As per the
New
Syllabus Effective
R 2015

Engineering Chemistry

First Edition

About the Authors

K N Jayaveera is retired Professor of Chemistry and former Director, JNTU Oil Technological Research Institute, Anantapur. He has a PhD degree in Chemistry from JNTU, Hyderabad (1991) and MSc in Chemistry from S V University, Tirupati (1975). He has more than 38 years of teaching and research experience at JNTU-A. He is a recipient of the state award as best teacher in university education for the year 2009 sponsored by the State Government of Andhra Pradesh. He was nominated by Department of Bio-technology, Govt. of India, New Delhi, as Member of Programme Review Committee of Bio-Engineering for Bio-Energy and Bio-Fuels; and also in, ICAR, Govt. of India, as a Research Advisory Committee Member for Directorate of Oil Seed Research, Hyderabad.

Dr Jayaveera has authored several books, and published and edited several journals under the Science-Tech Foundation. He has guided 35 PhD scholars, and 15 students are presently pursuing PhD under his supervision. He has operated several research projects and has many research publications—national (150) and international (125)—to his credit. He has handled several consultancy projects and is Life Member of Indian Technical Education, Life Fellow of Institution Chemists (INDIA), Member of BIS and Member of advisory body of Oil Technologists Association, Indian Chemical Society and Association of Food Scientists and Technologists (India). He was the former Chairman of Board of Studies of Chemistry and Pharmacy and Member of Board of Studies of Chemistry, JNTU, Hyderabad.

G V Subba Reddy is Professor & Head of Chemistry and also the Vice Principal, JNTU-A College of Engineering, Pulivendula. He has done his PhD in Chemistry (1997), MSc in Analytical Chemistry (1991), BSc (1989) from S V University, Tirupati, and B.Ed. (1992) from the Annamalai University, Tamil Nadu. He has more than 20 years of teaching experience with Sri Kalahasteeswara Institute of Technology (SKIT), Srikalahasti, Chittoor (District) and JNTU-A College of Engineering, Pulivendula; and rich industrial experience with Sumitra Pharmaceuticals & Fine Chemicals (A P) and Plant Organics Pvt Ltd. (A P). He is presently supervising 15 students, who are pursuing their PhD degrees. Presently, Dr. Reddy is the Vice Principal at JNTUA College of Engineering, Pulivendula.

Dr Subba Reddy is a Life Member, ISTE, Life Member, ASCI, Chairman Board of Studies, Chemistry, for JNTU Anantapur, JNTU Anantapur College of Engineering, Pulivendula and Member Board of Studies, Pharmacy. He is also the member of the Governing Body for affiliated Pharmacy and Engineering colleges. His research interest lies in the areas of analytical chemistry, electrochemistry, environmental chemistry, inorganic chemistry and synthetic chemistry. He has more than 50 research publications in various reputed National and International journals. Dr. Reddy has completed one major research project, funded by BRNS, Bombay in December, 2013. He has guided 6 PhD scholars, and 10 students are presently pursuing PhD under his supervision. He stood first in Analytical Chemistry for which he was awarded the Dr. Suryanarayana Murthy Memorial Award for the year 1991. He has been actively involved in the developments of drugs like Ibuprofen, Norfloxacin, Ciprofloxacin, Ranitidine and Pefloxacin, and also in the Electro-Analytical techniques in drug analysis.

Dr. C. Ramachandraiah is Assistant professor (Sr) & Head of chemistry, Sri Kalahasteswara Institute of Technology (SKIT), Srikalahasti, Chittoor (District). His educational qualifications are MSc, MPhil, BEd and PhD. His area of specialization is inorganic chemistry. His research interest lies in the area of Inorganic chemistry, Analytical chemistry and Environmental chemistry for both UG and PG. He is the member of Board of studies of Chemistry, JNTUA, Anantapur. He has more than 26 years of teaching experience in Applied Chemistry, Engineering Chemistry and Environmental Studies. He has contributed to several research publications in reputed National and International journals. He has attended various conferences, seminars and presented papers, both in national as well as international platforms. Several students are pursuing PhD degrees under his guidance.

As per the
New
Syllabus
Effective
R 2015

Engineering Chemistry

First Edition

K N Jayaveera
Retd Professor of Chemistry & Former Director of OTRI
JNTU Collage of Engineering Anantapur, A.P.

G V Subba Reddy
Vice Principal
Professor & Head
Department of Chemistry
JNTU-A College of Engineering
Pulivendula, A P

C Ramachandraiah
Assistant Professor (Sr)
Department of Chemistry
Srikalahsteeswara Institute of Technology (SKIT)
Srikalahsti, A P

McGraw Hill Education (India) Private Limited
NEW DELHI

McGraw Hill Education Offices

New Delhi New York St Louis San Francisco Auckland Bogotá Caracas
Kuala Lumpur Lisbon London Madrid Mexico City Milan Montreal
San Juan Santiago Singapore Sydney Tokyo Toronto

McGraw Hill Education (India) Private Limited

Published by McGraw Hill Education (India) Private Limited
P-24, Green Park Extension, New Delhi 110 016

Engineering Chemistry, 1e

Copyright © 2016, by McGraw Hill Education (India) Private Limited. No part of this publication may be reproduced or distributed in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise or stored in a database or retrieval system without the prior written permission of the publishers. The program listings (if any) may be entered, stored and executed in a computer system, but they may not be reproduced for publication.

This edition can be exported from India only by the publishers,
McGraw Hill Education (India) Private Limited.

