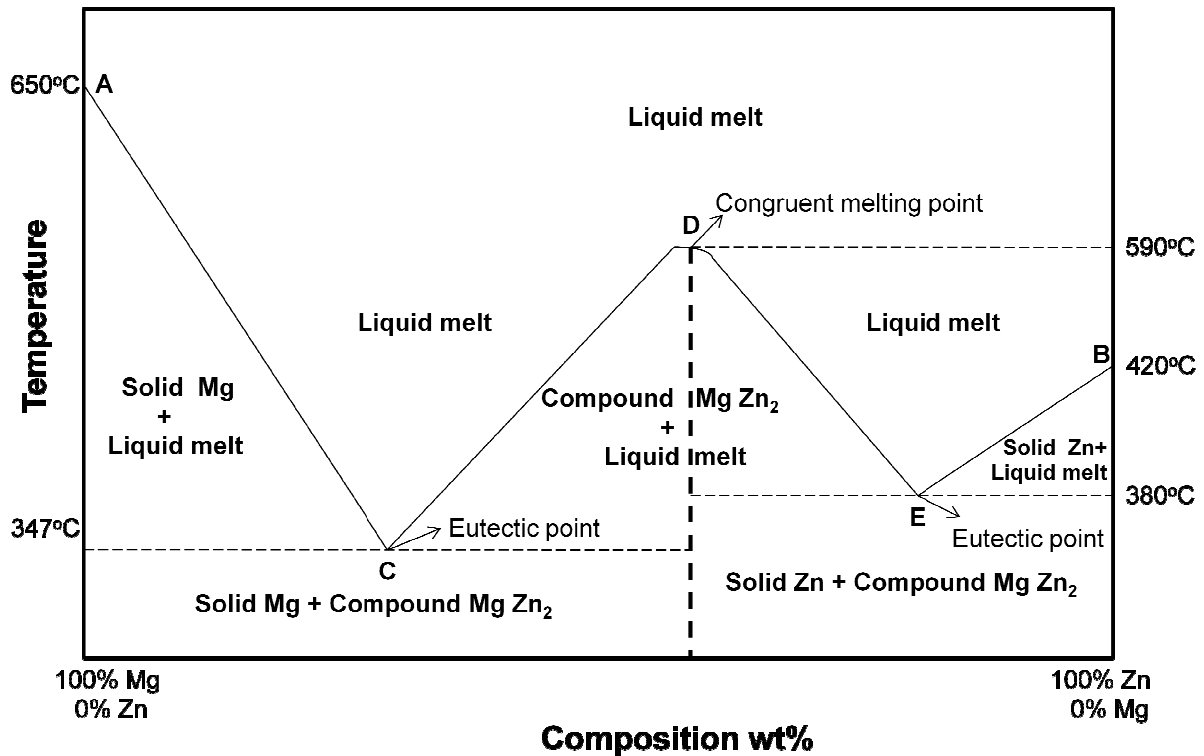
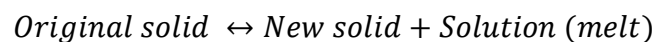


Fig. 7. Phase diagram of Zinc – Magnesium System

Phase Diagram of System Having Incongruent Melting Point

The system possesses an incongruent melting point if on heating it decomposes below its melting point and forms a new compound and a solution having different composition from the corresponding solid state. The system has no sharp melting point. The temperature at which the original solid decomposes into a new compound and solution melt (of different composition) is known as peritectic temperature and the reaction is known as peritectic reaction.



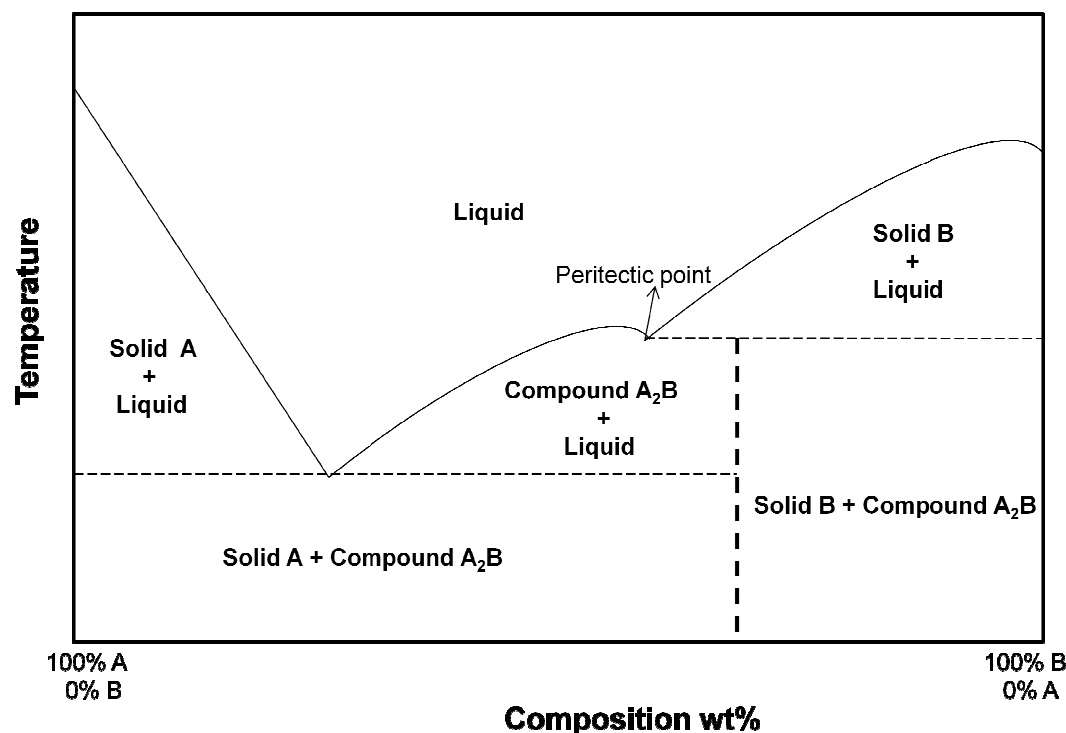


Fig. 8. Phase diagram of system with incongruent melting point

Sodium-Potassium System

It is a system having incongruent melting point. The sodium and potassium react in the ratio 2:1 to form a compound Na_2K . This compound is unstable and undergoes a peritectic reaction to form sodium and liquid melt. The corresponding temperature is the peritectic temperature of the system. This system consists of four phases namely Solid K, Solid Na, Solid Na_2K and liquid melt (Na and K in liquid state). Since pressure has no significance in this system reduced phase rule is applicable to Na – K system.

$$F = C - P + 1$$

The phase diagram of Na – K system consists of:

Curve AC represents the freezing point curve of potassium which shows the decrease in freezing point with the addition of Na. Along AC, Solid K separates out and at C new compound Na_2K separates out.

Thus $P = 2$ (Solid K and liquid melt) and $C = 2$

$$F = C - P + 1 = 2 - 2 + 1 = 1. \text{ Hence univariant.}$$

Curve CD represents the fusion curve of Na_2K along which Solid Na_2K and liquid melt are in equilibrium.

Thus $P = 2$ (Solid Na_2K and liquid melt) and $C = 2$

$$F = C - P + 1 = 2 - 2 + 1 = 1. \text{ Hence univariant.}$$

Curve BD represents the freezing point curve of sodium which shows the decrease in freezing point with the addition of K. Along BC Solid Na separates out and at C new compound Na_2K separates out.

Thus $P = 2$ (Solid Na and liquid melt) and $C = 2$

$$F = C - P + 1 = 2 - 2 + 1 = 1. \text{ Hence univariant.}$$

The Na – K system contains six areas above and below the curves. They are

Area above ACDB contains liquid melt of Na, K and Na_2K . Thus $P = 1$ and $C = 2$, hence $F = C - P + 1 = 2 - 1 + 1 = 2$ (Bivariant).

Area ACF contains Solid K and liquid melt. Area DCG contains Solid Na_2K and liquid melt. Area BDH contains Solid Na and liquid melt. Area below FCG contains Solid K and Solid Na_2K . Area IHLK contains Solid Na and Solid Na_2K .

All these areas have $P = 2$ and $C = 2$ and hence $F = C - P + 1 = 2 - 2 + 1 = 1$ (univariant).

This also contains eutectic point C at which Solid K, Solid Na_2K and liquid melt coexist comprising of $P = 3$ and $C = 2$, hence $F = C - P + 1 = 2 - 3 + 1 = 0$ (Invariant). The point D is the peritectic point where Solid Na, Solid Na_2K and liquid melt coexist having $P = 3$ and $C = 2$, hence $F = C - P + 1 = 2 - 3 + 1 = 0$ (Invariant).

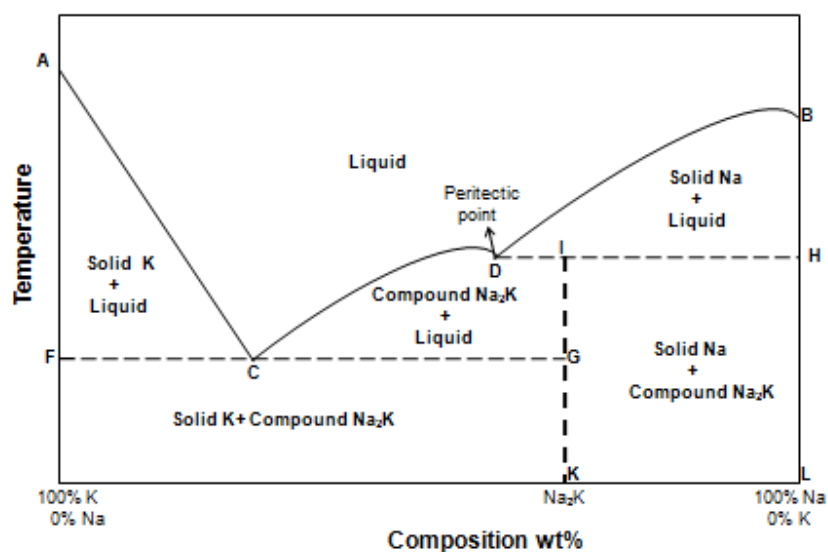


Fig. 9. Phase diagram of Sodium – Potassium system

Solved Problems

1. Determine the number of phases, components, and degrees of freedom present in:

- i. $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2 \text{NO}_2 (\text{g})$
- ii. Liquid Water and Water vapour in equilibrium
- iii. Liquid water and Water vapour at pressure of 1 atm

i. Number of phases P = 1

Number of components C = 1

Number of degrees of freedom F = $C - P + 2 = 1 - 1 + 2 = 2$ (Bivariant)

- ii. $\text{Water} \rightleftharpoons \text{Water vapour}$

Number of phases P = 2

Number of components C = 1

Number of degrees of freedom $F = C - P + 2 = 1 - 2 + 2 = 1$ (Univariant)

iii. $\text{Water} \rightleftharpoons \text{Water vapour}$ at pressure 1 atm

Number of phases $P = 2$

Number of components $C = 1$

Number of degrees of freedom $F = C - P + 1 = 1 - 2 + 1 = 0$ (Invariant)

2. Calculate the number of phases present in the following systems:

i. $\text{MgCO}_3 (\text{s}) \rightleftharpoons \text{MgO} (\text{s}) + \text{CO}_2 (\text{g})$

ii. $\text{Rhombic sulphur} (\text{s}) \rightleftharpoons \text{Monoclinic sulphur} (\text{s})$

iii. $\text{Solid ice} \rightleftharpoons \text{Liquid water} \rightleftharpoons \text{Water vapour}$

iv. $\text{Emulsion of oil in water}$

i. $\text{MgCO}_3 (\text{s}) \rightleftharpoons \text{MgO} (\text{s}) + \text{CO}_2 (\text{g})$

Number of phases $P = 3$

Number of components $C = 2$

Number of degrees of freedom $F = C - P + 2 = 2 - 3 + 2 = 1$ (Univariant)

ii. $\text{Rhombic sulphur} (\text{s}) \rightleftharpoons \text{Monoclinic sulphur} (\text{s})$

Number of phases $P = 2$

Number of components $C = 1$

Number of degrees of freedom $F = C - P + 2 = 1 - 2 + 2 = 1$ (Univariant)

iii. $\text{Solid ice} \rightleftharpoons \text{Liquid water} \rightleftharpoons \text{Water vapour}$

Number of phases $P = 3$

Number of components $C = 1$

Number of degrees of freedom $F = C - P + 2 = 1 - 3 + 2 = 0$ (Invariant)

iv. Emulsion of oil in water

Number of phases $P = 2$

Number of components $C = 2$

Number of degrees of freedom $F = C - P + 2 = 2 - 2 + 2 = 2$ (Bivariant)

3. 100 kg of a sample of argentiferous lead containing 0.5% Ag is melted and then allowed to cool. If eutectic contains 2.6% Ag, (1) what mass of eutectic will be formed and (2) what mass of lead will separate out?

Given: In 1 kg argentiferous lead, silver content is 0.5%; (i.e: 5 gm).

(or) In 100 kg argentiferous lead, silver content = 500 gm = 0.5 kg

In the given eutectic system, 2.6% is silver and hence 97.4% is lead.

Corresponding to 0.5 kg silver, the amount of lead (Pb)

present in eutectic
$$= \frac{0.5 \times 97.4}{2.6} = 18.73 \text{ kg}$$

1. The mass of eutectic formed from 100 kg ore = $0.5 + 18.73 = 19.23 \text{ kg}$
2. The mass of lead, which is separated out from 100 kg ore = $100 - 18.73$
$$= 81.27 \text{ kg}$$

Questions

1. State the phase rule. Explain the terms involved in it with suitable examples. What is condensed phase rule?
2. Derive an expression for phase rule.
3. What is "phase diagram"? With the help of phase diagram explain the following terms: (i) Triple Point (ii) Eutectic Point
4. Draw and explain the phase diagram of water system.
5. Draw a neat simple eutectic system and explain the various phases present in it?
6. Construct a phase diagram by thermal analysis.
7. Explain the differences among melting point, eutectic point and triple point. Give examples?
8. Draw the phase diagram of lead-silver system and explain the salient features and its application?

9. Discuss the general phase diagram of a two-component system from the standpoint of phase rule.
10. Explain the salient features of phase diagram of 2 component congruent system.
11. Write notes on phase diagram of 2 component in-congruent system.
12. 50 kg of a sample of argentiferous lead containing 0.5% Ag is melted and then allowed to cool. If eutectic contains 2.6% Ag, (1) what mass of eutectic will be formed and (2) what mass of lead will separate out?
13. $\text{Fe(s)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{FeO(s)} + \text{H}_2 \text{ (g)}$. Calculate P, C and F for the above system.
14. Write the number of phases and components in the following heterogeneous system: $\text{CuSO}_4 \text{ (s)} + 5 \text{ H}_2\text{O (l)} \rightleftharpoons \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O (s)}$.
15. A system consists of benzene and water. What is the number of phases?
16. Determine the number of phases, components and degrees of freedom available for the following systems:
 - i. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O(s)} \rightleftharpoons \text{Na}_2\text{SO}_4\text{(s)} + 10 \text{ H}_2\text{O (g)}$
 - ii. $\text{N}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightleftharpoons 2\text{NO (g)}$
 - iii. $\text{PCl}_5 \text{ (g)} \rightleftharpoons \text{PCl}_3 \text{ (g)} + \text{Cl}_2 \text{ (g)}$

References

1. Puri, L.R. Sharma and M.S. Pathania, Principles of Physical Chemistry, Vishal Publishing Co, 2004.
2. P. C. Jain and Monika Jain, Engineering Chemistry, Dhanpat Rai Publishing company (P) Ltd, 15th edition, 2008.
3. https://www.ikbooks.com/home/samplechapter?filename=195_Sample-Chapter.pdf
4. P. L. Soni, O. P. Dharmarha, Textbook of Physical Chemistry: A Modern Approach, Sultan Chand & Sons, 1981.

Introduction. Explosives: Requirements, Oxygen balance related problems, Classification of Explosives: Low explosives, primary explosives and high explosives, Properties of Detonators and high explosives, Assessment of explosives. Rocket engines: Types of rocket engines. Basic principle, Mass fraction, Specific impulse, Thrust, Effective exhaust velocity, Specific propellant consumption. Problems, Chemical propellants: Requirements, Classification: Liquid fuels, Liquid oxidizers, Solid fuels, Solid oxidizers.

INTRODUCTION

Explosives and propellants are chemical compounds that rapidly produce large volume of hot gases when properly initiated. Explosives and propellants have relatively large amount of available energy stored compactly and readily deliverable. The power output depends on the rate at which energy is liberated. Explosives are largely used for military purposes. However, they are also used for blasting mountains, for construction of tunnels, roads, mining and other civil engineering purposes. Propellants are used for putting space capsule into orbit and many other military applications.

EXPLOSIVES

An explosive is a substance or a mixture of substances which when subjected to mechanical or thermal shock gets rapidly oxidized exothermically into products of large amount of heat and gases.

REQUIREMENTS OF A GOOD EXPLOSIVE

The following requirements are to be fulfilled by an explosive.

- ✓ A good explosive must have at least one chemical bond that can be easily broken. Usually explosive molecules contain N-N, N-O, N-Cl, O-Cl bonds. The electro negativity difference in these cases is either zero or very small
- ✓ It must be stable under normal conditions of storage
- ✓ Its rate of decomposition must be fast to produce large amount of hot gases
- ✓ It must have high Brisance or Shattering power
- ✓ It must have a positive oxygen balance.

The oxygen balance is a measure of oxygen available in the molecule, which is used to oxidize C to CO and H to H₂O. It is numerically expressed as a percentage surplus or deficiency of oxygen by weight. For a molecule C_xH_yO_z, X-atoms of oxygen are required to oxidize C to CO and Y/2 atoms of oxygen are required to oxidize H to H₂O. Hence, surplus oxygen = Z-(X+Y/2) atoms.

$$\text{Oxygen balance} = \frac{\left[Z - \left(X + \frac{Y}{2} \right) \right] \times 16}{\text{Mol. wt. of } C_xH_yO_z} \times 100$$

The oxygen balance of some explosives is given in table 1.

TABLE 1 OXYGEN BALANCE FOR SOME EXPLOSIVES

S.No.	Substance	Molecular weight	$Z - \left(X + \frac{Y}{2} \right)$	Oxygen balance
1.	NH ₄ NO ₃	80	$3 - \left(0 + \frac{4}{2} \right) = 1$	$\frac{1 \times 16}{80} \times 100 = +20$
2.	C ₆ H ₃ (NO ₂) ₃	213	$6 - \left(6 + \frac{3}{2} \right) = -1.5$	$\frac{-1.5 \times 16}{213} \times 100 = -11.3$
3.	Pb(N ₃) ₂	290	Zero	Zero

Substances having negative oxygen balance (e.g: Trinitrobenzene) must be mixed with those having positive oxygen balance (e.g.: Ammonium nitrate). Lead azide, Pb (N₃)₂ does not get oxidized and it has no oxygen balance. However it is an explosive.

CLASSIFICATION OF EXPLOSIVES

Explosive are classified into (i) low explosives (ii) primary explosive and (iii) high explosives on the basis of their sensitivity and destructive power.

Important examples for different types of explosives are given in the following flow sheet diagram.

LOW EXPLOSIVES (or) PROPELLANTS

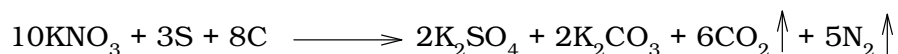
Low explosives burn rather than explode. The rate of combustion is low (0.25m/s.) The volume of gases evolved is predictable and controllable. They are used in fireworks, as propellants for rockets.

Examples: Gun powder, Gun-cotton

1. GUN POWDER (or) BLACK POWDER

Gun powder is a mixture of 75%KNO₃ + 15%Charcoal + 10%Sulphur. The main disadvantage of using gun powder is the formation of smoke.

The decomposition reaction of gun powder is:



2. GUN COTTON (or) CORDITE (or) SMOKELESS POWDER

Gun cotton is made by dissolving 65%Cellulose nitrate + 30%Glyceryl trinitrate + 5%Petroleum jelly in alcohol or ether. The resulting paste is extruded into cylindrical cords; hence its name is called cordite. The petroleum jelly acts as stabilizer. It produces CO, CO₂, N₂, water vapour and no smoke.

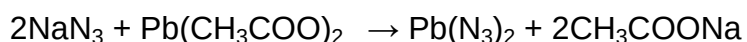
PRIMARY (or) INITIATING EXPLOSIVES (or) DETONATORS

Primary explosives are sensitive to both heat and shock. They are generally used for initiating the explosion (detonation) of high explosives.

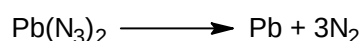
Examples: Lead azide, mercury fulminate, Diazodinitrophenol, Tetrazine, Silver acetylide.

1. LEAD AZIDE, Pb(N₃)₂

Lead azide is used for military purposes on account of its low cost, stability in storage, and excellent initiating action. It is manufactured by treating sodium azide with lead acetate.



Lead azide is a shock sensitive detonator which decomposes as follows:

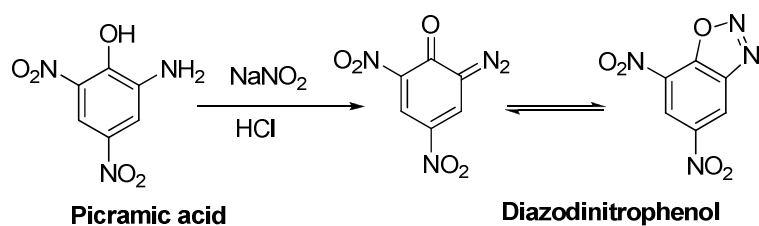


2. MERCURY FULMINATE, Hg (ONC)₂

Mercury fulminate is more sensitive, expensive and slightly toxic explosive than Pb(N₃)₂. It is obtained by dissolving mercury in excess nitric acid. The resulting solution when added to ethyl alcohol, mercury fulminate gets precipitated.

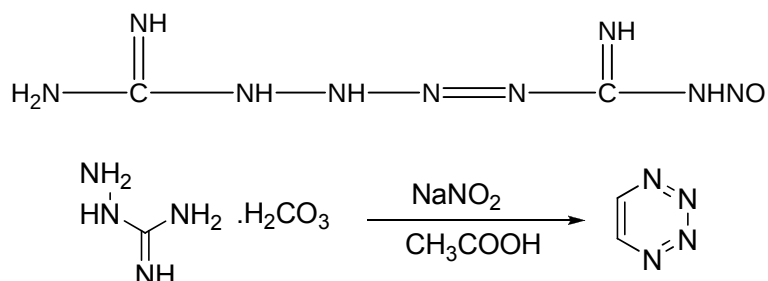
3. DIAZODINITROPHENOL (DDNP)

Diazodinitrophenol is obtained by diazotizing picramic acid with sodium nitrite and HCl. It is non-hygroscopic and sensitive to friction and impact. It is used as an initiator in commercial blasting caps.



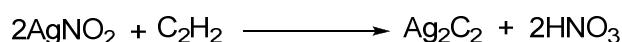
4. TETRAZINE

Tetrazine is obtained by treating 1-amino-guanidine hydrogen carbonate with sodium nitrite and dilute acetic acid. The compound is stable up to 75°C. It can be used as detonator for high explosives.

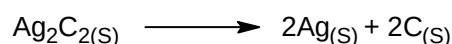


5. SILVER ACETYLIDE

It is a heat and shock sensitive high explosive. It is prepared by passing acetylene gas through a solution of silver nitrate.



It decomposes as follows upon ignition without evolving any gas



HIGH EXPLOSIVES

High explosives explode not on ignition, but only on detonation by primary explosives. They are less sensitive but the shattering power is high. They are used for military purposes, in blasting hills for roads and train tunnels etc.

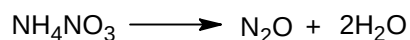
High explosives are classified into four groups

SINGLE COMPOUND EXPLOSIVES

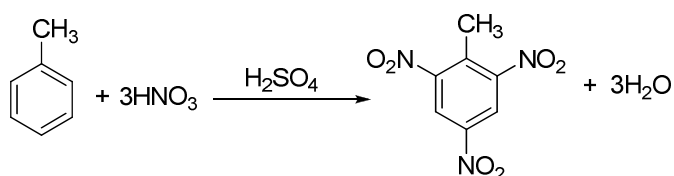
(i) AMMONIUM NITRATE (AN): Ammonium nitrate has a positive oxygen balance of +20 and hence it is mainly used for making binary explosives.

50%AN + 50%TNT is called as Amatol. It is widely used for military purposes.

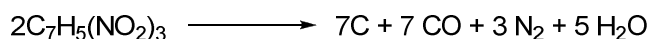
It decomposes as follows:



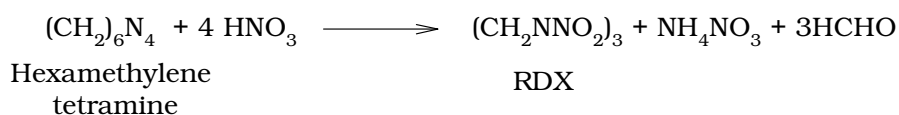
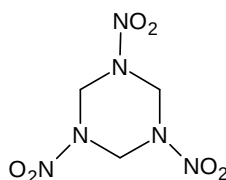
(ii) TRINITROTOLUENE (TNT): Trinitrotoluene is widely used as a military explosive. It can be prepared by nitration of toluene. TNT is safe explosive in manufacture, transportation and storage. Moreover it can be melted and poured into containers (meltloading). Most of the commercial explosives contain TNT as one of the components.



It decomposes as follows:



(iii) CYCLONITE (RDX): Cyclonite is cyclotrimethylene trinitramine. this can be obtained by nitration of hexamethylene tetramide with concentrated nitric acid. RDX is used for military and industrial purposes. Its advantages are less toxicity but greater sensitivity than TNT.



2. BINARY EXPLOSIVES

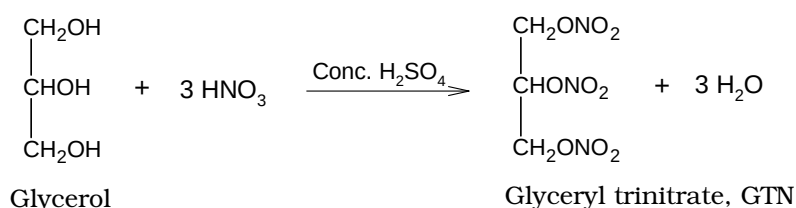
- (i) Amatol (50%AN + 50%TNT)
- (ii) Cyclotol (50%RDX + 50%TNT)
- (iii) Pentolite (50%PETN + 50%TNT) (PETN – Pentaerythritoltetranitrate)
- (iv) Ammonal (AN + TNT + Al – powder)
- (v) Tropex (RDX + TNT + Al – powder)

3. PLASTIC EXPLOSIVES

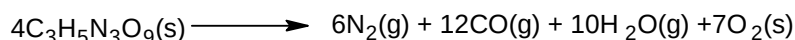
Plastic explosives are mainly used for industrial applications and military use. They can be moulded into any shape and press-loaded safely without any danger. They consist of high explosive, usually RDX or PETN (which gives destructive power) and wax or oil (which makes it less sensitive and more plastic).

4. NITROGLYCERINE (NG) (or) GLYCERYL TRINITRATE (GTN) AND DYNAMITES

Nitroglycerine (NG) is a poisonous liquid and is extremely sensitive to shock. It explodes violently on detonation. It is prepared by adding pure glycerol to a well stirred and cooled ($5-10^{\circ}\text{C}$) mixture of conc. HNO_3 and conc. H_2SO_4 . The nitration is completed within one and half hour.



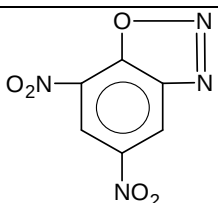
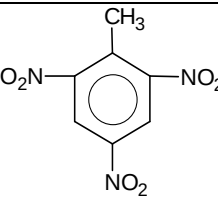
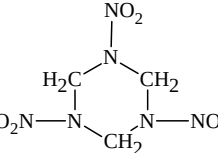
Nitroglycerine undergoes a rapid decomposition as follows:



To make NG safe and easy to handle, it is absorbed in a siliceous material like kieselguhr. *The stabilized NG is called as dynamite.* The dynamites are of different types.

- ✓ **Original dynamite:** It is a mixture of 75%NG + 25%kieselguhr (stabilizer). It is used for rock blasting, gold mining etc.
- ✓ **Straight dynamite:** It is a mixture of 60%NG + 40%wood flour, sodium nitrate (absorbent). It is used for rock blasting.
- ✓ **Gelatin dynamite:** It is a mixture of 82– 3%NG + 7–18%nitrocellulose. It is used for making train tunnel, for demolition etc.
- ✓ **Cordite:** It is a mixture of 65%nitrocellulose + 30%NG + 5%petroleum jelly (stabilizer). It is used as propellant in submarines.

TABLE 2: SELECTED PROPERTIES OF SOME DETONATORS AND HIGH EXPLOSIVES

S. No.	Name of the explosive	Chemical structure	Method of preparation	VOD ms^{-1}	Drop height in cm using 2kg
1.	Lead azide	$\text{Pb}(\text{N}_3)_2$	NaN_3 + Lead acetate	5100	11
2.	Diazodinitrophenol (DDNP)		$\text{C}_6\text{H}_2\text{NH}_2(\text{NO}_2)_2(\text{OH})$ (Picramic acid) + HNO_2 + HCl (at low temperature)	6900	5
3.	Mercury fulminate	$\text{Hg}(\text{ONC})_2$	Hg + conc. HNO_3 + Ethanol	5400	5
4.	Ammonium nitrate	NH_4NO_3	NH_3 gas + 40-60% HNO_3	2700	>100
5.	Glyceryl trinitrate (GTN) or Nitroglycerine (NG)	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{CHONO}_2 \\ \\ \text{CH}_2\text{ONO}_2 \end{array}$	Glycerol + 40% HNO_3 + 60% H_2SO_4	7700	15
6.	Trinitrotoluene (TNT)		Nitration of toluene	6900	>100
7.	Cyclonite (RDX)		Nitration of hexamethylene tetramine	8350	33

8.	Pentaerythritol tetranitrate (PETN)	$ \begin{array}{c} \text{CH}_2\text{ONO}_2 \\ \\ \text{O}_2\text{NOH}_2\text{C} - \text{C} - \text{CH}_2\text{ONO}_2 \\ \\ \text{CH}_2\text{ONO}_2 \end{array} $	Pentaerythritol + $\text{HNO}_3 + \text{H}_2\text{SO}_4$	8300	17
----	-------------------------------------	--	---	------	----

ASSESSMENT OF EXPLOSIVES

In order to compare the performance characteristics of explosives, certain empirical tests have been described.

1. BRISANCE (or) SHATTERING POWER

A good explosive must have high brisance or shattering power. The shattering power can be measured by sand bomb test.

In sand bomb test, the sample is kept inside the steel bomb containing a known weight of sand of uniform particle size (to be retained on 30 meshes).

After explosion, the pulverized sand is sieved and weight of sand that passes through the 30 mesh is taken as a measure of the shattering power of the explosive.

2. VELOCITY OF DETONATION (VOD)

The velocity of detonation is determined by measuring electronically. It is the time taken for the detonation to travel between two pairs of wires planted at a known distance apart.

3. DROP HEIGHT

The sensitivity to impact which is especially important for initiating explosives (detonators), and is measured in terms of the minimum height from which a standard weight usually 2kg must be dropped in order to cause detonation of the explosive.

ROCKET ENGINES

The Essential parts of a rocket engine (Fig. 1) are

1. A container or shell or containers for propellants
2. Combustion chamber or Thrust chamber
3. Exhaust nozzle
4. Payload (Satellites, Spacecraft etc.,)

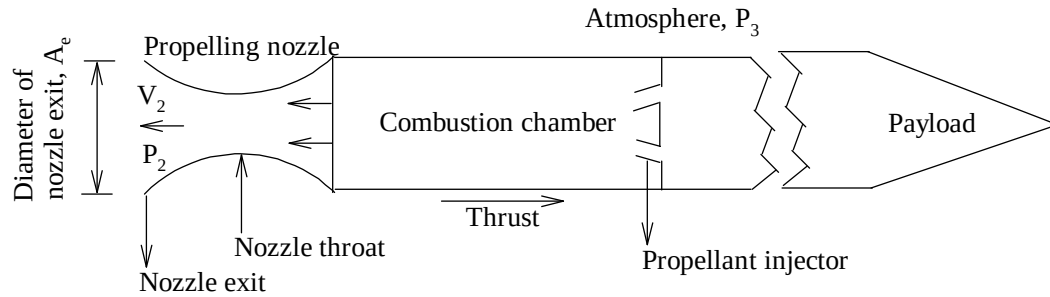


Fig. 1: A Rocket Engine

CLASSIFICATION OF ROCKET ENGINES

Rocket engines or simply rockets are classified in the following manner.