ISBN (13): 978-93-392-2333-5
ISBN (10): 93-392-2333-0

Managing Director: *Kaushik Bellani*

Director—Higher Education Publishing and Marketing: *Vibha Mahajan*

Manager—Product Development: *Koyel Ghosh*
Manager—Regional Product Development: *Sushil K Mathews*

Head—Production: Higher Education and Professional: *Satinder S Baveja*
Asst. Manager—Editorial Services: *Sohini Mukherjee*

AGM—Product Management: *Shalini Jha*
Asst. Product Manager (SEM & Tech Ed.): *Tina Jajoriya*
Sr. Graphic Designer—Cover: *Meenu Raghav*

General Manager—Production: *Rajender P Ghansela*
Manager—Production: *Reji Kumar*

Information contained in this work has been obtained by McGraw Hill Education (India), from sources believed to be reliable. However, neither McGraw Hill Education (India) nor its authors guarantee the accuracy or completeness of any information published herein, and neither McGraw Hill Education (India) nor its authors shall be responsible for any errors, omissions, or damages arising out of use of this information. This work is published with the understanding that McGraw Hill Education (India) and its authors are supplying information but are not attempting to render engineering or other professional services. If such services are required, the assistance of an appropriate professional should be sought.

Typeset at Text-o-Graphics, B-1/56, Aravali Apartment, Sector-34, Noida 201 301, and printed at

Cover Printer:

Visit us at: www.mheducation.co.in

Contents

Preface

Science knows no country, because knowledge belongs to humanity, and is the torch which illuminates the world.

– **Louis Pasteur**

Chemistry affords two general methods of determining the constituent principles of bodies, the method of analysis, and that of synthesis. When, for instance, by combining water with alcohol, we form the species of liquor called, in commercial language, brandy or spirit of wine, we certainly have a right to conclude, that brandy, or spirit of wine, is composed of alcohol combined with water. We can produce the same result by the analytical method; and in general it ought to be considered as a principle in chemical science, never to rest satisfied without both these species of proofs. We have this advantage in the analysis of atmospherical air, being able both to de-compound it, and to form it anew in the most satisfactory manner

– **Antoine-Laurent Lavoisier**
(Father of Chemistry)

Order and simplification are the first steps towards the mastery of the subject.

– **Thomas Mann**

The priest persuades the humble people to endure their hard lot, the politician urges them to rebel against it and the scientist thinks of a method that does away the hard lot altogether.

– Max Perutx (Nobel Laureate)

Chemistry is a branch of science that deals with preparation, composition, properties, structures and reactions of material substances. Since diverse substances are available in nature, the chemical processes are ubiquitous with a vast scope. Chemistry has interfaces with all scientific disciplines and thus, knowledge of the subject is essential for understanding nature as well as for the progress of society. Today, a well-trained chemist contributes not only to the growth of chemical science and industry but also in various emerging areas of sciences such as material science and biotechnology, nanotechnology and engineering technology. It is rightly said that no branch of science has done more, or promises more in this respect than chemistry. Moreover, thorough knowledge of chemistry provides the requisite expertise to deal with challenges in disciplines of engineering related to design and development of new materials. Many constituents of quality control—an important aspect of engineering—are basically chemical in nature.

New developments in the field of chemistry such as ion-exchange resins, high polymers, quantum chemistry, nuclear chemistry, surface chemistry, catalysis, spectroscopy, chromatography, nanomaterials, liquid crystals and metallurgy have their roots deeply embedded in the development of engineering and technology. Chemistry has played a vital role in creating new materials such as fibers, composites, refractories, bonding materials, insulators, conducting polymers, liquid crystals, superconductors, alloys, paints, batteries, fuels, fuel cells, explosives, propellants, semiconductors and lubricants that have varied engineering applications. These materials are scaled to nano size for use in electronics and computer science, for example, minimisation of supercomputers and electronics components. Hence, we see that chemistry makes important contributions in the development of science and technology.

Readers

This book is intended for use in **all branches of Engineering and Technology.** It serves as an introductory text to **first-year students**, enabling them to understand basic principles and updating them on the advancements in the ever-growing field of chemistry. The contents of this book have been carefully planned to cover the syllabi of most Indian universities, **particularly the foundation course in the first year at Jawaharlal Nehru Technological University, Anantapur** . It would also serve as a ready reference for preparation of competitive examinations.

Rationale

In many universities, Engineering Ehemistry has been introduced as a paper at the undergraduate level. But there are hardly any books available that provide requisite syllabus compatibility and right pedagogy. Therefore, this **book has been structured as per the revised syllabus (current academic year 2014–15) for the first-year students of JNTU, Anantapur**. Focused coverage of syllabus, a variety of solved and unsolved numerical problems and exercises make this book student-friendly.

While preparing this textbook, due attention has been given to provide comprehensive coverage of all topics at the depth needed for the undergraduate students. Further, we have emphasised on presenting the content in the light of modern developments and in a very simple language and structured manner, so that students can easily understand the topics. A variety of solved problems and exercise problems, short questions with answers (115), review questions (365) includes short type and essay type questions, multiple choice questions (277) and fill in the blanks (111) are given in the chapters to aid students in understanding the subject precisely and thus, appear for university examinations with confidence.

Organisation

The book has been carefully crafted as per the new syllabus of Engineering Chemistry for the foundation course (first year) at Jawaharlal Nehru Technological University, Anantapur. The structuring provides a logical flow of concepts supplemented with clear illustrations. **Chapter 1** on ***Electrochemistry*** provides a detailed exposition of review of electrochemical cells, Numerical calculations, Batteries which includes rechargeable batteries (Lead acid, Ni-Cd, Lithium Ion Batteries), Fuels cells with specific examples of hydrogen-Oxygen and methanol-oxygen fuel cells. The latest topics like Electrochemical Sensors included which are working based on electrochemistry. Further, Corrosion topic included with basics of electrochemical theory of corrosion, factors affecting the corrosion, prevention of corrosion using anodic and cathodic protection and electro and electroless plating techniques.

Chapter 2 on ***Polymers*** covered with basic concepts of polymerisation process, mechanisms, elastomers which includes natural rubber, compounding of Rubber, synthetic rubbers with preparation, properties and engineering applications, plastomers including thermosetting and thermoplastics with suitable example were discussed at a length. Further, new materials finding extensive applications in the field of engineering like Conducting polymers and mechanism, synthesis and applications of some selective conducting polymers presented. In addition to this, Liquid Crystals, their classification and applications, inorganic Polymers with suitable examples and applications illustrated.