1. On the basis of source of energy employed
 - ✓ Chemical rockets
 - ✓ Solar rockets
 - ✓ Nuclear rockets
 - ✓ Electrical rockets
2. On the basis of propellants used
 - ✓ Liquid propellant rockets
 - ✓ Solid propellant rockets
 - ✓ Hybrid propellant rockets
3. On the basis of application
 - ✓ Space rockets
 - ✓ Military rockets (missiles)
 - ✓ Weather rockets
 - ✓ Booster rockets
4. On the basis of number of stages
 - ✓ Single stage rockets
 - ✓ Multi - stage rockets
5. On the basis of size and range
 - ✓ Short range small rockets. They are generally solid propellant type
 - ✓ Long range large rockets. They are generally liquid propellant type

BASIC PRINCIPLE OF A ROCKET ENGINE

The combination of a fuel and an oxidizer is called as a propellant. The rocket engine carries both its fuel and oxidizer. It is completely independent of the atmosphere for its combustion. Therefore, the rocket can operate in a vacuum.

In the combustion chamber, the propellant burns and creates very high pressure and high temperature of 200atm and 4000K respectively. When the hot pressurized gaseous reaction products are ejected at a high velocity through the nozzle exit, thrust force is produced which in turn propels the rocket in the opposite direction.

MASS FRACTION

The mass of the propellant of the rocket divided by the total mass of the rocket gives the mass fraction. Total mass of the rocket includes mass of propellants, mass of structures (propellant tank, engines etc.), and mass of payload. For a typical rocket, the total mass is distributed in the following way.

90 propellant mass + 6%Structure + 4%Payload

Significance: The large the mass fraction number the less payload a rocket can carry. The smaller the mass fraction number the less is the range, the rocket can reach. The mass fraction of typical rocket is therefore optimized to about 0.82 so that a good balance can be obtained between payload carrying capability and range.

SPECIFIC IMPULSE, I_{sp}

Specific impulse is defined as the thrust force obtained by burning unit weight of the propellant.

The burning of a propellant depends upon the rate at which it flows into the thrust chamber.

Mathematically, I_{sp} is defined as

$$I_{sp} = \frac{F \text{ (Thrustforce)}}{\dot{w} \text{ (Weight flowrate of propellant)}}$$

But $\dot{w} = \dot{m} g$, where $\dot{m}$ is the mass flow rate of propellant, Kg/sec and g is the acceleration due to gravity at sea level, m/sec^2 .

$$\therefore I_{SP} = \frac{F}{\dot{m}g}$$

Unit: $F \rightarrow$ Thrust force (Newtons, N)

$$I_{sp} = \frac{N}{kg/sec \times m/sec^2}$$

But $Kg.m/sec^2$ is Newton, N

(or)
$$\therefore I_{SP} = \frac{N}{N/Sec}$$

$I_{SP} = \text{Seconds}$

THRUST

Thrust is the force that propels the rocket at a given velocity.

Momentum thrust and Pressure thrust: The burning of a propellant produces huge amount of hot gases with great pressure inside the combustion chamber.

The actual force (thrust force) required for rocket propulsion depends upon

- ✓ the momentum of hot exhaust gases
- ✓ the rate at which the gases expands at the exit of the nozzle

The momentum of exhaust gases is the product of mass flow rate of exhaust gases and the velocity at which the gases escape through the nozzle exit. This is known as “**momentum thrust**”.

$$F_{mom} = \dot{m} \times V_2$$

But the exhaust gases expand at the nozzle exit depends upon the diameter of the nozzle exit (A_e) and the pressure difference between exhaust pressure of gases (P_2) and ambient (atmospheric) pressure (P_3). This is known as “**pressure thrust**”

$$F_{press} = A_e (P_2 - P_3)$$

Therefore, the total force acting on the rocket is the sum of momentum thrust and pressure thrust.

$$F = \dot{m}V_2 + A_e(P_2 - P_3)$$

Significance: For effective propulsion of a rocket, the momentum thrust must be maximum and the pressure thrust must be minimum.

The large difference in the exhaust gas pressure (P_2) and ambient pressure (P_3) at the nozzle exit creates the expansion shock waves which in turn develops stress at the nozzle exit areas. Further it also decreases the momentum thrust responsible for propulsion. This condition is known as “**negative thrust**”.

When the exhaust gas pressure (P_2) is equal to ambient pressure (P_3), the exhaust gases escape through the nozzle exit expand smoothly in atmosphere with great velocity and provides maximum force (thrust) to propel the rocket.

When the atmospheric pressure decreases with increasing altitudes, about 10-30% change in pressure thrust is observed. Therefore the rocket exhaust nozzle is so designed that the exhaust gas pressure is equal to or slightly higher than the atmospheric pressure in order to propel the rocket with maximum thrust at a higher altitude.

i.e: When $P_2 = P_3$, the pressure thrust term $A_e (P_2 - P_3)$ becomes zero and hence

$$F = \dot{m}V_2.$$

This shows that the thrust force is proportional to the mass flow rate of exhaust gases and the exhaust velocity.

EFFECTIVE EXHAUST VELOCITY, (C)

The average equivalent velocity of the reaction products of combustion when expand at the nozzle exit of the rocket is known as effective exhaust velocity (C). The expansion tendency of hot gases at the nozzle exit depends upon the thrust force produced by burning unit mass flow rate of propellant. Hence,

$$C = \frac{F}{\dot{m}}$$

Unit:

$$C = \frac{N}{Kg/sec}$$

But, $N = Kg.m/sec^2$,

$$\therefore C = \frac{Kg.m/sec^2}{Kg/sec} = \frac{Kg.m}{sec^2} \times \frac{sec}{Kg} = m/sec.$$

RELATIONSHIP BETWEEN C AND V_2 :

The thrust force and actual exhaust velocity, V_2 are interrelated as

$$F = \dot{m} V_2 + A_e (P_2 - P_3) \quad \dots(1)$$

By definition, we have,

$$C = \frac{F}{\dot{m}} \quad \dots(2)$$

$$(or) F = C \dot{m}$$

Substituting (2) in (1), we get

$$C \dot{m} = \dot{m} V_2 + A_e (P_2 - P_3)$$

$$(or) C = V_2 + \frac{A_e}{\dot{m}} (P_2 - P_3) \quad \dots(3)$$

(i) When the exhaust pressure of gases (P_2) is equal to ambient (atmospheric) pressure (P_3), C becomes V_2 .

i.e: The effective exhaust velocity is the actual exhaust velocity.

(ii) When $P_2 \neq P_3$, $C \neq V_2$.

At this condition the effective exhaust velocity is disturbed because of pressure thrust.

SPECIFIC PROPELLANT CONSUMPTION

The weight flow rate of the propellant required to produce a thrust of one Newton is known as the specific propellant consumption (SPC). Reciprocal of I_{sp} is also known as SPC.

Mathematically, SPC is given by

$$SPC = \frac{\dot{w}}{F}$$

(or)

$$SPC = \frac{1}{F / \dot{w}} = \frac{1}{I_{sp}}$$

Significance: SPC value for a rocket determines the size of the propellant tanks and hence its total size.

REQUIREMENTS OF A GOOD PROPELLANT

1. A good propellant must have high specific impulse.
2. A good propellant must have high density or specific gravity. This minimizes the size of the propellant tank required and offer lower value of mass fraction ratio.
3. The freezing point of a good propellant must be less. This makes the handling of cryogenic propellants easier and avoids freezing of propellants at high altitudes and in cold weather.
4. Good propellants must be non-corrosive for the materials used in various parts of the rockets.
5. A good propellant must have low value of vapour pressure and viscosity. Low vapour pressure avoids cavitations problems in the feed pumping systems. Lower viscosity decreases the power required for pumping.
6. Good propellant should be chemically stable. It should not undergo any kind of decomposition with time. It should not absorb moisture. No ignition should start with slight shock, impact or pressure.
7. A good propellant should not be poisonous and hazardous. Handling, transportation, storage should be simple, convenient and safe.
8. Products of combustion of a good propellant must have lower values of the molecular weight to enhance exhaust velocity.
9. A good propellant should be cheap and abundantly available.

CLASSIFICATION OF PROPELLANTS

Rocket propellants are classified in to three groups

(1) Liquid propellants (2) Solid propellants (3) Hybrid propellants

LIQUID PROPELLANTS

Liquid propellants consist of fuel and oxidizer in liquid form. They are stored in separate storage tanks and are injected as spray in to the combustion chamber under pressure. They are further classified into monopropellants and bipropellants.

1. MONOPROPELLANTS

A liquid propellant consisting of a single substance or a mixture of substance that contains both fuel and oxidizer in itself is defined as a monopropellant.

Examples: Hydrogen peroxide, Hydrazine, Nitro methane, Nitroglycerine

2. BIPROPELLANTS

A two-component rocket propellant that is fed separately to the combustion chamber as fuel and oxidizer is defined as bipropellant.

Examples:

S.No.	Oxidizer	Fuels
1.	Liquid oxygen	Liquid hydrogen
2.	Hydrogen peroxide	Hydrazine
3.	Nitrogen tetroxide	Unsymmetrical dimethyl hydrazine (UDMH)

Bipropellants are of two types

(a) Cryogenic propellants: Those fuels and oxidizers which must be stored at extremely low temperature to remain in liquid form are called cryogenic propellants.

Example: Liquid oxygen (LOX) – Liquid hydrogen

(b) Hypergolic propellants: When a fuel and oxidizer ignite simply on contact with one another, is called as hypergolic propellants.

Example: Nitrogen tetroxide – Mono methyl hydrazine (MMH)

SOLID PROPELLANTS

They consist of solid fuel and solid oxidizer in premixed form. The mixture is then casted in fluid state and packed into the steel shell or case of the combustion chamber. They are further classified into homogeneous propellants and heterogeneous propellants.

1. HOMOGENEOUS SOLID PROPELLANTS

Homogeneous solid propellants are of either simple – base type or double – base type.

A Simple base propellant consists of a single substance which has both the fuel and oxidizer in it.

Example: cellulose nitrate.

A double base propellant consists of an intimate and uniform mixture of two different organic substances. This mixture contains sufficient amount of oxygen required for combustion and has properties of both fuel and oxidizer.

Example: Nitroglycerine – nitrocellulose mixture.

2. HETEROGENEOUS (or) COMPOSITE PROPELLANTS

When a fuel is dispersed in an oxidizer and held by a polymer binder is known as composite propellant.

Example: Aluminium Powder (16%) + Ammonium perchlorate (69.3%) + Polybutadiene-acrylic acid-acrylonitrile (PBAA) (14%) + Iron oxide (0.7%).

In this example, the fuel (aluminium powder) is dispersed in the oxidizer, (ammonium perchlorate). This mixture is held together by the polymer binder, PBAA. The binder also burns as a fuel. Presence of iron oxide acts as catalyst to increase the burning rate of this mixture. The final product is rubber like substance with consistency of a hard rubber eraser.

HYBRID PROPELLANTS

Hybrid propellants consist of a liquid oxidizer and a solid fuel. The liquid oxidizer is injected into the central region of the solid fuel shell where the chemical reaction between the two takes place. This type of propellant has the advantage of both the solid and liquid propellant rockets.

Examples:

S.No.	Liquid oxidizer	Solid fuels
1.	Fluorine	Beryllium hydride
2.	Nitrogen tetroxide	Lithium hydride

LIQUID OXIDIZERS**1. LIQUID OXYGEN (LOX)**

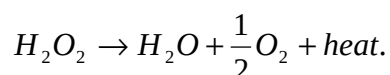
- ✓ Liquid oxygen (LOX) is a cryogenic propellant (Boiling point = 90K)
- ✓ It requires proper insulation of containers and feed lines to prevent evaporation
- ✓ It is non-corrosive but harmful to personnel.
- ✓ It is used with large number of liquid fuels such as gasoline, hydrazine, UDMH, liquid hydrogen and ethanol
- ✓ Its specific gravity is 1.14

2. LIQUID FLUORINE

- ✓ Liquid fluorine has low boiling point of 84.8K
- ✓ It also requires proper insulation equipment to avoid evaporation
- ✓ It is extremely toxic and corrosive in nature. Therefore, special passive coatings have to be used on containers, pipelines, valves etc.
- ✓ It is compatible with most of the liquid fuels
- ✓ Further it has high specific gravity of ~ 1.5

3. HYDROGEN PEROXIDE (H₂O₂)

- ✓ Hydrogen peroxide is a highly reactive liquid and hence it requires special materials and handling systems
- ✓ It has a high boiling point of 424K
- ✓ Its specific gravity is 1.4
- ✓ Highly concentrated form of H₂O₂ is used in rocket engines. This is harmful to the skin of personnel
- ✓ Presence of many impurities such as *MnO₂*, *KMnO₄*, *iron oxide*, *calcium permanganate* either in the containers or in the feed system acts as catalyst in decomposing H₂O₂ in to steam and oxygen gas. This reaction is exothermic and therefore often employed as mono propellant.



4. NITROGEN TETROXIDE (N_2O_4)

- ✓ Nitrogen tetroxide is a storable propellant oxidizer
- ✓ Its high specific gravity (1.44) is an advantage but its high vapour pressure (0.958bar) is a serious disadvantage for the feed system
- ✓ It is compatible with a number of fuels like hydrogen, unsymmetrical dimethyl hydrazine etc.
- ✓ It is hypergolic with several rocket fuels

5. NITRIC ACID

- ✓ Red fuming nitric acid (RFNA) and white fuming nitric acid (WFNA) are used as oxidizers in rockets
- ✓ They are highly reactive, corrosive and poisonous causing storage and handling problems
- ✓ They are compatible with large number of fuels such as hydrogen, UDMH, hydrazine etc. RFNA contains a significant percentage of N_2O_4
- ✓ Its specific gravity is 1.5 and vapour pressure is 0.1378bar

LIQUID FUELS

1. LIQUID HYDROGEN

- ✓ Liquid hydrogen is a cryogenic propellant
- ✓ Its low specific gravity (0.07) and extremely low boiling point temperature (20K) cause several technological problems
- ✓ It requires larger and well insulated storage tanks. Its mixture with air due to leakage can cause explosion
- ✓ All common liquids and gases solidify in liquid hydrogen. These solids may plug the orifices and valves. Therefore, care must be taken to scavenge all lines and tanks of air and moisture (flush with helium or pull vacuum) before use liquid hydrogen as a fuel

2. HYDROCARBONS

- ✓ Petroleum products such as kerosene, diesel oil and gasoline can be used as rocket fuels
- ✓ They are compatible with LOX and N_2O_4
- ✓ Ethyl alcohol along with some water is also used as a rocket fuel with several oxidizers such as LOX , H_2O_2 , N_2O_4 , $RFNA$
- ✓ It gives lower combustion temperature with slightly lower performance

3. HYDRAZINE (N_2H_4)

- ✓ Hydrazine is a colourless, toxic liquid and harmful to personnel
- ✓ Since N_2H_4 is highly reactive with many materials, storage and handling have to be done in a special type of materials. On leakage, it forms an explosive mixture with air leading to fires and accidents
- ✓ Another problem with N_2H_4 is high freezing point (275K). Therefore some chemicals must be used to lower freezing point
- ✓ By using suitable catalysts like Fe , Co and Ni , hydrazine can easily be decomposed. This property make use of N_2H_4 as monopropellant

4. MONO METHYL HYDRAZINE, CH_3NHNH_2 , (MMH)

- ✓ Monomethyl hydrazine (MMH) also ignites easily with air. Its inflammable limit is 2.5–98%. It means, minimum concentration of 2.5% MMH in air is sufficient for explosion (ignition) to occur
- ✓ MMH is the most toxic when inhaled
- ✓ MMH with N_2O_4 is used as a propellant in short range rocket engine

5. UNSYMMETRICAL DIMETHYL HYDRAZINE, $(CH_3)_2NNH_2$, (UDMH)

- ✓ Unsymmetrical dimethyl hydrazine (UDMH) is often used as a 50:50 mixture with N_2H_4 (this mixture is more stable particularly at high temperatures) in combination with oxidizer N_2O_4 or $RFNA$
- ✓ UDMH has a high vapour pressure of 1.117bar at 339K. This can cause cavitations if proper measures in the design of the feed system are not taken
- ✓ The freezing of 50:50 $UDMH-N_2H_4$ mixtures causes a separation into two distinct layers. Therefore, a special remixing operation is required for re-blending if freezing occurs in a space vehicle
- ✓ It is the least toxic when compared to N_2H_4 and MMH

SOLID OXIDIZERS

Solid oxidizers are characterized by high density, high amount of available oxygen, high heat of formation, not or slightly hygroscopic and smooth burning characteristics over a wide pressure range.

Examples of inorganic oxidizers: Ammonium perchlorate (NH_4ClO_4), Potassium perchlorate ($KClO_4$), Nitronium perchlorate (NO_2ClO_4), Sodium perchlorate ($NaClO_4$), Hydrazine perchlorate ($N_2H_3ClO_4$), Ammonium nitrate (NH_4NO_3), Potassium nitrate (KNO_3).

Examples of organic oxidizers: Cyclotrimethylene trinitramine (RDX), Cyclotetramethylene tetranitramine (HMX).