Classification and characteristics of fuel, solid fuels, liquid fuels, gaseous fuels, Power alcohol, octane and cetane numbers, calorific values, combustion and flue gas analysis by Orsat's apparatus are presented with solved problems in **Chapter 3** on ***Fuels Technology.***

Semiconducting and Super conducting materials, magnetic materials , cement, refractories, lubricants and rocket Propellants, nanomaterials, insulators and explosives are dealt with in **Chapter 4** on ***Chemistry of Engineering Materials.***

Chapter 5 on ***Water Treatment*** offers comprehensive coverage of important topics such Impurities in water, Hardness of water, estimation of hardness by EDTA method, Alkalinity, acidity and chlorides in water, Water treatment for domestic purpose, industrial use of water, for steam generation, troubles of Boilers like Scale & Sludge, Priming and Foaming, Caustic Embrittlement and Boiler Corrosion. Further, treatment of Boil. Lastly, ***Chapter 6*** on ***Phase Rule*** provides with basic concepts, Gibbs Phase equation, Phase diagrams, eutectic systems, iron-carbon alloy systems and heat treatment of alloys.

Acknowledgements

We are indebted to Jawaharlal Nehru Technological University, Anantapur, for giving us an opportunity to write this textbook. We extend our appreciation to the McGraw Hill Education (India) team, especially Shalini Jha, Sohini Mukherjee, Satinder S Baveja and Anuj K Shriwastava for their courtesy, cooperation and willingness to go the extra mile so that we could bring out an outstanding product.

This book will highly appeal to teachers and students alike. We look forward to suggestions and criticism, which may be forthcoming from colleagues, friends, teachers and students for further refinement of the text.

K N JAYAVEERA
G V SUBBA REDDY
C RAMACHANDRAIAH

Publisher's Note

McGraw Hill Education (India) invites suggestions and comments from you, all of which can be sent to *info.india@mheducation.com* (kindly mention the title and author name in the subject line).

I

Electrochemistry

Electrochemistry is a branch of science that deals with conversion of chemical energy into electrical energy and vice versa. A substance, which decomposes as a result of passage of electric current is called ‘electrolyte’ and the phenomenon of decomposition of electrolyte through passage of electricity is called ‘Electrolysis’. The electrical conductivity of solutions has been well explained by Arrhenius in 1884 and given satisfactory mechanism of electrolytic conduction. The salient points of theory of electrolytic dissociation are given below:

(i) Salts, bases and acids when dissolved in water, yield two kinds of particles, one carrying positive charge and the other equal but negative charge. The charged particles are called ‘ions’.

$AB \rightarrow A^+ + B^-$ (old)

$A^+B^+ \rightarrow A^+ + B^-$ (solid electrolyte is a combination of charged ions) (modern view)

(ii) Ions present in a solution constantly reunite to form neutral molecules and thus, there is a state of equilibrium between dissociated and undissociated molecules.

$AB \rightarrow A^+ + B^+$

(iii) When an electric current is passed through an electrolytic solution, the positive ions move towards cathode and the negative ions move towards anode.

The electrical conductivity of solution depends upon the number of ions present in the solution. The fraction of total number of molecules present in a solution as ions is known as degree of ‘ionisation’.

(iv) The properties of electrolytes in solution are the properties of the ions. In aqueous solution, acid properties are due to H^+ ions, basic properties are due to OH^- ions and chemical properties of the salt is due to the ions constituting them.

1.1

ELECTROCHEMICAL CELLS

Electrochemistry is a science which deals with transformation of chemical energy is to electrical energy and vice versa. An electrochemical cell is a device in which redox reactions is utilised to get electrical energy. This type of cell is also known as voltaic cell or Galvanic cell. Oxidation and reduction (Redox) reactions happen in many chemical systems. Examples include our own respiratory system and complementary photo synthetic systems in plants. In addition rusting of iron, the action of leach on stains and production and combustion of petroleum that heat us, generate electricity and move our cars. Because electricity plays a role in these systems, the processes involved are described as "Electrochemical changes". The study of such changes is called "electrochemistry".

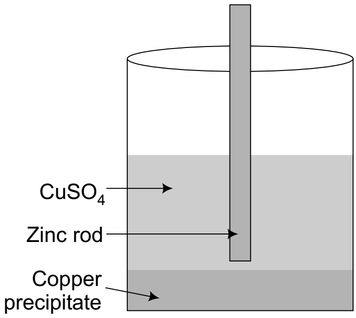


Fig. 1.1 *Zinc-$CuSO_4$ reaction*

Electric current in an electrochemical cell results from a chemical reaction in which oxidation occurs at one electrode and reduction at the other. The substance which loses electrons is said to be oxidised. The substance which gains electrons is said to be reduced. In redox chemical reactions, oxidation can take place only if reduction can also take place at the same time.

For example, Zn – $CuSO_4$ reaction in a beaker. Oxidation of zinc metal by Cu^{2+} ions. If a zinc rod is placed in a solution of $CuSO_4$, the following observation will be made.

The zinc strip starts dissolving forming Zn^{2+} ions in solution.

$$Zn(s) \rightarrow Zn^{2+}\,(aq) + 2e^- \qquad \text{(a)}$$

At the same time, copper starts to precipitate out from the solution.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(S) \qquad \text{(b)}$$

The reactions (a) and (b) are called half-reactions.

The overall reaction is a redox reaction and obtained by adding two half reactions (a) and (b).

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(S)$$

Zinc metal can be oxidised by Cu^{2+} ions. Copper metal cannot be oxidised by Zn^{2+} ions.

Electrochemical cell is defined as 'a device in which a redox reaction takes place indirectly and the decrease in potential energy of the reaction appears largely in the form of electrical energy'.

1.1.1 Electrode Potential

It is known that metal atoms have a tendency to go into solution as metal ions. Electrode potential is a measure of the tendency of metal atoms to go into solution as metal ions. When a metal strip (M), immersed in a solution of its own ions (M^{n+}), either of the following three possibilities occurs (Fig. 1.2).