1. AMMONIUM PERCHLORATE (AP)

- ✓ At present, ammonium perchlorate (AP) is the most commonly used oxidizer for composite propellants
- ✓ AP is produced by the reaction between ammonia and perchloric acid. The material is considered as hazardous if ground under 15 μ m.
- ✓ When AP is mixed with fuel, it can generate self sustained combustion under atmospheric air. Its oxygen content is 27.2wt%

2. AMMONIUM NITRATE (AN)

- ✓ Inorganic nitrates are relatively low performance oxidizer than perchlorates
- ✓ Ammonium nitrate (AN) is relatively non-toxic, cheap and can produce smokeless gases with the fuels. Its oxygen content is 20wt%
- ✓ AN is used in gas generator for turbo pump of liquid rocket engines and emergency starter for jet aircraft.

3. ORGANIC OXIDISERS

- ✓ Organic oxidizers are single compound high explosives
- ✓ They contain sufficient quantity of available oxygen for oxidation
- ✓ They are used in composite based and double based propellants
- ✓ They are characterized by efficient combustion, high and uniform burning rate and high specific impulse

Examples: RDX and HMX (Cyclotetramethylene tetranitramine)

3.7.7 SOLID FUELS

The choice of solid fuel is mainly determined by a high energy content, good shelf life, and good thermal properties at low and high temperatures.

Examples: Aluminium powder, Boron, Beryllium, Aluminium hydride (AlH_3), Beryllium hydride (BeH_2).

1. ALUMINIUM POWDER

- ✓ Aluminium powder is widely used in composite type propellants
- ✓ During combustion, it is oxidized into aluminium oxide. This vapour is toxic when inhaled.
- ✓ Also, the solidification of vapour in the nozzle region (due to the temperature difference) affects the vehicle's mass ratio.

2. BORON

- ✓ Boron is lighter than aluminium. It is a high energy fuel
- ✓ However, it is difficult to burn (its melting point is 2304°C) in combustion chamber to obtain high energy for the reasonable length of time

3. BERYLLIUM

- ✓ Beryllium burns much easier than boron. But its vapour is extremely toxic when inhaled. Therefore, it has not been tested experimentally in rockets

4. ALUMINIUM HYDRIDE (AlH₃) AND BERYLLIUM HYDRIDE (BeH₂)

- ✓ Aluminium hydride and beryllium hydride are theoretically attractive fuels, because they release huge volume of heat and hot gases on combustion
- ✓ But, their manufacture is not much easier. They deteriorate chemically during storage.

TABLE 3: MERITS AND DEMERITS OF SOLID PROPELLANTS AND LIQUID PROPELLANTS

S.No.	Solid propellants	Liquid propellants
1.	Solid propellants have relatively lower values of I_{SP}	Liquid propellants have relatively higher values of I_{SP}
2.	Solid propellants are dense and therefore larger quantity of propellants can be packed into a small space	On account of lower density, the liquid propellants need large storage space
3.	Solid propellant rockets are simple in design and construction. There is no need of pumps and propellant feeding system	Liquid propellant rockets are more complicated. They require turbo pump systems, container, valves etc., which increase the total weight of the rocket
4.	It is more difficult to control combustion of solid propellants and regulate thrust	It offers more flexible and greater control over the thrust. The operation is more stable
5.	In case of emergency, it is difficult to turn off the combustion of solid propellants in midway	It is much easier to stop the operation of liquid propellants in case of malfunctioning
6.	Solid propellant rockets are smaller ones, meant for short range military applications	Liquid propellant rockets are more economical for long range space and military applications

SOLVED PROBLEMS

1. A rocket has the following data: Propellant flow rate = 5 Kg/s, Thrust = 7 KN. Calculate I_{SP} , C and SPC.

Given: $\dot{m} = 5 \text{ kg/sec}$; $F = 7000 \text{ N}$; $g = 9.81 \text{ m/sec}^2$

(i) Specific impulse,
$$I_{SP} = \frac{F}{\dot{w}} = \frac{7000}{5 \times 9.81} \quad \left[\because \dot{w} = \dot{m} \times g \right]$$

$$I_{SP} = 142.7 \text{ sec.}$$

(ii) Effective exhaust velocity, $C = \frac{F}{\dot{m}}$

$$C = \frac{7000}{5}$$

$$C = 1400 \text{ m/sec}$$

(iii) Specific propellant consumption, $\text{SPC} = \frac{1}{I_{SP}} = \frac{1}{142.7}$

$$\text{SPC} = 0.007 \text{ sec}^{-1}$$

Determine the oxygen balance for the following compounds:

S.No .	Substance	Molecular weight	$Z - \left(X + \frac{Y}{2} \right)$	Oxygen balance
i.	Glyceryl trinitrate, $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	227	$9 - \left(3 + \frac{5}{2} \right) = 3.5$	$\frac{3.5 \times 16}{227} \times 100 = +24.7$
ii.	Picric acid, $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$	229	$7 - \left(6 + \frac{3}{2} \right) = -0.5$	$\frac{-0.5 \times 16}{229} \times 100 = -3.5$
iii.	Glycol Dinitrate	152	$6 - \left(2 + \frac{4}{2} \right) = +2$	$\frac{+2 \times 16}{152} \times 100 = +21.03$

	$C_2H_4N_2O_6$			
iv.	Diethylene Glycol Dinitrate $C_4H_8N_2O_7$	196	$7 - \left(4 + \frac{8}{2}\right) = -1$	$\frac{-1 \times 16}{196} \times 100 = -8.16$
v.	RDX $C_3H_6N_6O_6$	222	$6 - \left(3 + \frac{6}{2}\right) = 0$	zero
vi.	PETN $C_5H_8N_4O_{12}$	316	$12 - \left(5 + \frac{8}{2}\right) = +3$	$\frac{+3 \times 16}{316} \times 100 = +15.2$

TEST YOUR UNDERSTANDING

- Write a note on the classification of explosives.
- What is meant by oxygen balance ? How is it important ? Determine the oxygen balance for the following :
 - Glyceryl trinitrate ($C_3H_5N_3O_9$)
 - Picric Acid ($C_6H_3N_3O_7$)
 - PETN ($C_5H_8N_4O_{12}$)
- Describe the classification of rocket propellants.
- Write briefly on liquid propellants.
- Write short notes on (i) Detonators (ii) Rocket Fuels (iii) Dynamites.
- Define an explosive. How are explosive classified? What are the requirements of a good explosive?
- What are rocket propellants? How are they classified? What are the requirements for the selection of a propellant?
- Write a note on explosives.
- Explain the classification of propellants with suitable examples.
- How are rocket engines classified?
- Explain the basic principle of a rocket engine.
- Define the terms: (i) Specific impulse, (ii) Thrust, (iii) Effective exhaust velocity, (iv) Specific propellant consumption.
- What are the requirements of a good propellant?
- Write an account on liquid oxidizers.
- Write an account on liquid fuels used in rocket engines.

16. What are solid propellants? Explain their components with suitable examples.
17. Compare the merits and demerits of solid propellants and liquid propellants.
18. Write an account on assessment of explosives.
19. What are high explosives? Explain the different types of high explosives with suitable examples.
20. Write a short note on dynamites.
21. Compare low explosives, primary explosives and high explosives.
22. In a rocket engine, a thrust force of 15KN is produced by burning 10Kg of propellant per sec. Calculate its specific impulse and specific propellants consumption.
23. Calculate effective exhaust velocity of a rocket engine when 10KN thrust force is produced by burning 5 Kg of propellant per sec.
24. Determine the oxygen balance for the following compounds:
 - (i) Cyclonite, $C_3H_6N_6O_9$
 - (ii) Mercury fulminate, $Hg(ONC)_2$
 - (iii) Diazo dinitrophenol, $C_6H_2N_4O_5$.

Lubricants: Introduction - Properties and functions of lubrication. Lubrication mechanism: Hydrodynamic lubrication, Boundary lubrication, Extreme pressure lubrication. Properties of lubricants: Viscosity index (VI), Flash and fire point, Cloud and pour point, Aniline point, Oiliness, Sligh oxidation test, Corrosion stability. Classification of lubricants: Liquid lubricants, Compounding of oil. Semisolid lubricants: Greases, Types of greases. Solid lubricants: Graphite and Molybdenum disulphide (MoS_2). Solved Problems and Excercises.

INTRODUCTION

Efficient operation of machinery depends on the nature of the lubricant and its application. Most modern machinery requires application of lubricants in a precise controlled manner. Most modern machinery utilizes different lubrication methods and different types of lubricants are employed for different parts. A lubricant may be oil, grease, graphite or any substance in gaseous, liquid, semisolid or solid forms which permits free action of mechanical devices and prevents damage by abration and seizing of metal or other components through unequal expansion caused by heat. In other words, a lubricant is also defined as a substance which is capable of reducing friction between two surfaces which are sliding over the other.

Lubrication is a process in which friction is reduced between any two surfaces which are sliding one over the other with the help of a lubricant as shown in Fig 1.

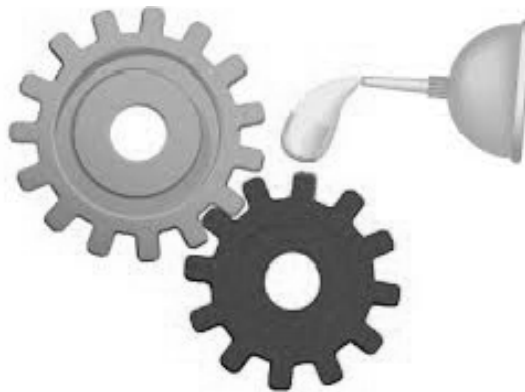


Fig. 1. Lubrication process

PROPERTIES OF A LUBRICANT

- A lubricant should not change its own properties during lubrication.
- It should not undergo oxidation, decomposition, emulsification during lubrication.

- It should not corrode the parts of the machine.
- It should be cheap and readily available.
- It should not be toxic to the operating person.
- It should have high viscosity index, oiliness and aniline point.
- It should have high flash and fire points than the operating temperature of the machine.
- The cloud and pour points should be lower than that of the operating temperature of the machine.
- A lubricating oil should have low volatility.
- It should deposit least amount of carbon during use.

FUNCTIONS OF A LUBRICANT

- A lubricant reduces surface deformation, wear and tear as there would be no direct contact between the surfaces.
- It helps in preventing the entry of moisture, dust and dirt between the moving parts of the machine
- It acts as a coolant and reduces the loss of energy in the form of heat
- It enhances the efficiency of machine by reducing the wastage of energy.
- It decreases the liberation of frictional heat.
- It reduces the maintenance, operating and running cost of machine.

MECHANISM OF LUBRICATION

The working phenomenon of lubrication can be explained by the following three mechanisms:

- (a) Thick-Film lubrication (Fluid-Film or hydrodynamic lubrication)
- (b) Thin Film lubrication (Boundary lubrication) and
- (c) Extreme Pressure lubrication

FLUID-FILM OR THICK FILM OR HYDRODYNAMIC LUBRICATION

Hydrodynamic lubrication was first studied by Osborne Reynolds (1842 - 1912). When two moving or sliding surfaces are separated from each other by a thick film of fluid about $1000 \text{ \AA}$ to avoid direct metal to metal contact for reducing the friction is termed as fluid film lubrication. The diagrammatic representation of this mechanism is shown in Fig 2. Here, the lubricant film covers the irregularities of the moving surfaces and forms a thick layer in between them thereby reducing the wear and tear between the surfaces. This reduction in wear and tear is due to the internal resistance between the particles of the lubricant moving over each other. The coefficient of friction is as low as 0.001 to 0.03. This type of lubrication depends mainly on the viscosity of the lubricant. A lubricant should have minimum viscosity

under working conditions and should remain in place while separating the surfaces. In such cases, friction depends on the viscosity, thickness of the lubricant, relative velocity and the area of the moving / sliding surfaces. This type of lubrication is observed in the case of a shaft running at a fair speed and in well lubricated bearing with low load. This lubrication mechanism is used in machineries working under low load and fair speed conditions. Delicate instruments and machines like watches, clocks, guns, sewing machines and scientific instruments require this type of lubrication. **Examples:** Hydrocarbon oils blended with selected long chain polymers.

Hydrocarbon oils are mineral oils having low molecular weight with about 12 to 50 carbon atoms. They are considered to be a good lubricant for thick-film lubrication. To maintain the viscosity and to make it suitable for all seasons, it is blended with selected long chain polymers.

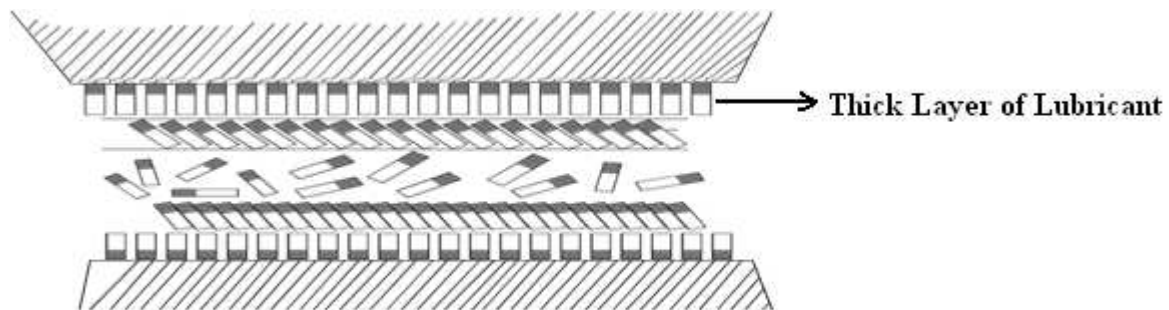


Fig. 2. Fluid-film or thick film or hydrodynamic lubrication

BOUNDARY LUBRICATION

When the load is high and under low speed conditions, the hydrodynamic pressure may not be sufficient to support the load when the surfaces come into contact with each other. This type of contact occurs at the hilly regions and is called as asperities. The extent of asperity contact depends on the surface roughness, fluid film pressure, normal load, hardness and elasticity of the asperities. Many of the asperities undergo elastic deformation under the contacting conditions and the normal load is supported by the asperities and the fluid film. This condition is referred to as the elasto hydrodynamic lubrication (EHL) and it describes the surface temperature, fluid film thickness and the pressure supporting the load. Increase in the contact pressure above the EHL conditions causes deformation of the contacting asperities, increases the number of contacts and decreases the thickness of the fluid film. When the thickness of the fluid film falls below the average relative surface roughness, the contact surface becomes the major load supporting system. This results in wear, deformation, abrasion and fatigue under dry sliding condition. Due to frictional heating, chemical reactions occur between the lubricant and the asperity surface

forming a boundary chemical film which can be either beneficial or detrimental in terms of wear. The load sharing by the asperities and the occurrence of the chemical reactions together constitute the lubrication process which is commonly referred to as the boundary lubrication (BL). This type of lubrication depends upon the oiliness of the lubricants. For boundary lubrication, the lubricant should have low viscosity index, high resistance to heat and oxidation, good oiliness and low pour point. The lubricant must also have long hydrocarbon chain with lateral attraction between the chains, active groups for the formation of chemical linkages with the surfaces. Boundary lubrication is seen in railway track joints, rollers, tractors.

Examples: Graphite, molybdenum disulphide

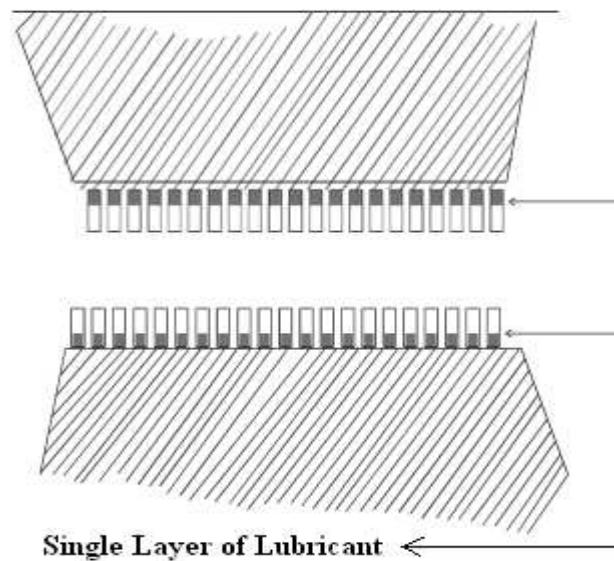


Fig. 3. Boundary Lubrication showing a layer of adsorbed thin layer of a lubricant (vegetable or animal oil)

EXTREME PRESSURE LUBRICATION

When the moving or sliding surfaces are under very high pressure and speed, a high local temperature is attained. Under such conditions, a liquid lubricant stick on to the moving parts, may decompose or may even vaporize. In order to meet the extreme pressure condition, special additive is added to the lubricant and is called as extreme pressure lubrication. The extreme pressure additive forms a durable film and is capable of withstanding high load and high temperatures. The additives are organic compounds containing sulphur, chlorine, lead, phosphorous etc. The additives are not effective with surfaces like chromium, silver, titanium etc. which are chemically inert. They react with metallic surfaces existing at high temperatures forming metallic chlorides, sulphides or phosphides.

The extreme pressure additives are of the following types:

- i) Compounds containing oxygen - fatty acids, esters and ketones.
- ii) Compounds containing sulphur alone or sulphur and oxygen.
- iii) Organo chlorine compounds – chlorinated wax.
- iv) Organo sulphur compounds - sulphurised fats, sulphurised olefins.
- v) Organic compounds containing lead.
- vi) Organic compounds containing trivalent and pentavalent phosphorous.

PROPERTIES OF LUBRICANTS

VISCOSITY INDEX (VI)

It is the measure of the resistance offered by a liquid to its own flow and is an important property of a liquid lubricant. Unit is poise. Viscosity determines the operating characteristics of a lubricant. If the viscosity is too low, a liquid film cannot be maintained between the moving / sliding surfaces and consequently results in excessive wear. If the viscosity of the lubricant is too high, it will result in excessive friction. Viscosity of liquid decreases with the increase in temperature and the liquid lubricant becomes thin. Hence viscosity of a good lubricant should not change with the change in temperature. The rate at which the viscosity of an oil changes with temperature is called the viscosity-index (V.I). For an oil of low viscosity-index, the viscosity of the oil decreases rapidly with the increase in temperature. If the viscosity-index of an oil is high, then the viscosity of the oil is slightly affected on raising the temperature.

Viscosity measurement is made by determining the time required for a given volume of oil to flow from a given height through a calibrated capillary tube under its own weight at a given temperature. The viscosity thus measured is called the kinematic viscosity and is equal to the absolute viscosity divided by the density of the oil and is expressed in centistokes (cm²/s) where, 1 centistoke = centipoises/density oil in g/cm³. A schematic diagram of redwood viscometer is shown in Fig. 4. An arbitrary scale known as the viscosity index (VI) is used to indicate the effect of temperature on viscosity. In order to assess the viscosity of oils, two standard oils such as paraffinic-base Pennsylvanian oils (VI = 100) and naphthenic-base Gulf oils (VI = 0) are used. The scale is based on the arbitrary fixing of a value 100 for Pennsylvanian oils containing paraffins and for which the viscosity is slightly affected with the increase in the temperature. The VI is fixed as zero for the Gulf oil containing naphthalene and for which the viscosity decreases to the maximum with the increase in temperature. A high VI for an oil indicates that the viscosity of the oil is affected by the increase in the temperature. For low VI, the viscosity of the oil changes with the increase in the temperature.

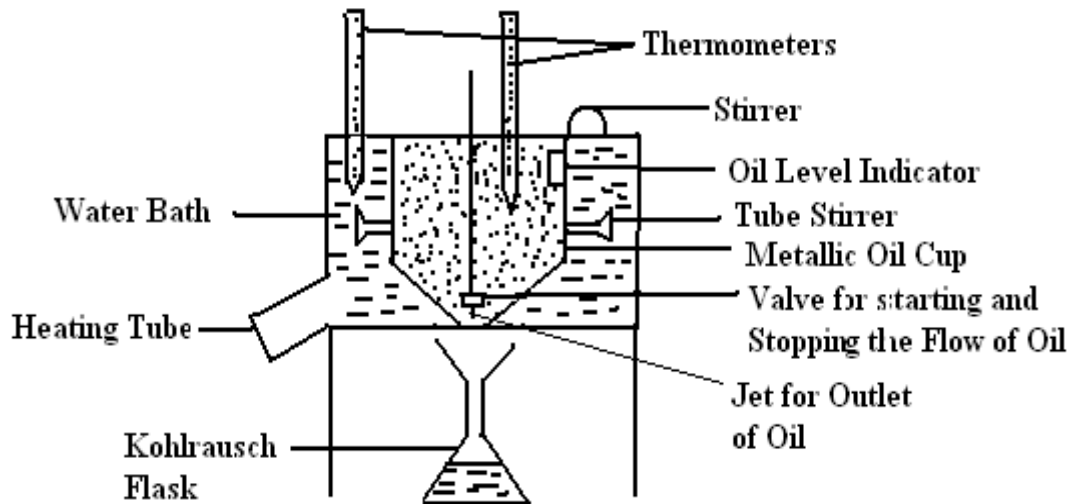


Fig.4. Redwood Viscometer

The VI of a test oil is assigned by comparing the viscosity of oil having VI = 0 with the viscosity of oil having VI = 100 at 38°C. They both have the same viscosity as that of the test oil at 99°C.

The VI of the test oil is given by the formula

$$VI = (L - U / L - H) \times 100$$

where H is the viscosity at 38°C of the standard oil with 100 VI, L is the viscosity at 38°C of the standard oil with 0 VI and U is the viscosity of the test oil at 38°C. The VI of an oil can be improved by the addition of linear polymers.

FLASH AND FIRE POINT

Flash and fire points are of importance to determine the use of lubricating oil at higher temperatures. Flash point is defined as the lowest temperature at which the lubricant oil gives off enough vapours to give a flash when the vapours come into contact with a test flame. Fire point is defined as the lowest temperature at which the vapours of the oil burn continuously, atleast for five seconds, when the vapours come into contact with a test flame. In most cases, the fire-points are 5 to 40° higher than the flash points.

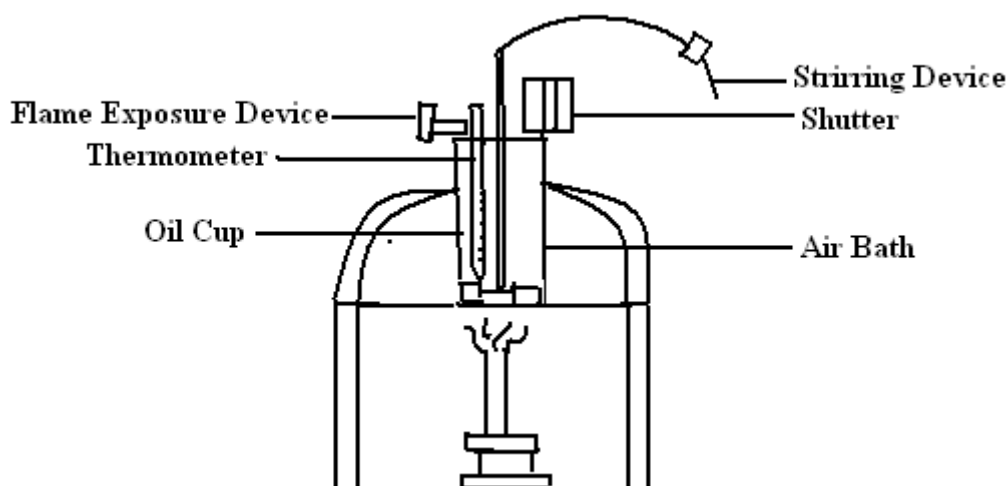


Fig.5. Pensky- Martins Apparatus

The flash and fire points of a lubricant are determined using Pensky-Martins apparatus is shown in Fig. 5, which essentially consists of:

An oil cup is about 5 cm in diameter and 5.5 cm deep. The level to which oil is to be filled is marked inside the cup. The cup lid is provided with four openings of standard sizes. Through one of these passes a thermometer; while the second opening is used for introducing test flame. Through third opening passes stirrer carrying two brass blades; while the fourth is meant for admission of air.

- a) **Shutter** is a lever mechanism, provided at the top of the cup. By moving the shutter, opening in the lid open and flame (carried by a flame exposure device) is dipped into this opening, thereby bringing the flame over the oil surface.
- b) **Flame exposure device** is a tiny flame, connected to the shutter by a lever mechanism.
- c) **Air bath** is supported by its flange over an air-bath, which is heated by a gas burner.
- d) **Pilot burner** produces a test flame automatically when it gets extinguished.

Working: An oil under examination is filled upto the mark in the oil cup and then heated by heating the air bath by a burner. Stirrer is worked between tests at a rate of about 1 to 2 revolutions per second. Heat is applied so as to raise the oil temperature by about 5°C per minute. At every 1°C rise of temperature, test flame is introduced for a moment, by working the shutter. The temperature, at which a distinct flash (combination of a weak sound and light) appears inside the cup is recorded as the flash point. The heating is continued and the test flame is applied as before. When the oil ignites and continues to burn for at least 5 seconds, the temperature reading is recorded as the fire point of the oil.

CLOUD AND POUR POINT

When the oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance, is called its cloud point. The temperature, at which the oil ceases to flow is called its pour point. Cloud and pour points indicate the suitability of lubricants in cold conditions. Lubricant used in a machine working at low temperatures should possess low pour point and the wax present in the lubricating oil raise the pour point.

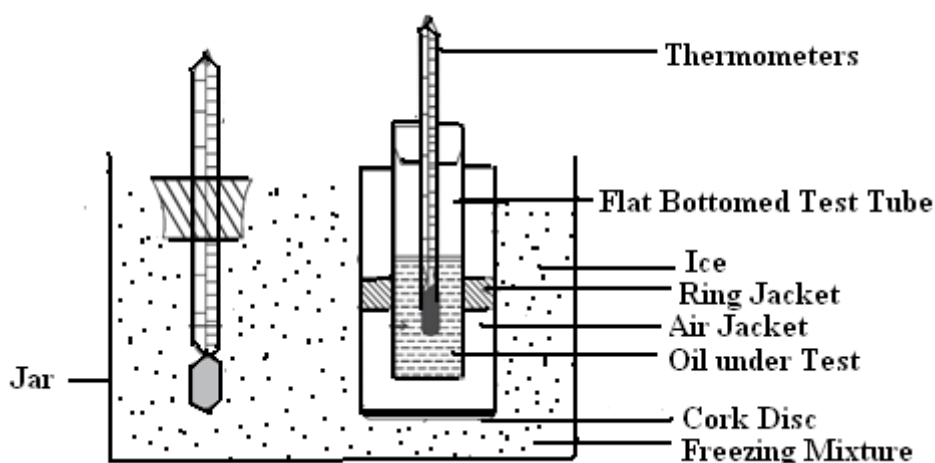


Fig. 6. Cloud and Pour Point Apparatus

Determination of cloud and pour point is carried out with the help of pour point apparatus shown in Figure. 6. It consists of essentially a flat bottomed tube (about 3 cm in diameter and 2cm high) enclosed in an air jacket. The jacket is surrounded by freezing mixture (ice + CaCl_2) contained in a jar. The tube is half filled with oil. A thermometer is introduced in the oil. As the cooling proceeds slowly via the air jacket, the temperature falls continuously. With every degree fall of temperature of the oil, the tube is withdrawn from the air jacket for a moment (2 – 3 seconds) and examined. It is then replaced immediately. The temperature at which cloudiness is noticed is recorded as the cloud point. After this, cooling continues and the test tube is withdrawn after every 3°C fall off temperature and tilted to observe the flow or pour of oil. The temperature at which oil does not flow in the test tube, even when kept horizontally for 5 seconds, is recorded as the pour point.

ANILINE POINT

The aniline point is a physical characteristic of oil, and refers to the minimum temperature at which the oil and the same amount of the compound aniline ($\text{C}_6\text{H}_5\text{NH}_2$) are perfectly miscible.

Aniline point indicates the possible deterioration of the lubricating oil in contact with

rubber surfaces. Aromatic hydrocarbons tend to dissolve rubber and hence lubricating oils with a lower aromatic hydrocarbon should be used. Aniline point of oil is defined as the minimum equilibrium solution temperature for equal volumes of aniline and the oil sample. The test for finding the aniline point of given oil is relatively simple. It is determined by mixing equal volumes of aniline and the sample oil in a test tube and heating the mixture till a homogeneous solution is obtained. The solution is then allowed to cool at a controlled rate and the temperature at which the oil and aniline phases separate out is recorded as the aniline point of the oil.

OILINESS

The term “oiliness” is defined as the property of lubricants by virtue of which one fluid gives lower coefficients of friction (generally at low speeds or high loads) than another fluid of the same viscosity. Oiliness of a lubricant is a measure of its capacity to stick on to the surfaces of machine parts, under conditions of heavy load and pressure. Lubricants with good oiliness stick on and remain between the surfaces even under high operating pressures. Mineral oils are generally poor in their oiliness while animal and vegetable oils have good oiliness. The mineral oils tend to be squeezed out from machinery parts at operating pressures thereby stopping their lubrication action. Hence additives such as vegetable oils (possesses good oiliness) or the higher fatty acids (oleic or stearic acids) are added to mineral oils to improve their oiliness. No direct test is available for detecting oiliness of lubricant.

SLIGH OXIDATION TEST

A good lubricant should have low sligh oxidation number. Low sligh number indicates high resistance towards oxidation. Because oxidation and pyrolysis are the main cause of decomposition of lubrication. The harmful effect of contamination of the lubricant by this oxidation process can be minimized by the use of oil filtration and periodic change of the oil. The common test for oxidation stability of oils can be determined by “Sligh oxidation test”. In this test, a known weight (10gm) of oil is taken in a long necked flask filled with sufficient amount of oxygen. The flask is heated to a temperature of 200°C in the oil bath and maintained it for 2 hour. The flask is then removed and cooled. The sample is diluted with naphtha and allowed to stand for undisturbed for an hour in order to precipitate the oxidized impurities. The precipitate formed is filtered, washed, dried and weighed. The weight of the precipitate, in milligrams per 10 gram of the sample, is expressed as sligh number in percentage.

CORROSION STABILITY

Corrosion stability of the lubricant oil is estimated by carrying out corrosion test. A polished copper strip is placed in the lubricant oil for a specified time at a particular temperature. After the stipulated time, the strip is taken out and examined for

corrosion effects. If the copper strip is tarnished, indicates the lubricant oil contains chemically active substances which cause the corrosion of the copper strip. A good lubricant oil have no effect on the copper strip. To retard corrosion effects of the lubricant oil, inhibitors like organic compounds of P, As, Cr, Bi or Pb.

CLASSIFICATION OF LUBRICANTS

Lubricants can be broadly divided , on their natural state of existence into (1) Liquid lubricants or lubricating oils (2) Semi-solid lubricants or greases (3) Solid lubricants.

LIQUID LUBRICANTS

Liquid lubricants are mainly oils derived from higher boiling fractions of petroleum, as well as from animal and vegetable oils. They are used to reduce the friction by providing a continuous fluid film between moving metallic surfaces. They act as coolant, sealing agent and corrosion preventer. A lubricating oil should have high boiling temperature (low pressure), low freezing point, adequate viscosity for the chosen application, stability against heat, high resistance to oxidation and non-corrosive characteristics.

Liquid lubricants include three main classifications,

- (i) Mineral or petroleum oils
- (ii) Animal and vegetable oils, and
- (iii) Blended oils derived from petroleum oils containing a variety of derivatives.

MINERAL OR PETROLEUM OILS

Mineral or petroleum oils are derived from the three petroleum fractions such as light, medium, and heavy fractions obtained by fractional distillation of petroleum. The fractions contain wax, asphalt and other oxidisable impurities.

Purification of petroleum fractions is carried out in the refinery by

1. Solvent extraction
2. Dewaxing
3. Finishing operations

Solvents such as phenol, p-cresol, nitrobenzene, dichloro ethyl ether, liquid propane, furfural and liquid sulphur di oxide which are immiscible with the oils are used to remove asphalt and other impurities. Mineral or petroleum oils consist of a mixture of paraffins, naphthalenes and aromatic hydrocarbons. The physical properties of the oils depend on the relative proportions of the constituent hydrocarbons. Paraffinic oils have low viscosity and density and tend to oxidize easily under certain

conditions. Aromatic oils are dark in colour, having low viscosity index, and high density. They are relatively more stable to oxidation. Naphthalenic oils exhibit characteristics properties in between the paraffinic and aromatic oils. They have a low pour point.

ANIMAL AND VEGETABLE OILS

Animal and vegetable oils are essentially glycerides of higher fatty acids and are called fixed oils as they decompose on heating. These oils are mainly used as additives for petroleum based lubricating oils because of their high oiliness and for the manufacture of soaps in the preparation of greases. Before the advent of the petroleum industry, oils of the animal and vegetable origins were the most commonly used lubricants. They possess high good oiliness. Normally, they are used as “blending agent” with other lubricating oils (like mineral oil) to produce desired products for present applications. However, they are rarely used because (i) they are costly;(ii) they undergo oxidation easily and form gummy and acidic products and (iii) they have a tendency to undergo hydrolysis when allowed to remain in contact with moisture or aqueous medium.