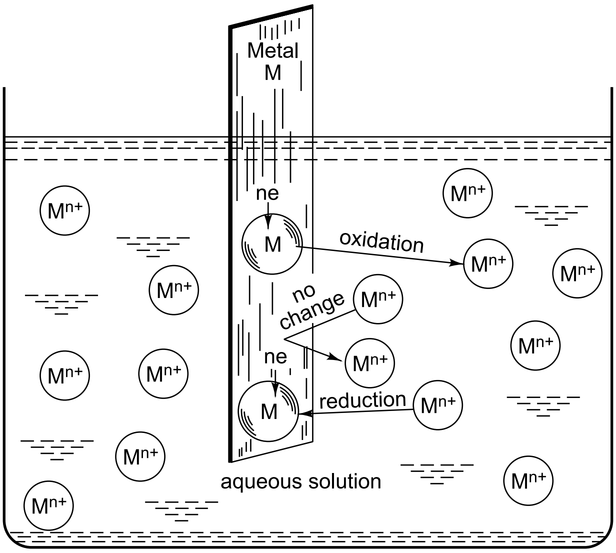


Fig. 1.2 *Electrode equilibrium*

(i) A metal ion (M^{n+}) may collide with the electrode and undergo no change.
(ii) A metal ion (M^{n+}) may collide with the electrode, gain 'n' electrons and converted into a metal atom (M) (the ion reduced).
(iii) A metal atom on the electrode (M) may lose 'n' electrons to the electrode and enter the solution as M^{n+} (the metal is oxidised).

If the tendency of the metal to get oxidised is specially high, there may be slight increase in the number of metal ions (M^{n+}) in solution and increase slightly number of electrons at the electrodes. Therefore, the electrode develops a small negative potential with respect to the solution. The electrode equilibrium is represented as:

$$M(S) \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^-$$

If the situation is established for two different metals (say Cu and Zinc) and if electrical contact is established between the two metals, metal electrodes and two solutions, an electric current will flow.

Note: $Cu(aq) + 2e^- \rightarrow Cu(S)$ occurs more readily than $Zn^{2+}(aq) + 2e^- \rightarrow Zn(S)$, and $Zn(S) \rightarrow Zn^{2+}(aq) + 2e^-$ occurs more readily than $Cu(S) \rightarrow Cu^{2+}(aq) + 2e^-$

1.1.2 Galvanic Cells

The energy from a battery comes from a spontaneous redox reaction in which the electron transfer is forced to take place through a wire. The apparatus that provides electricity through redox reaction is called Galvanic cell, after Luigi Galvane (1737–1798), an Italian anatomist who discovered that electricity can cause the contraction of muscles. It also called a voltaic cell after Alessandro Volta (1745–1827) whose inventions led ultimately to the development of modern batteries.

A galvanic cell is made up of two half-cells as shown in Fig. 1.3. On the left, a silver electrode dips into a solution of $AgNO_3$, and on the right, a copper electrode dips into a solution of $Cu(NO_3)_2$. The two electrodes are connected by an external electrical circuit and two solutions are connected by a salt bridge. When the circuit is completed by a closing switch, the reduction of Ag^+ to Ag occurs spontaneously in the half cell on the left and oxidation of Cu to Cu^{2+} occurs spontaneously in the half cell on the right. The overall cell reaction is as follows:

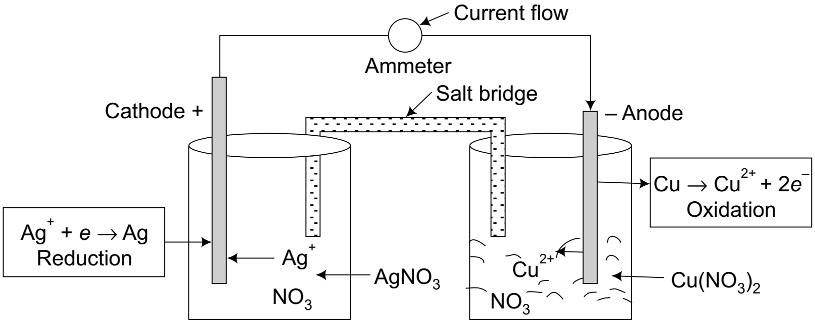


Fig. 1.3 *Galvanic cell*

$$\begin{array}{rll} 2Ag^+(aq) + 2e^- & \rightarrow 2Ag(S) & \text{Reduction} \quad (a) \\ Cu(S) & \rightarrow Cu^{2+}(aq) + 2e^- & \text{Oxidation} \quad (b) \\ \hline 2Ag^+(aq) + Cu(S) & \rightarrow 2Ag(S) + Cu^{2+}(aq) & \text{Cell reaction} \end{array}$$

When electrons appear as a reactant, the process is reduction, when they appear as a product, it is oxidation.

When these reactions take place, electrons left behind by oxidation of the copper, travel through an external circuit to the other electrode where they are transferred to the silver ions, as Ag^+ is reduced to the shiny sliver metal. The overall reaction that takes place in the galvanic cell is called the cell reaction. The electrons lost in the oxidation of the gram atom of copper metal in (b) are gained in the reduction of two gram ions of silver to yield two gram atoms of silver metal ion (a).

Electric current flows from negative electrode (oxidation) to positive electrode (reduction occurs). Thus, in the cell, copper electrode is called negative electrode while the silver electrode is called positive electrode.

Hence, the direction of flow from copper electrode to silver electrode through external circuit but long standing convention defines that current flows from positive to negative electrode. The flow of electricity from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials. The difference of potential which causes the flow of current from one electrode which is at higher potential to another electrode which is at lower potential is called the 'Electromotive force (EMF)' of the cell.

1.1.3 Nernst Equation for Electrode and Cell Potential

Electrode potential for the electrode reaction,

$$M^{n+}\ (aq) + ne^- \rightarrow M(s)$$

Relative to the hydrogen electrode is given by a simple form of the Nernst equation as

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} + \frac{RT}{nF}\ln\,(M^{n+})$$

Here $E^\circ_{M^{n+}/M}$ is the standard electrode potential for a molar solution of a metal ion (M^{n+}) at 298° K which is determined by using the standard hydrogen electrode *R* is the gas constant and is 8.31 J/K/mol, *T* is the temperature in Kelvin '*n*' is the number of moles of electrons indicated in the balanced equation and *F* is the Faraday (96,500 C/mol).