COMPOUNDING OF OIL OR BLENDED OIL

Compounding of oils or blended oils is derived from petroleum based lubricating oils. The petroleum oils are incapable of satisfying the lubricating properties for modern machineries. Therefore, additives are essential to improve the properties of the oils. A variety of chemical compounds are added to the extent of 10%. The additives are oiliness carriers, pour point depressants, viscosity index improvers, thickeners, antioxidants, corrosion inhibitors, anti-wear agents or extreme pressure additives, detergents, anti foaming agents, emulsifiers and deposit inhibitors.

Oiliness carriers: Oiliness of a lubricant can be increased by addition of a vegetable oils like coconut oil, castor oil and fatty acids e.g., palmitic acid, stearic acid, oleic acid, etc.

Pourpoint depressants: Pourpoint depressants enable the oil to remain fluid even at low temperature by preventing the precipitation of wax. Phenol and polyesters are used as pourpoint depressants.

Viscosity index improvers: Viscosity index improvers are certain high molecular weight linear polymers and they reduce the rate of change of viscosity with temperature. Examples are polyisobutylenes, polymethacrylates and n-hexanol.

Thickeners: Thickeners are substances of molecular weight between 300 and 3000. They are added to increase the viscosity in the lubricating oil. Polystyrene, polyesters are used as thickeners.

Antioxidants or oxidation inhibitors: Antioxidants or oxidation inhibitors retard the oxidation of oils during combustion process. It is particularly added to lubricants used in internal combustion engines and turbines etc where oxidation of oil is a serious problem. The antioxidants are aromatic, phenolic or amino compounds like 2-naphthol and phenyl-1-naphthylamine.

Corrosion inhibitors: Corrosion inhibitors are organic compounds of phosphorous or antimony. They prevent the metal from corrosion in contact between the metal surfaces and the corrosive surfaces. Alkyl succinic acids, metallic salts of thio phosphoric acid, metal phenates are the examples of corrosion inhibitors.

Anti-wear agents or extreme pressure additives: These substances are adsorbed on the metal surfaces or react with metal surface by minimizing friction and wear under boundary lubrication conditions. Examples are tri cresyl phosphate and zinc dialkyl dithio phosphate. They act as both anti wear agents and anti corrosive agents. For extreme pressure conditions organic compounds containing sulphur, phosphorous and chlorine are used as extreme pressure additives.

Detergents: At 2-10% concentrations of detergents the deposits are removed particularly in internal combustion engines. They form colloidal suspensions preventing the formation of deposits. Barium phenoxides and sulphonates are the detergents used for automotive engines.

Antifoaming agents: Anti foaming agents are the chemical substances used to decrease the foam formation. Examples are glycol and glycerol.

Emulsifiers: Emulsifiers are the chemical substances tendency to separate dirt, grit, foreign matter. Example: sodium salts of sulphonic acid.

Deposit inhibitors: Sometimes deposits are formed in internal combustion engine due to imperfect combustion. Deposit inhibitors are the additives used to disperse and clean the deposit. Examples are detergents such as the salts of phenol and carboxylic acids.

SYNTHETIC LUBRICANTS

Synthetic lubricants are formed from chemically prepared pure chemicals rather than refined from crude oil. This gives them significant advantages over refined oils. Synthetic lubricants can meet the most drastic conditions such as those existing in aircraft engines, in which they are used in the temperature range of -50°C and 250°C . A lubricant should possess low freezing point, high viscosity index and also should be non-inflammable.

Synthetic lubricants can be used under the following conditions:

1. High temperature,
2. When atmosphere is chemically reactive
3. Under certain specific operating conditions

Characteristics of synthetic lubricants

- It is non-flammable
- It has high flashpoint
- It has high thermal stability at high temperature
- It has high viscosity index
- It is chemically stable.

Some of the important synthetic lubricants are given below:

Polymerized hydrocarbons

Polymerized hydrocarbons are polymers in the molecular weight ranging from 500–50,000. It is residue free, light in colour, free from non-hydrocarbon impurities, chemically non-reactive and high temperature lubricants. Examples are polyethylene, polypropylene, polybutylene.

Polyglycols and its compounds

They are water soluble as well as water insoluble lubricants and are used in rubber bearings and joints. They are not used at high temperature conditions since they undergo thermal decomposition to form volatile compounds. Examples are polyethylene glycol, polypropylene glycol and polyglycidyl ethers.

Organic amines, imines and amides

They are good synthetic lubricants as they possess low pour point and high viscosity index. It can be used under the temperature range of -50°C to 250°C.

Silicones

Silicones are effective synthetic lubricants as they are not easily oxidizable below 200°C and possess high viscosity index. They are not employed for high temperature applications.

Fluorocarbons

They are effective at high temperature as they are inert and resistant to heat and chemicals.

GREASES OR SEMI-SOLID LUBRICANTS

Lubricating grease is a semi-solid, consisting of soap dispersed throughout the liquid lubricating oil. It is obtained by combining lubricating oil with thickening agents. The liquid lubricant may be petroleum oil or even synthetic oil with additives for specific requirements.

Greases are prepared by saponification of tallow or fatty acid (fat) with lime or caustic soda (alkali) followed by addition of hot lubricating oil under agitation. The consistency of finished grease is determined by the addition of mineral oil. Generally, the structure of grease is gel. Soaps are gelling agents, which provide inter-connect structure (intermolecular forces) containing the added oil. At high temperature, the soap dissolves in the oil, the inter-connected structures ceases to exist and the grease liquifies. The nature of the soap decides the temperature upto which the grease can be used, its consistency and its resistance to water and oxygen. In order, to improve the heat resistance of grease, inorganic solid thickening agents (finely divided clay, bentonite, colloidal silica and carbon black etc.) are added. Grease supports the operating condition as much heavier load at lower speeds due to its higher shear or frictional resistance than oil. Internal resistance of grease is much higher than that of lubricating oils; therefore it is better to use oil instead of grease. Compared to lubricating oils, grease cannot effectively dissipate heat from the bearings, so work at relatively lower temperature.

Grease is used in following situations

- a) The situation where oil cannot remain in place due to high load, low speed, intermittent operation, sudden jerks etc
- b) In bearing and gears that work at high temperatures
- c) In situations where bearing needs to be sealed against of entry of dust, dirt, grit or moisture, because greases are less liable to contaminate
- d) In situations where dripping or spurting of oil is undesirable.

IMPORTANT TYPES OF GREASES ARE

Calcium based greases or cup greases are emulsions of petroleum oil with calcium soaps. They are prepared by adding required amount of calcium hydroxide to a hot oil (like tallow) under agitation. These greases are cheap and most commonly used. They are insoluble in water, because they are water resistant. They are used at low temperature while above 80°C, oil and soap begins to separate out.

Soda based greases are petroleum oils , thickened by mixing sodium soaps. They are soluble in water, so they are not water resistant. They can be used upto 175°C. They are used in ball bearings where lubricant is heated by friction.

Lithium based greases are petroleum oils, thickened by mixing lithium soaps. They are water-resistant and suitable for use at low temperatures (up to 15°C) only.

Axle greases are very cheap resin greases, prepared by adding lime to resin and fatty acids. They are water resistant and suitable for less delicate equipments working under high loads and at low speeds.

SOLID LUBRICANTS

Solid lubricants are solids applied to friction surfaces to reduce friction and wear and prevent surface damage. They may be powders, films, or composite materials. Solid lubricants are roughly classified as shown in Table 1.

Table 1: Classification of solid lubricants

Type	Examples
Metals and inorganic compounds (a) Layered structure compounds (b) Non-layered compounds (c) Soft metals	Molybdenum disulfide, graphite, boron nitride PbO, CaF ₂ Pb, Sn, Au, Ag, Cu
Organic compounds (a) Fats, soaps, waxes (b) Polymers (c) Malleable substances	Beef tallow, lithium stearate, bee wax, Polytetrafluoroethylene (PTFE), polyimide Phthalocyanine

Substances with layered structures such as molybdenum disulfide and graphite, are widely used and their structures are shown in Figure 2.7. These solid lubricants are highly anisotropic, with weak bonding between particular crystal planes or molecules. Their self-lubrication properties provide low friction coefficients. A variety of solid materials such as inorganic and organic solids with inherent lubricating capability are available for use in solid lubricants. The characteristic properties of solid lubricants are

- (i) Strong adhesion to the applied surface
- (ii) Low shear strength
- (iii) Chemically inert

- (iv) Good thermal conductivity
- (v) Stability at operating temperatures.

Solid lubricants are used where

- A lubricating film cannot be formed by use of lubricating oils or greases
- Contamination (by the entry of dust or grit particles) of lubricating oil or grease is unacceptable.
- The operating temperature or load is too high
- Combustible lubricants

Both molybdenum di sulfide and graphite are used either in the dry powder state or mixed with water or oil. The solids occupy the low spots in the surfaces of moving parts and form films in the state of solid, have low frictional resistance. The co-efficient of friction of solid lubricants is between 0.005 and 0.01 resulting in an efficient lubrication action. Other solid lubricants are tungsten disulfide, boron nitride, leadoxide, antimonyoxide, lead, silver, fluorinated ethylene propylene (FEP), perfluoroalkoxy copolymer (PFA), etc. Solid lubricants have the properties of low coefficient of friction, highest load carrying capacity, corrosion resistance (susceptibility to galvanic corrosion) and electrical conductivity.

Solid lubricants are used primarily as extreme pressure (EP) or anti-wear type additives and are applied in one of three ways. The first and most popular application of solid lubricants, particularly molybdenum disulfide and graphite, is an Extreme Pressure additive in grease formulations. The plate-like structure of these solid lubricant reduces friction by allowing the surfaces in motion to easily slide over each other and are used in pins and bushings. Other method of applying solid lubricants is the bonding or impregnation of these friction modifiers onto the surface of various machine components, such as cylinder liners and piston in large stationary natural gas engines. The bonded film of solid lubricant forms a sacrificial wear film on the surface of the component subjected to friction.

GRAPHITE

Graphite consists of a multitude of flat layers, one atom thick which are held together by only weak bonds so that the force to shear the crystals parallel to the layers is low. Consequently, the parallel layers slide over one another easily. The structure of graphite is given in fig 2.7. Normally, some organic substances are used with solid lubricants so that they may stick tightly onto the metal surface. The layer structure of graphite consists of a hexagonal arrangement of carbon atoms within each layer and the layers held by weak attractive forces. Graphite will not exhibit its lubricating action in high vacuum. It is classified into two groups: natural and synthetic. Synthetic graphite is a high temperature sintered product and is characterized by its high purity of carbon (99.5-99.9%). Natural graphite is derived

from mining. Graphite consists of carbon (high grade graphite 96-98% carbon), sulfur, SiO_2 and ash. The higher the carbon content and the degree of graphitization (high crystalline) the better the lubricity and resistance to oxidation. Graphite is best suited for lubrication in a regular atmosphere. Water vapor is a necessary for graphite lubrication. The adsorption of water reduces the bonding energy between the hexagonal planes of the graphite to a lower level than the adhesion energy between a substrate and the graphite. It is used as a solid powder for lubrication in oil less bearings, colloidal dispersions in water or oil or as grease. The dispersion of graphite solid powder in water is aqua dag and where as the powder in oil is oil dag. The aqua dag is used in air compressors, lathes and machines used in food processing where the lubricant is free from oil required. Oil dag is used in internal combustion engines as it forms a film between the piston rings and the cylinder bringing a tight-contact for increasing the compression of the air-fuel mixture. The effective lubrication by graphite is due to the presence of adsorbed water and gases between layers which decrease the inter-laminar attraction.

Advantages

- It accelerates the galvanic corrosion of the surfaces.
- In an oxidative atmosphere graphite is effective at high temperatures up to 450°C continuously and can withstand much higher temperature peaks.
- The thermal conductivity of graphite is generally low as $\sim 1.3 \text{ W/mK}$ at 40°C .

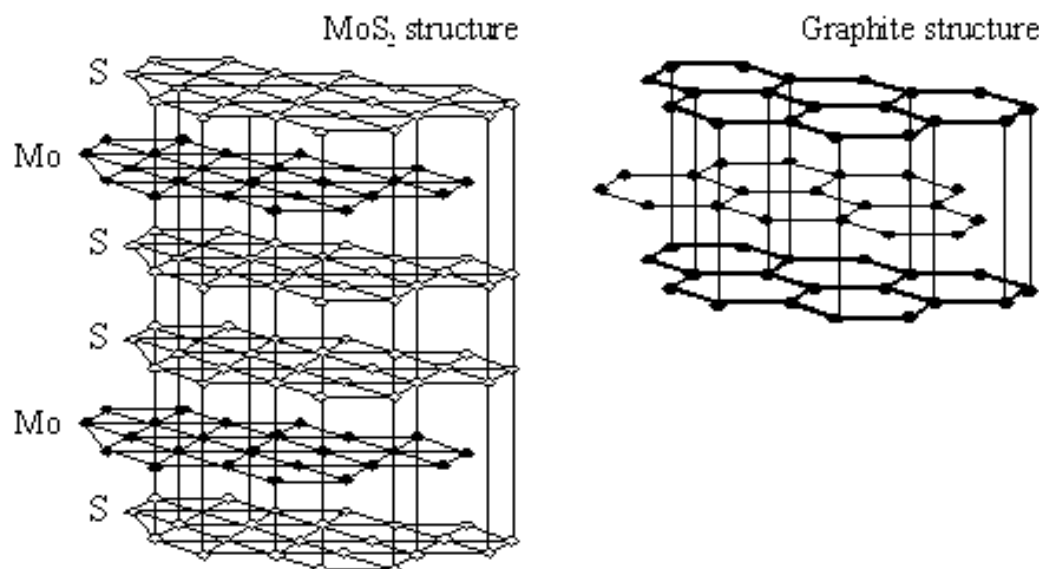


Fig. 2.7 Structure of graphite and molybdenum disulphide (MoS_2)

MOLYBDENUM DISULPHIDE (MoS_2)

Molybdenum disulphide consists of a layer of Mo atoms sandwiched between two layers of S atoms is shown in fig.2.7. The Mo-Mo layer distance is about $3.15 \text{ \AA}$

while the sulphur layers are separated by a distance of 3.08 Å. It is used in the form of powder in oil-less bearings or as dispersion in water, isopropanol, petroleum oils or synthetic oils. It possesses very low coefficient of friction and is stable in air up to 400°C. Its fine powder may be sprinkled on surfaces sliding at high velocities, and it forms film when it fills low spots in metal surfaces. It is also used along with solvents and in greases.

Molybdenum disulphide possess low co-efficient of friction. But in an oxidative atmosphere in excess of 400 °C (750 ° F), it begins to decompose. Molybdenum disulphide frequently used as anti-wear additives blended with engine oils or other lubricants. MoS_2 is a mined material found as thin veins within granite and highly refined in order to achieve purity suitable for lubricants. Like graphite, MoS_2 has a hexagonal crystal structure with the intrinsic property to shear. MoS_2 lubrication performance often exceeds that of graphite and is effective in vacuum. The temperature limitation of MoS_2 is 400°C. The particle size and film thickness are important parameters that should be matched to the surface roughness of the substrate. Large particles may result in excessive wear by abrasion while small particles may result in accelerated oxidation.

Advantages

- Molybdenum disulphide is used in lubrication of airframes and wire drawing dies.
- It is stable up to 800°C above which it gets oxidized to the abrasive oxide MoO_3 .
- It is susceptible to hydrolysis and accelerates the corrosion of the surfaces.

Mixture of graphite (7%) and MoO_2 (70%) bonded with silicates (23%) are capable of withstanding high temperatures, low pressures and nuclear radiations. Hence, it is used in space vehicles. Other inorganic soft solids includes white lead, zinc oxide and lead mono oxide are used as lubricants along with grease. Lead and tin in the form of bearing alloys and indium in steel bearings. Other substances like soapstone, talc, mica are also used as solid lubricants. Metals and alloys with low melting points provide lubrication between moving metal surfaces as they melt during sliding.

Solved Example

1. An oil sample under test has a Saybolt universal viscosity of 64 seconds at 210°F and 564 seconds at 100°F. The low viscosity standard (Gulf oil) possesses a Saybolt viscosity of 64 seconds at 210°F and 774 seconds at 100°F. The high viscosity standard (Pennsylvanian oil) gave a Saybolt viscosity value of 64 seconds at 210°F and 414 seconds at 100°F. Calculate the viscosity in dex of the oil sample under test.