Fig. 1.4 provides a better understanding of all oxidation-reduction reactions in solutions irrespective of whether they take place in a compartment of a battery or by direct contact in a beaker. It is possible to demonstrate that any metal can displace the metals given below it from their salt solution.

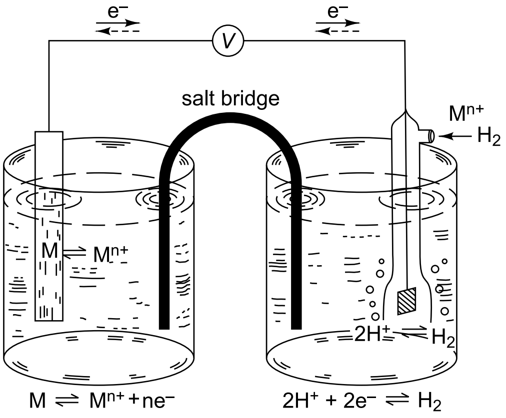


Fig. 1.4 *Scheme for determining electrode potential of a voltaic cell. The standard electrode potential of the half cell (of which electrode potential is to be determined) equals the standard cell e.m.f. and if the hydrogen electrode is positive electrode then* E°_{cell} *will be equal to* $(-E_{M^{n+}/M})$.

In the Daniell cell,

(left) $Zn(s)|\ Zn^{2+}\ (aq)\ ||\ Cu^{2+}\ (aq)\ |\ Cu(s)$ (Right),

the electrode potential of the right hand electrode (half cell) is written as:

$$E_{Cu^{2+}/Cu} = E^{\circ}_{Cu^{2+}/Cu} + \frac{RT}{2F}\ln\,[Cu^{2+}(aq)]$$

and the left hand electrode is written as:

$$E_{Zn^{2+}/Zn} = E''_{Zn^{2+}/Zn} + \frac{RT}{2F}\ln\,[Zn^{2+}(aq)]$$

$\therefore$ The cell potential E_{cell} = Electrode potential of right electrode – Electrode potential of left electrode

$= E_{right} - E_{left}$

$$\therefore\ E_{cell} = \left\{E^{\circ}_{Cu^{2+}/Cu} + \frac{RT}{2F}\ln\,[Cu^{2+}(aq)]\right\} - \left\{E^{\circ}_{Zn^{2+}/Zn} + \frac{RT}{2F}\ln\,[Zn^{2+}(aq)]\right\}$$

$$= (E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn}) + \frac{RT}{2F}\ln\frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]}$$

$$E_{cell} = E^{\circ}_{cell} + \frac{RT}{2F}\ln\frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]} \qquad (\because\ E^{\circ}_{cell} = E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn})$$

E°_{Cell} is cell potential in standard state. By converting natural logarithm to the base 10, and substituting the values R, T (298 K) and F, we get

$$E_{cell} = E^{\circ}_{cell} + \frac{0.0592}{2}\log\frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]}$$

This equation is also written as

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

For a reaction which involves monovalent and bivalent ions,
Let us consider the cell,

$$Ni(s)\ |\ Ni^{2+}\ (aq)\ ||\ Ag^{+}\ (aq)\ |\ Ag(s)$$

The expression for e.m.f. of cell is written as

$$E_{cell} = E^{\circ}_{cell} + \frac{RT}{2F}\ln\frac{[Ag^{+}(aq)]^2}{[Ni^{2+}(aq)]}$$

(or) for a general electrochemical change of the type

$$aA + bB \xrightarrow{ne^-} cC + dD$$

The Nernst equation can be written as

$$E_{cell} = E°_{cell} - \frac{2.303}{RT} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

1.1.4 EMF Measurement

The EMF of a cell can be measured by connecting two electrodes to the two terminals of a voltmeter. This method is inaccurate due to the following reasons: (i) some current drawn from the cell by voltmeter causes alteration of chemical equilibrium (ii) with flow of current, a part of EMF is used in overcoming the internal resistance of the cell. To measure EMF value accurately without disturbing the electrochemical equilibrium, Poggendorff's compensation principle is widely used. In this technique, the EMF to be measured is balanced by equal and opposite EMF from another cell or battery and there is no net flow of current in the circuit. The electrical assembly used is known as potentiometer. It consists of a uniform wire *AB* of high resistance connected to a storage battery of constant emf which should be longer than the EMF of cell to be measured is connected at the ends *A* and *B* of the wire (Fig. 1.5). The cell '*X*', the EMF of which is to be determined is included in the circuit by connecting the positive pole at the same point '*A*' and then through a galvanometer '*G*' to a sliding contact '*D*' as shown in Fig. 1.5.

The sliding contact is moved along the wire '*AB*' till there is no current flow in the galvanometer. The position '*D*' is then noted. The emf of the cell say E_x is proportional to the distance '*AD*', i.e.,

$$E_x \propto \text{AD} \tag{1}$$

The cell '*X*' is now replaced by standard cell '*S*', the EMF of which say *Es* is known. The position of sliding contact is readjusted by moving it over the wire *AB* till the point of no current in the galvanometer, i.e. the 'null point' is reached again say at '*D′*' as shown in Fig. 1.5.

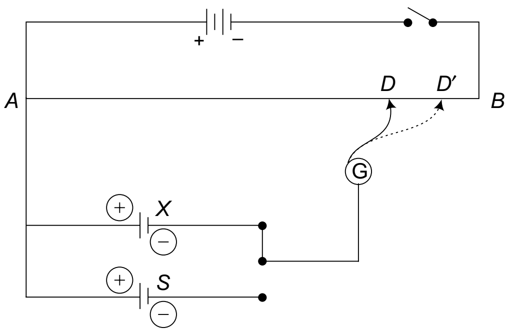


Fig. 1.5 *Potentiometric method for the measurement of EMF*

Then evidently, $$E_s \propto AD' \quad (2)$$

∴ From (1) and (2) $$\frac{E_x}{E_s} = \frac{AD}{AD'} \quad (3)$$

∴ Therefore EMF of 'X' (E_x) is $$\frac{AD}{AD'} \times E_s \quad (4)$$

Knowing E_s, E_x can be calculated easily.

The standard cell must be capable of giving constant and reproducible emf and its variation with temperature will be negligibly small.

1.1.5 Standard Electrode Potential

The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution is called 'electrode potential'. The magnitude of acquired electrons and proceed as a reduction is expressed by the half-reaction's potential. When it is measured under standard conditions namely 25°C, concentration of 1.0 M for all solute and pressure of 1 atmosphere, the reduction potential is called 'Standard Reduction Potential'. Standard reduction potentials are also called "Standard Electrode Potentials". To represent standard electrode potential, add subscript to the symbol $E°_{cell}$.

When two half-cells are connected to make a galvanic cell, one with the larger standard reduction potential (the one with the greater tendency to undergo reduction) acquires electrons from the half-cell with lower standard reduction potential, which is therefore forced to undergo oxidation.

$$E°\text{cell} = \begin{pmatrix}\text{Standard reduction potential}\\ \text{of the substance reduced}\end{pmatrix} - \begin{pmatrix}\text{Standard reduction potential}\\ \text{of the substance oxidised}\end{pmatrix}$$

The standard electrode potentials of a number of electrodes are given in Table 1.1. These values are said to be on hydrogen scale since in these determinations, potential of the standard hydrogen electrode used as the reference electrode has been taken as zero. The values of standard potentials arranged in the decreasing order is called the 'Electrochemical Series'.

Table 1.1 *Electrochemical series standard electrode potentials (Reduction) at 25°C.*

Electrode	*Electrode Reaction (Reduction)*	*E°(volts)*
F_2 (g); $2F^-$	$F_2 + 2e^- \rightleftharpoons 2F^-$	+ 2.87
CO^{3+}; CO^{2+}; Pt	$CO^{3+} + e^- \rightleftharpoons CO^{2+}$	+ 1.82
Cl_2 (g); $2Cl^-$; Pt	Cl_2 (g, 1 atm.) + $2e \rightleftharpoons 2Cl^-$	+ 1.36
Br_2; $2Br^-$ (l); Pt	Br_2 (l) + $2e^- \rightleftharpoons 2Br^-$	+ 1.06
Ag^+; Ag	$Ag^+ + e \rightleftharpoons Ag(s)$	+ 0.80

Contd.

$Fe^{3+}; Fe^{2+}; Pt$	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+ 0.77
$Ag_2SO_4(s), SO_4^{2-}; Hg$	$Hg_2SO_4(s) + 2e \rightleftharpoons 2Hg + SO_4^{2-}$	+ 0.61
$I_2; 2I^- (s); Pt$	$I_2 (s) + 2e \rightleftharpoons 2I^-$	+ 0.53
$Cu^{2+}; Cu$	$Cu^{2+} + 2e \rightleftharpoons Cu(s)$	+ 0.34
$Hg_2Cl_2 (s); Cl^-; Hg$	$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	+ 0.28
$AgCl (s); Cl^-; Ag$	$AgCl (s) + e \rightleftharpoons Ag(s) + Cl^-$	+ 0.22
$Sn^{4+}; Sn^{2+}; Pt$	$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	+ 0.14
$Hg_2Br_2 (s); Br^-; Hg$	$Hg_2Br_2 (s) + 2e \rightleftharpoons 2Hg + 2Br^-$	+ 0.13
$AgBr(s); Br^-; Ag$	$AgBr(s) + e \rightleftharpoons Ag(s) + Br^-$	+ 0.07
$2H^+; H_2(g); Pt$	$2H^+ + 2e \rightleftharpoons H_2$ (g, 1 atm.)	± 0.0000
$Pb^{2+}; Pb$	$Pb^{2+} + 2e \rightleftharpoons Pb (s)$	– 0.13
$Sn^{2+}; Sn$	$Sn^{2t} + 2e \rightleftharpoons Sn (s)$	– 0.14
$AgI (s), I^-; Ag$	$AgI (s) + e \rightleftharpoons Ag (s) + I^-$	– 0.15
$Ni^{2+}; Ni$	$Ni^{2+} + 2e \rightleftharpoons Ni (s)$	– 0.24
$Cd^{2+}; Cd$	$Cd^{2+} + 2e \rightleftharpoons Cd (s)$	– 0.40
$Fe^{2+}; Fe$	$Fe^{2+} + 2e \rightleftharpoons Fe (s)$	– 0.44
$Zn^{2+}; Zn$	$Zn^{2+} + 2e \rightleftharpoons Zn (s)$	– 0.76
$Na^+; Na$	$Na^+ + e \rightleftharpoons Na (s)$	– 2.71
$Ca^{2+}; Ca$	$Ca^{2+} + 2e \rightleftharpoons Ca (s)$	– 2.87
$K^+; K$	$K^+ + e \rightleftharpoons K (s)$	– 2.92
$Li^+; Li$	$Li^+ + e \rightleftharpoons Li (s)$	– 3.04

Table 1.1 above shows that fluorine has maximum positive value of the standard electrode potential and hence it has maximum tendency to accept electrons and thus get reduced to fluoride ion.

The negative sign indicates that half-cell reaction occurs in the opposite direction, the reduced form has a greater tendency to get oxidised and leave electrons. Lithium has maximum negative value of the electrode potential and hence it has the maximum tendency to lose electrons and get oxidised Li^+ ions. The standard electrode potentials serve many applications.

(a) Calculation of standard EMF of a Galvanic cell and determination of cell reaction.

(i) Standard EMF of a cell (E° cell) is equal to the standard electrode potential of the right hand electrode minus the standard electrode potential of the left hand electrode. Thus

$$E^\circ_{cell} = E^\circ_R - E^\circ_L$$

(ii) The electrode at the right is written in the order: Ion–Electrode (e.g., Cu^{2+}, Cu) and the electrode at left is written in the order: Electrode, Ion (Zn, Zn^{2+}).