Solution: Here, $L = 774$ s, $H = 414$ s and $U = 564$ s

$$VI = [(L-U)] / (L-H)] \times 100 = [(774-564) / (774 - 414)] \times 100 = 58.33$$

Exercises:

1. An oil sample of unknown viscosity has a Saybolt universal viscosity of 58 seconds at 210°F and 580 seconds at 100°F. The high viscosity standard possesses a Saybolt viscosity of 58 seconds at 210°F and 430 seconds at 100°F. The low viscosity standard gave a Saybolt viscosity values of 58 seconds at 210°F and 780 seconds at 100°F. Calculate the viscosity index of the unknown.
2. A Lubricating oil has a Saybolt universal viscosity of 59 seconds at 210°F and 564 seconds at 100°F. The low viscosity-index standard Gulf oil has a Saybolt universal viscosity of 59 seconds at 210°F and 758 seconds at 100°F. The high viscosity-index standard Pennsylvanian oil has a Saybolt universal viscosity value of 59 seconds at 210°F and 420 seconds at 100°F. Find the viscosity index of the lubricating oil.

QUESTIONS**PART-A**

1. Define lubricant.
2. What are oiliness carriers?
3. List the requirement of lubricants.
4. What is the role of antioxidants in hydrocarbon oils?
5. Give the examples of solid lubricants.
6. What are the main classifications of lubricants?
7. Define the terms viscosity and viscosity index.
8. Define Flash and fire point.
9. Define Cloud and pour point.
10. What is grease? Give examples.
11. Define the term Aniline point.
12. List any two properties of lubricants.
13. What are extreme pressure additives? Give examples.
14. What are viscosity index improvers? Give examples.
15. What are pour point depressants? Give examples.
16. Differentiate soda base grease and lime soda grease.
17. How does graphite differ from molybdenum disulphide in lubrication?
18. Define sligh oxidation number.

PART-B

1. How are lubricants classified? Mention the additives added to the lubricants and their functions?
2. Write a note on solid lubricants.
3. Explain briefly about grease as a lubricant.

4. Describe briefly about synthetic lubricants.
5. What is lubrication? Discuss the mechanism of lubrication?
6. Describe thick film or hydrodynamic lubrication mechanism.
7. Explain boundary lubrication with a neat diagram.

Introduction: Definition. Constituents of composites: Matrix phase and dispersed phase –spatial arrangement of the matrix and dispersed phases - Classification of composites based on the type of matrix material used and the geometry of the dispersed phase - Examples. Metal matrix composites: Al matrix; Mg matrix and Ti matrix composites. Ceramic matrix composites: SiC matrix and Alumina matrix composites. Polymer matrix composites: Fibre reinforced plastics (FRP) and its types. Carbon/Carbon composites: Characteristics and Fabrication – Chemical Vapour Infiltration Method – Disadvantages and applications of composites. Cermets: Characteristics – Types -Oxide based cermets - Carbide based cermets– Properties and applications. Abrasives: Definition - Properties: Mohs scale of Hardness. Classification: Natural and synthetic abrasives. Manufacture of abrasive paper and abrasive cloth.

COMPOSITES

A composite material is a combination of two or more materials and has characteristics superior to that of the individual components.

Properties

- Composites possess excellent strength and stiffness
- They are lightweight materials
- They have low coefficient of expansion
- They have a high strength to weight ratio
- They are highly resistant to corrosion, chemicals and the weather
- They have low thermal conductivity
- They can be moulded to any shape and size with required mechanical properties
- Composites are recyclable, reliable and consume less energy

Disadvantages of Composites

- Properties of many important composites are anisotropic i.e., the properties differ depending on the direction in which they are measured.
- Composites based on polymers are susceptible to attack by chemicals.
- Composite materials are expensive.
- Manufacture of composite materials are tedious and expensive.

Applications

Composite materials are extensively used in

- Manufacturing advanced aerospace structures
- Light weight construction materials
- High speed and fuel efficient transport vehicles
- Electronic components and sporting goods

CONSTITUENTS OF COMPOSITES

Composites generally consist of two phases namely, the matrix phase (bulk phase) and the reinforcement phase (dispersed phase).

MATRIX PHASE

The matrix phase is the continuous phase. It surrounds and holds the individual reinforcing elements providing stiffness to the material. It provides the bulk form of the product made of the composite material. It holds the dispersed phase in place, usually enclosing and often concealing it. On application of a load, the bulk phase bears the weight along with the dispersed phase. Hence, deformation takes place in some cases such that the reinforcement agent bears the stress. **Examples:** Polymers, Metals, Ceramics

Characteristics

- Matrix phase gives protection against surface damage by mechanical abrasion and corrosion by environment
- Matrix phase takes the load and stress and transfers it into the reinforcement phase.
- Matrix phase gives shape to the composites.
- Ductile matrix prevents formation of cracks between fibres or particles, even after hard wear and tear.

REINFORCEMENT PHASE/DISPERSED PHASE

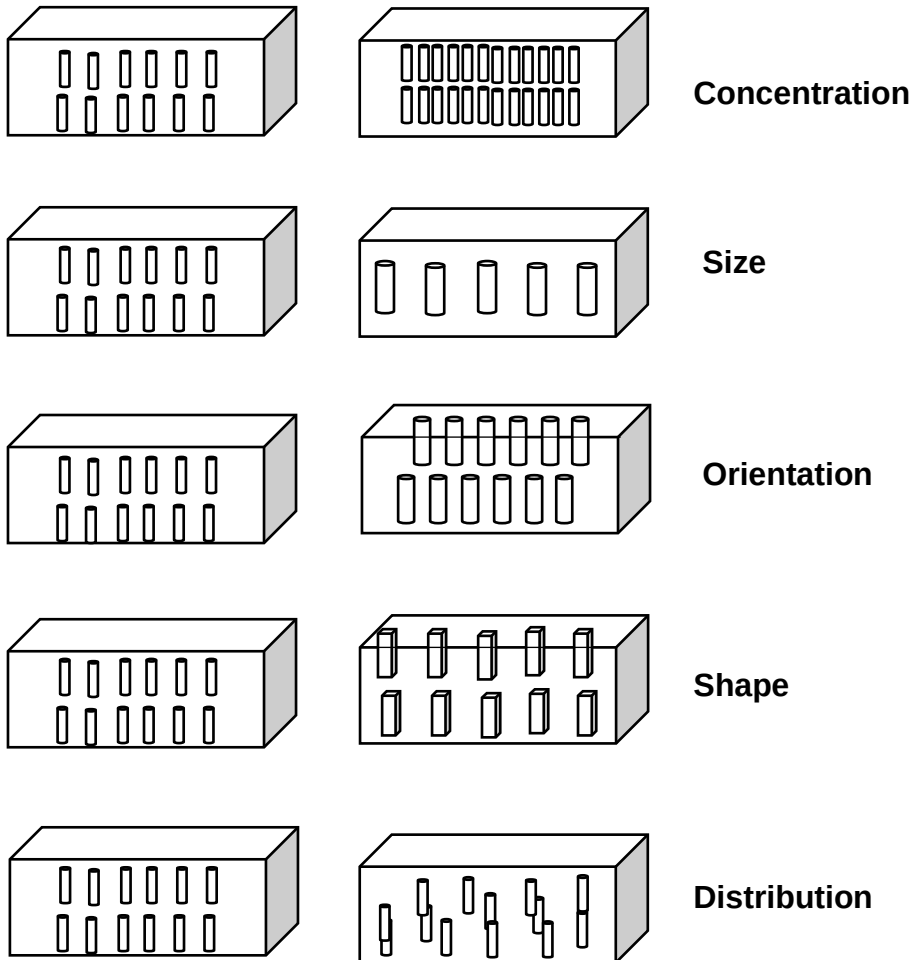
The dispersed phase is also called the reinforcement phase if it is added to increase strength. It can be in the form of fibres, sheets or particles.

Characteristics

- Reinforcement phase imparts mechanical properties like light weight, strength, stiffness, toughness and thermal stability.
- Packing of the dispersed phase is determined by the size and shape of the particles and fibres.
- Longer fibres give better reinforcement and smaller particles give more surface area for contact.
- Reinforcement phase acts as the major load bearing constituent.
- The characteristics of the composite is determined by the interface between the two phases.
- Composite strength is determined not only by the matrix properties but also on how it adheres to the particles and fibres of the reinforcement phase.

The various geometrical and spatial characteristics of the dispersed phase that may influence the properties of composites are

- Concentration
- Size
- Orientation
- Shape
- Distribution



CLASSIFICATION OF COMPOSITES

Composites can be classified based on the type of matrix material used and on the geometry of the reinforcement or dispersed phase.

Classification based on the type of matrix material used

1. Polymer Matrix Composites (PMC)
2. Metal Matrix Composites (MMC)
3. Ceramic Matrix Composites (CMC)

4. Carbon/Carbon Composites (C/Cs)

Classification based on the geometry of the reinforcement phase

1. Particle Reinforced Composite
 - Large particle
 - Dispersion strengthened
2. Fibre Reinforced Composite
 - Continuous (aligned)
 - Discontinuous (short)
 - o Aligned
 - o Randomly oriented
3. Structural Reinforced Composite
 - Laminates
 - Sandwich panels

POLYMER MATRIX COMPOSITES (PMC)

Polymer matrix composite (PMC) is a material that consists of a fibre dispersed in a polymer matrix.

Examples of polymer matrix materials: Thermosetting resins are widely used in PMCs such as unsaturated polyesters, vinyl esters, etc.

Advantages

- high tensile strength
- high stiffness
- high fracture resistance
- light weight
- good corrosion resistance
- low cost

Disadvantages

- low thermal resistance
- high coefficient of thermal expansion

FIBRE REINFORCED PLASTICS (FRP)

FRP are composite materials that typically consist of strong fibres embedded in a resin (polymer) matrix.

Examples of FRP (PMC):

- Glass fibre reinforced polymers (GFRP)
- Aramid fibre (Kevlar) reinforced polymers (AFRP)
- Carbon fibre reinforced polymers (CFRP)

GLASS FIBRE REINFORCED POLYMERS (GFRP)

GFRP is a polymer matrix composite that is reinforced by glass fibres

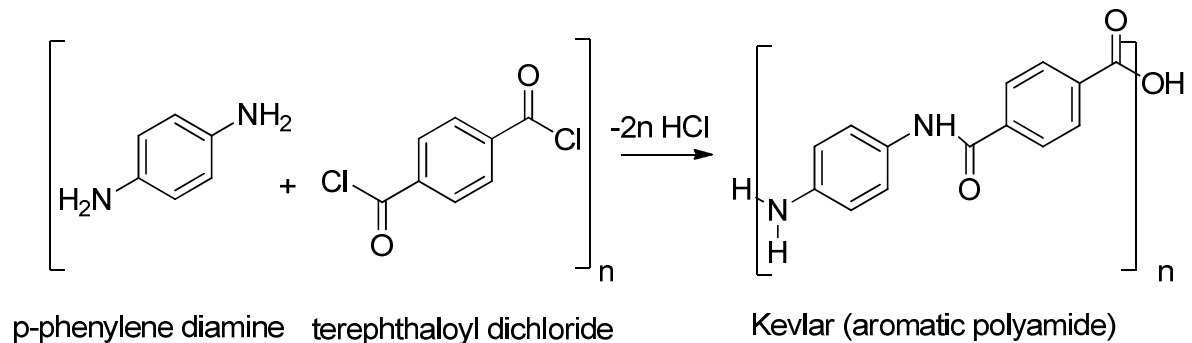
Properties and Applications: There are basically four varieties of glass fibres used in composites. They are E-glass (electrical grade), S-glass (high strength), AR-glass (alkaline resistant) and Z-glass (zirconia containing glass fibres).

Type of Glass fibre	Properties	Applications
E-glass (electrical grade)	High electrical insulating properties, low susceptibility to moisture and good mechanical properties	Used for structural and electrical applications
S-glass (Strength)	Very strong even at high temperatures, higher fatigue strength and superior mechanical properties than E-glass	Used in defense and aeronautical applications
AR-glass (alkaline resistant)	Resistant to alkaline environments. They also provide strength and flexibility to concrete.	Used as reinforcement to cement matrix composites
Z-glass (containing Zirconia)	Highly alkali and acid resistant. Contains a large percentage of ZrO_2 . Excellent workability characteristics. They provide strength and flexibility to concrete.	Can be used as asbestos replacement

ARAMID FIBRE (KEVLAR) REINFORCED POLYMERS (AFRP)

AFRP is a polymer matrix composite reinforced by aramid fibres. Aramid is an aromatic polyamide.

Preparation: Kevlar is the trade name of aramid [Poly (para-phenylene-terephthalamide)] fibres. Aramid fibres are synthesized through low temperature polycondensation of p-phenylene diamine and terephthaloyl dichloride.

**Properties**

- Has high tensile strength
- High stiffness and toughness
- Light weight
- Low density
- High modulus
- Thermal stability

Applications

- Used in the manufacture of panels and wings of fighter jets
- Used in automotive and marine applications
- Used in sports equipment

CARBON FIBRE REINFORCED POLYMERS (CFRP)

CFRP is a polymer matrix composite reinforced by carbon fibres.

Preparation: Carbon fibres are made by heating filaments of polyacrylonitrile(PAN) at 500K, under an atmosphere of air to form oxidized PAN. The oxidized PAN is then placed in a furnace with an inert gas such as argon, and heated to 2000 K in the absence of air. The product, carbon fibre, containing chains of carbon atoms are formed.

Properties

- High strength and rigidity
- Light weight
- High elastic modulus
- Low thermal expansion
- Conductive and corrosion resistant

Applications

- In high quality sports equipment
- In laptops and cameras
- In the construction of aircraft
- In the automotive industry
- In golf clubs, fishing rods, etc

METALMATRIX COMPOSITES (MMC)

A metal matrix composite (MMC) is a composite material that consists of a metal or ceramic dispersed in a metal matrix.

Examples of metal matrix: Al, Mg, Ti, Cu etc.

Examples of reinforcements

- Ceramics – Oxides (Al_2O_3), Carbides (SiC, TiC), Borides (TiB_2)
- Metals – Pb, W, Mo etc.

Characteristics

- High strength at elevated temperatures
- High stiffness (modulus of elasticity)
- High thermal stability
- Good creep resistance
- High thermal conductivity
- Low density

TYPES OF MMC

S.No.	Types	Reinforcement	Properties	Applications
1.	Al-matrix composites	SiC particles, Al_2O_3 fibres and Boron carbide (B_4C)	SiC reinforcement increases the tensile strength, hardness, density and wear resistance. Al_2O_3 reinforcement has good compressive strength and wear resistance. B_4C is one of the hardest known elements and has high elastic modulus and fracture toughness.	Used for manufacturing automotive parts, brake rotors for high speed trains, bicycles, electronic substrates, cores for high voltage electrical cables
2.	Mg-matrix composites	SiC particles, Al_2O_3 and Titanium carbide (TiC)	SiC reinforcement increases the ultimate tensile strength, yield strength, hardness, ductility and wear resistance of Mg and its alloys. Reinforcement of TiC particles results in an improvement of yield strength, tensile strength and elastic modulus significantly, while ductility is reduced to some extent. Reinforcement of Al_2O_3 induces good creep resistance and compressive strength.	Used for manufacturing components for racing cars, aircraft parts, gearboxes.
3.	Ti-matrix composites	Continuous, monofilament SiC, Titanium monoboride (TiB), and titanium carbide (TiC) particles	SiC offers high strength and light weight replacement materials for super alloys. TiB offers superior thermodynamic properties and excellent physical and mechanical properties. TiC reinforcement provides elevated hardness, good wear and corrosion resistance.	Used in aerospace applications, turbine engine components, automotive engine components, etc.

CERAMIC MATRIX COMPOSITE (CMC)

Ceramic Matrix Composite (CMC) is a material that consists of a ceramic dispersed in another ceramic phase.

Examples of ceramic matrix: Alumina (Oxide matrix), SiC (Non-oxide matrix)

Examples of reinforcements: Whiskers (Fine single crystal materials) of SiC, TiB₂, AlN, ZrO₂.

Characteristics

- High strength at elevated temperatures
- High stiffness (modulus of elasticity)
- High thermal stability
- High thermal conductivity
- High corrosion resistance even at elevated temperatures

TYPES OF CMC

S.No.	Types	Reinforcement	Properties	Applications
1.	Silicon carbide matrix composite	SiC fibres	SiC/SiC composites exhibit toughness, can withstand high temperatures, thermal shock resistance, high thermal conductivity, creep and oxidation resistance	In combustion and turbine section components of aero-propulsion and gas turbine engines, in heat exchangers, reformers, reactors, and filters for the chemical industry, in nuclear fission and fusion reactors as fuel cladding and radiation blankets

2.	Alumina matrix composite	SiC particles or SiC whiskers	SiC reinforcement improves strength, fracture toughness, wear resistance and creep resistance	Used to control gas flow in high temperature furnaces, in flame tubes, heat exchangers, protective tiles and various high temperature holders, in thermo-photovoltaic burners, burner stabilizers, and combustion liners of gas turbine engines.
----	--------------------------	-------------------------------	---	--

CARBON/CARBON COMPOSITES (C/Cs)

Carbon/Carbon composites are composed of a carbon matrix reinforced with carbon yarn fabric, 3-D woven fabric, 3-D braiding, etc. They are developed specifically for parts that must operate at extreme temperature ranges. It is the only elemental composite since it is made up of only carbon.