(iii) Half-cell reaction taking place at left hand electrode is written as an oxidation reaction and half cell reaction taking place at the right hand electrode is written as reduction reaction. The complete cell reaction is given by the sum of these two half-cell reactions.

(b) *Predicting spontaneity or feasibility of the cell reaction:* If the standard emf of the cell is positive, the cell reaction written as per the rule, is spontaneous or feasible.

Let us consider the Zn-Cu cell, the cell would be represented as

Zn, Zn^{2+}; Cu^{2+}, Cu

$$\begin{aligned} E^\circ_{cell} &= E^\circ_R - E^\circ_L = E^\circ(Cu^{2+}, Cu) - E^\circ\,(Zn^{2+}, Zn) \\ &= 0.34 - (-0.76) \\ &= +1.10 \text{ volts.} \end{aligned}$$

The positive value (E°_{cell}) suggests that the redox reaction is spontaneous in the forward direction.

Let us test spontaneity of the reaction

$$Fe^{2+}\,(aq) + Ni(s) \rightarrow Fe\,(s) + Ni^{2+}\,(aq)$$

Two half cells reaction are

$$\begin{array}{ll} Fe^{2+} + 2e \rightarrow Fe & E^\circ_{Fe^{2+}/Fe} = -0.44\text{ V} \\ Ni \quad\ \rightarrow Ni^{2+} + 2e & E^\circ_{Ni^{2+}/Ni} = -0.25\text{ V} \\ \hline \end{array}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{Fe^{2+}/Fe} - E^\circ_{Ni^{2+}/Ni} \\ &= -0.44 - (-0.25) \\ E^\circ_{cell} &= -0.19\text{ V} \end{aligned}$$

Since, the EMF for the above cell is negative, hence the cell reaction as represented above is not feasible.

(c) The standard electrode potential data is helpful in the designing cells through which required voltage can be drawn.

For example, Zn^{2+}, Zn; $2Cl^-$, Cl_2 (g); Pt

$$\begin{array}{rl} Cl_2\,(g) + 2e \rightarrow 2Cl^- & E^\circ = 1.36\text{ V} \\ Zn(s) \rightarrow Zn^{2+} + 2e^- & E^\circ = -0.76\text{ V} \\ E^\circ_{cell} = E_R - E_L & \quad\ = 1.36 - (-0.76) \\ & \quad\ = 2.12\text{ V} \end{array}$$

(d) From the Standard Electrode Potentials, a non-spontaneous electrode is made by spontaneous suitable changes in the sign of the electrode.

$$Fe^{2+}\,(aq) + Ni\,(s) \rightarrow Fe\,(s) + Ni^{2+}(aq) \text{ – Non-spontaneous}$$

$$Ni^{2+}\,(aq) + Fe\,(s) \rightarrow Fe^{2+}\,(aq) + Ni\,(s)$$

which has a cell potential of + 0.19 V, leads to spontaneity.

(e) An oxidising agent with a higher reduction potential will oxidise any reducing agent with a lower reduction potential. In other words, any substance on the left in the table will oxidise any substance above it and on the right.

(f) A reducing agent with a lower reduction potential will reduce any oxidising agent with a higher reduction potential. In other words, any substance on the right will reduce any substance below it and on the left.

(g) No two substances on the same side (left or right) will react with each other.

Solved Problems

1. **Calculate the emf of the concentration cell consisting of zinc electrodes one immersed in a solution of 0.01 molality and the other in a solution of 0.1 molality at 25ºC. The solutions are separated by a salt bridge. The mean activity coefficient of the electrolyte may be assumed to be unity.**

Solution

The cell is represented as:

$$Zn(s) \mid Zn^{2+}\,(aq)\,(cm_1 = 0.01) \parallel Zn^{2+}\,(aq),\, m_2 = 0.1) \mid Zn(s)$$

The emf of the cell (E_{cell}) is given by equation

$$\begin{aligned} E_{cell} &= \frac{RT}{nF} \ln \frac{[Zn^{2+}(0.1)]}{Zn^{2+}(0.01)} \\ &= \frac{2.303RT}{2F} \log \frac{(0.1)}{0.01} \text{ at 25”C} \\ &= 0.0295 \text{ V} \end{aligned}$$

2. **Calculate the standard emf of the cell: Cd(s) | Cd^{2+} (aq) || Cu^{2+} (aq) | Cu and determine the cell reaction.**

Solution

The standard emf of the cell is given by

$E^\circ_{cell} = E^\circ_{cell\ (right)} - E^\circ_{cell\ (left)}$

= [Reduction potential of right hand electrode] – [Reduction potential of left hand electrode]

$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Cd^{2+}/Cd}$

= 0.34 – (–0.40) = 0.74 volts

The various reactions would be as follows:

Left hand electrode: $Cd(s) \rightleftharpoons Cd^{2+} + 2e^-$ (Oxidation)

Right hand electrode: $Cu^{2+}\,(aq) + 2e^- \rightarrow Cu(s)$ (Reduction)

Cell reaction: $Cd(s) + Cu^{2+}\,(aq) \rightleftharpoons Cd^{2+}\,(aq) + Cu(s)$

3. **Calculate the emf of the cell represented the cell as Zn(s) | Zn^{2+} (aq) || H^+ (1M) | H_2 (Atm) | at ($E_{Zn^{2+}/Zn} = -0.7618$ V)**

Solution

EMF of the cell $E_{cell} = E_R - E_L$

E°_R standard hydrogen electrode potential is zero

E_L standard zinc electrode potential is –0.7618 V

$\therefore\ E_{cell} = 0 - (-0.7618\ V) = 0.7618\ V$

4. **Calculate the emf of the cell Cd | Cu^{2+} || Cu^{2+} | Cu at 25ºC. The standard reduction potential of cadmium and copper electrodes are –0.40 and 0.34 volts, respectively**