Characteristics

- Extremely high temperature resistance (1930°C – 2760° C).
- Strength actually increases at higher temperatures (up to 1930°C).
- High strength and stiffness.
- Good resistance to thermal shock.
- High modulus of elasticity
- Low coefficient of thermal expansion
- High electrical conductivity

Matrix Phase: Carbon or Graphite

Reinforcement Phase: Carbon or graphite fibres (can be single strands, abundant strands or plaited)

Applications of Carbon/Carbon composites

- They can be used in the manufacture of components for missiles and military aircraft.
- They are used in rocket nozzles, exit cones for strategic missiles, and brake discs for military aircraft.

- In industries, they are used in hot glass handling tools and hot press dies and pistons.
- They are used in special automobile brakes and clutches, forging dies and molding crucibles, corrosive chemical reactors and heat exchangers, fuel cells, prosthetic devices, and components for internal combustion engines.

Fabrication of Carbon/Carbon composites

Chemical Vapour Infiltration (CVI) Process

Chemical vapour infiltration is a CVD (chemical vapour deposition) process. The inner surfaces of a porous material are coated by this method. Gaseous precursor chemicals penetrate the pores / fibres of the material and a solid coating is deposited on the internal surfaces. In CVD, deposition takes place on the surface whilst in CVI, it takes place within a body. This method is also used to make ceramic matrix composites.

Process

A fibrous structure called the porous preform is placed in a reactor. This acts as the reinforcement phase. The preform not only imparts rigidity to the composite, but also incorporates the properties of a fibre that determine the properties of the composites. The preforms are usually made using polyacrylonitrile (PAN) carbon fibres. Reactant gases or vapours (methane precursor) are supplied to the reactor which flow around and diffuse into the preform. The decomposition of the reactants fills the space between the fibres, forming composite material in which the matrix is the deposited material and dispersed phase is the fibres of the preform. The diameter of the fibres gradually increases as the reaction progresses.

There are different types of CVI process

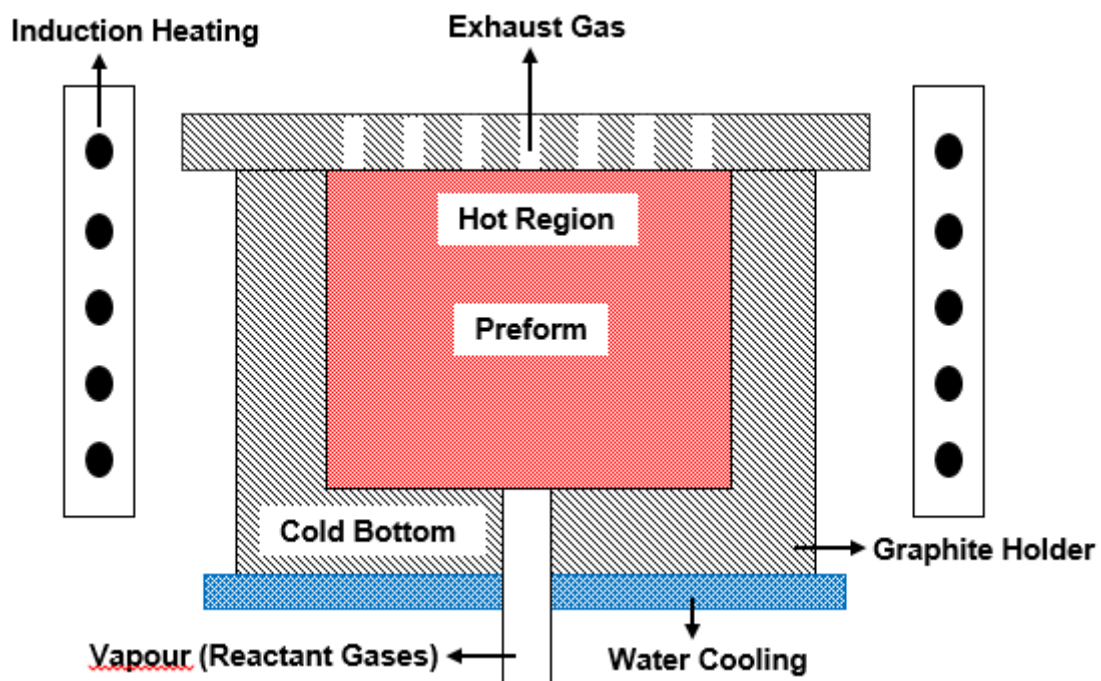
1. **Isothermal/isobaric CVI process** - The reactant gas is supplied to the preform at a uniform temperature and pressure. It is a very slow process as it has a low rate of diffusion.
2. **Temperature gradient (TG-CVI) process** - In this process the vapour diffuses initially to the hotter surface of the preform and then to the cooler surface.
3. **Isothermal-forced flow (IF-CVI) process** - In this process, the vapours are forced onto the uniformly heated preform. Infiltration of the reactant gases is increased thus increasing deposition rate.
4. **Pulsed flow (P-CVI) process** - In this process, the surrounding gas pressure changes rapidly. The pressure changes repeatedly during each cycle. Each cycle consists of the evacuation of the reactor vessel followed by its filling with the reactant gas.

Advantages

- Large, complex shapes product can be produced
- Various matrices can be fabricated
- Gives enhanced mechanical properties, corrosion resistance and thermal shock resistance

Disadvantages

- Production rate is very low
- Residual porosity is very high (10-15%)
- High capital and production costs



CERMETS

Cermets are composite materials composed of ceramic particles dispersed in a refractory metal matrix. They bring together the useful characteristics of ceramics such as hardness, oxidation and heat resistance with those of metals such as toughness and impact strength. Cermets basically consist of a combination of oxides, carbides, nitrides and carbonitrides with binders such as aluminium, iron, chromium, cobalt and nickel.

Characteristics of cermets

- Cermets possess high tensile strength and high density.
- They are characterized by high thermal shock resistance.

- They have high modulus, high shapeability
- They show uniform wear and chemical stability.
- They have high thermal stability.

Classification of cermets

Cermets are classified into two groups

- Oxide based cermets
- Carbide based cermets.

Oxide based cermets: These cermets are a dispersion of alumina particles in chromium or its alloys and in stainless steel, MgO dispersed in nickel-cobalt alloy, dispersion strengthened stainless steel with UO_2 , TiO_2 and ThO_2 .

Class	Ceramic	Metal addition
Oxides	Al_2O_3	Al, Be, Co, Fe, etc
	Cr_2O_3	Cr
	MgO	Al, Be, Co, Fe, Mg
	SiO_2	Si, Cr
	ZrO_2	Zr
	UO_2	Zr, Al, stainless steel

Characteristics

- Specific gravity between 4.5 and 9
- High tensile strength and thermal shock resistance
- Metal or ceramic can be the matrix phase
- Oxide based cermets are easy to fabricate

Applications

- As tools for high speed cutting of materials
- In thermocouple protection tubes and molten metal processing equipment parts.
- In mechanical seals and gas-turbine flame holders

Carbide based cermets: It is classified based on the carbides present in the cermet

Class	Ceramic	Metal addition
Oxides	TiC	Mo, W, Fe, Ni, Co
	WC	Co
	Cr_3C_2	Ni, Si
	SiC	Ag, Si, Cr, Co

Tungsten carbide cermets: They are a dispersion of tungsten carbide in cobalt matrix. They contain about 30% cobalt as the matrix binder.

Characteristics

- High compressive strength
- High hardness
- Rigidity
- Abrasive resistance.

Applications

- They are used for gauges and valves.
- In wire drawing dies and precision rolls.

Chromium carbide cermets: They are a dispersion of chromium carbide in nickel matrix. They contain from 80 to 90% chromium carbide, with the balance being either nickel or nickel alloys. It is used as spray nozzles, bearing seal rings, bearings and pump rotors.

Characteristics

- High tensile strength
- High hardness
- Superior resistance to oxidation
- Excellent corrosion resistance
- Low density

Applications

- They are used for gauges, oil-well check valves, valve liners, spray nozzles, bearing seal rings, bearings and pump rotors.

Titanium based cermets: Most TiC cermets have nickel or nickel alloys as the metallic matrix. This results in high-temperature resistance.

Characteristics

- High tensile strength
- High stiffness
- High temperature resistance
- Low density

Applications

- They are used for integral turbine wheels, hot-spinning tools, thermocouple protection tubes, gas-turbine nozzle vanes and buckets, torch tips, valves, and valve seats.

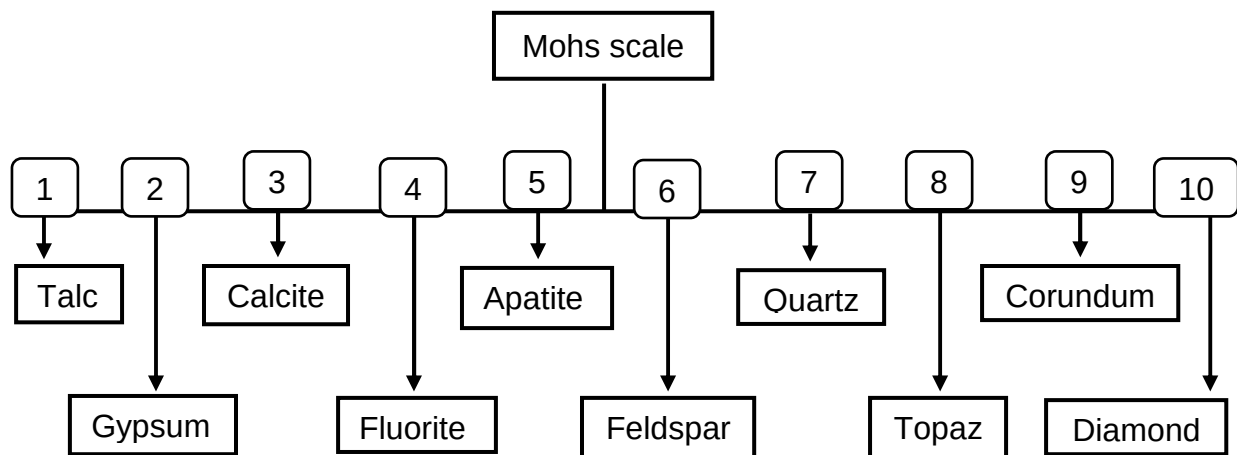
ABRASIVES

Abrasives are substances characterized by their hardness and used for cutting, grinding and polishing softer surfaces. For example, cutting tools are sharpened on abrasives (grinding wheels), emery is used for polishing surfaces, etc. Examples of abrasives include sand paper, honing stones, polishes, ball mills, etc.

Properties of Abrasives

1. **Hardness:** It is the ability or capacity of an abrasive to cut or grind another surface. The abrasive must be harder than the material it should cut or grind. Hardness is measured using a variety of scales, but the most common is the Mohs scale, Vickers scale and the Knoop hardness test.

Mohs scale of Hardness: Different substances possess varying hardness. For example, talc, the softest material, has a hardness of 1 while the hardest material, diamond has a hardness of 10 on the Mohs scale. The hardness of any material on the Mohs scale lies between 1 and 10.



2. **Abrasive power:** it is the strength of an abrasive to cut or grind another surface. It depends on the hardness of the abrasive.

Classification of Abrasives

Natural Abrasives			
Abrasive	Hardness on Mohs scale	Chemical composition	Uses
Diamond	10	Crystallized carbon and chemically inactive. Not attacked by acids or alkalis. Borts –faulty diamond. Carbonado – black diamond from Brazil	Borts and carbonado are used for cutting rocks, stones, grinding wheels
Corundum	9	Crystallized aluminium oxide (Al_2O_3)	Used for grinding glasses, gems, lenses, etc.
Emery	8	55 – 75% crystalline alumina + 20 – 40% magnetite + 12% other minerals	Used as tip for drilling tools and cutting tools. Emery paper is used

			for polishing metal surfaces
Garnet	6 – 7.5	Mixture of trisilicates of alumina, magnesia and ferrous oxide	Abrasive paper and abrasive cloth are used for polishing metals, finishing hard woods, etc.
Quartz	7	Pure Silica (SiO ₂). An impure hydrated form of quartz is called abrasive flint and is used in sand paper	Used for grinding floor, pigments, ores, etc.

Artificial Abrasives			
Abrasive	Hardness on Mohs scale	Chemical composition	Uses
Carborundum or silicon carbide (SiC)	9.3	Chemically inactive. It can withstand high temperature. It is brittle and prepared by heating silica and coke at 1650 – 2200°C in an electric furnace. $\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$	Used for grinding low tensile strength materials like cast iron, brass, bronze, marble, glass, etc.
Boron carbide or Norbide (B ₄ C)	9	Chemically inert. It is prepared by heating boron oxide and coke at 2700°C in an electric furnace. $2\text{B}_2\text{O}_3 + 7\text{C} \rightarrow \text{B}_4\text{C} + 6\text{CO}$	Used for cutting and sharpening hard high-speed tools and for making grinding dies
Alundum (Artificial corundum)	-	It is less hard and brittle than carborundum Hard crystallized aluminium oxide It is prepared by heating a mixture of calcined bauxite, coke and iron at 4000°C in an electric arc furnace	Trade name – Aloxite Used in preference to carborundum for grinding hard steel and high tensile strength materials

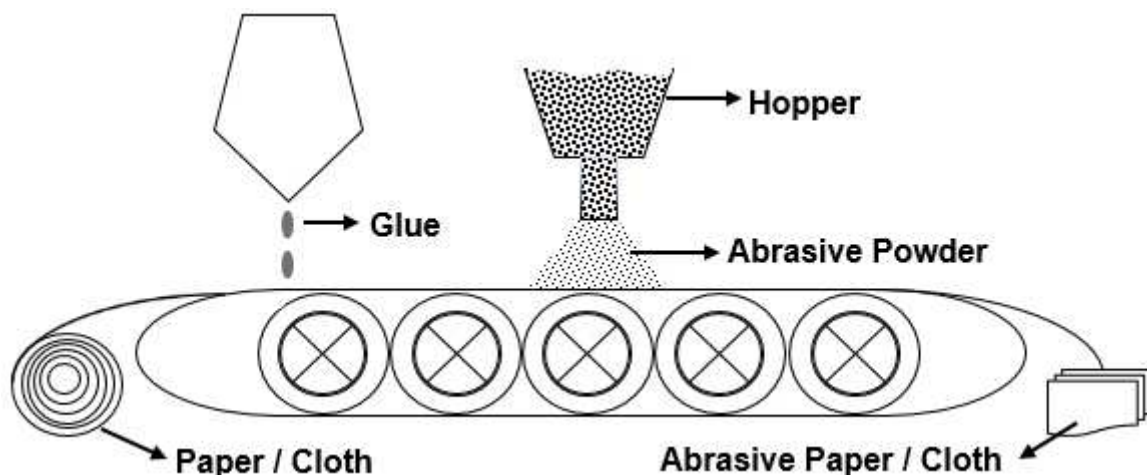
ABRASIVE PAPER AND ABRASIVE CLOTH

Abrasive paper and abrasive cloth are commonly used for cleaning and polishing of different materials, removing corrosion products and rust from metal surfaces. There

are different varieties of abrasive paper and cloth depending upon the hardness, abrasive grain size, chemical composition and purity.

MANUFACTURE OF ABRASIVE PAPER AND ABRASIVE CLOTH

The common method for manufacturing any type of abrasive paper and abrasive cloth is given below. A roll of paper or cloth is made to pass through a series of rollers. This paper or cloth is called the backing to which the abrasive material is attached. In the first stage a thin coating of adhesive or glue is applied on the upper surface of the paper or cloth. The glued paper or cloth is passed through rollers under a hopper. The abrasive powder of uniform grain size is dropped from the hopper and is spread evenly over the glued paper or cloth. The abrasive coated paper or cloth is cured for about a week which fixes the abrasive firmly on the backing. Finally the abrasive paper or cloth is cut into sheets of desired sizes.



TEST YOUR UNDERSTANDING

1. Discuss the characteristics and spatial arrangement of the matrix and dispersed phases in composites.
2. Discuss polymer matrix composites.
3. What are fibre reinforced plastics? Explain the various types with suitable examples and applications.
4. What are metal matrix composites? Describe MMC with their types and applications.
5. What are ceramic matrix composites? Describe CMC with their types and applications.
6. What are carbon/carbon composites? Discuss their characteristics, fabrication and applications.
7. Explain the chemical vapour infiltration process with a suitable diagram.
8. What are cermets? Explain its types with suitable examples.

9. What are abrasives? Explain the classification of abrasives with suitable examples.
10. Explain the manufacture of abrasive cloth and abrasive paper.
11. Write short notes on the properties of abrasives.