Solution

The cell representation is Cd(s) | Cu^{2+} (aq) || Cu^{2+} (aq) | C_u(s)

The standard reduction potential of cadmium $(E^\circ_{Cd^{2+}/Cd}) = -0.40$ V

The standard reduction potential of copper $(E^\circ_{Cu^{2+}/Cu}) = 0.34$ V

The cell emf is $E_{cell} = E_R - E_L = 0.34 - (-0.40) = 0.744$ V

5. **Calculate the emf of the Zinc – Silver Cell at 25ºC when $[Zn^{2+}] = 0.10$ M and $[(Ag^+)] = 10.0$ M (E°_{cell} at 25ºC = 1.56 V)**

Solution

The cell reaction in the Zn – Ag cell would be

$$2Ag^+ + Zn \rightleftharpoons 2Ag + Zn^{2+}$$

The Nernst equation for the above cell reaction may be written as

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Ag]^2[Zn^{2+}]}{[Ag^+]^2[Zn]}$$

$$= E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$= E^\circ_{cell} - \frac{2.303\,RT}{nF}\log\frac{[Zn^{2+}]}{[Ag^+]^2} \quad (\because \text{conc. of solids taken as unity})$$

Substituting the various values in Nernst equation, we have

$$E_{cell} = 1.56 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500}\log\frac{0.1}{10} = 1.62 \text{ Volts.}$$

6. **Calculate the standard emf of Ni – Ag cell whose E°_{Ni} and E°_{Ag} are – 0.25 and 0.83 V respectively. Also write the cell representation.**

Solution

The cell representation is:

$$Ni(s)\,|\,Ni^{2+}(aq)\,|\,|\,Ag^+(aq)\,|\,Ag(s)$$

At anode	$Ni(s) \rightarrow Ni^{2+} + 2e$	Oxidation, $E^\circ_{Ni} = -0.25$ V
At cathode	$2Ag^+ + 2e^- \rightarrow 2Ag(s)$	Reduction $E^\circ_{Ag} = +0.83$ V
Overall cell reaction	$Ni(s) + 2Ag^+(aq) \rightleftharpoons Ni^{2+}(aq) + 2Ag(s)$	

$$\therefore \quad E^o_{cell} = E^o_{Ag(R)} - E^o_{Ni(L)}$$
$$= 0.83 - (0.25\ V)$$
$$= 1.08\ V$$

7. **The emf of a cell, Mg/Mg^{2+} (0.01M || Cu^{2+} (M) | Cu is found to 2.78 V at 300 K. The standard electrode potential of Mg electrode is –2.371 V. What is the electrode potential of copper electrode?**

Solution

The electrode potential of 'Mg' is (according to Nernst equation)

$$E_{Mg} = E^o_{Mg^{2+}/Mg} + \frac{0.0591}{n} \log [Mg^{2+}]$$
$$= -2.37 + \frac{0.0591}{2} \log (0.01) \Rightarrow -2.37 - 0.0591$$
$$= -2.4290\ V$$
$$\therefore \quad E_{cell} = E_{Cu} - E_{Mg}$$
$$2.78 = E_{Cu} - (-2.4290)$$
$$E_{Cu} = 2.78 - 2.4290 \Rightarrow 0.3509\ V$$

1.1.6 Reference Electrodes

The electrode of standard potential, with which one can compare the potentials of another electrode of interest is called a reference electrode. The standard hydrogen electrode is used as reference electrode for determining single electrode potentials, whose potential arbitarily taken as zero. But it is not always convenient to set up this electrode on account of the difficulties involved in maintaining activity of hydrogen ions at unity and keeping the pressure of the gas uniformly at one atmosphere. Hydrogen electrode also gets 'poisoned' even if traces of impurities in the gas. To overcome this, some other electrodes called secondary reference electrodes have been employed. Some of the important reference electrodes are as follows:

(a) Hydrogen electrode It is the primary electrode. It consists of a small platinum strip coated with platinum black to absorb hydrogen gas. A platinum wire welded to the electrode and sealed through a glass tube makes contact with the outer circuit. The platinum strip is surrounded by an outer glass tube which has an inlet for hydrogen at the top and number of holes at the base for the escape of excess gas. The electrode is placed in a dilute solution of an acid. Pure hydrogen gas is then passed into it at one atmosphere pressure. Apart of hydrogen gas absorbed by the platinised electrode, while the excess is escapes through the lower holes. Then results an equilibrium between the adsorbed hydrogen on the electrode surface and hydrogen ions in the solution

$$H_2 \rightarrow 2H^+ + 2e^-$$

By convenient, the potential of this standard hydrogen electrode when hydrogen at one atmosphere pressure is bubbled through a solution of hydrogen ions of unit concentration is arbitarily fixed as zero. The hydrogen electrode may be used to find the pH of a solution. The only practical difficulties in setting this electrode is maintenance of the pressure of the gas uniformly at one atmosphere and activity of hydrogen ions at one gram ion per litre.

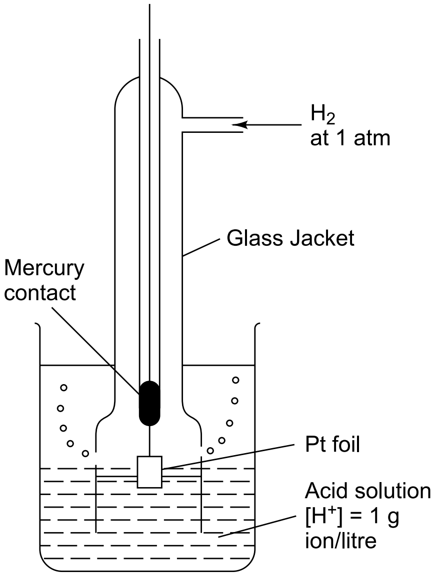


Fig. 1.6 *Hydrogen electrode*

(b)* *Calomel electrode It is a secondary electrode, consists of a glass tube having a side tube on each side as shown in Fig. 1.7. Mercury of high degree of purity is placed at the bottom of this tube and is connected to the other circuit by means of platinum wire sealed in a glass tube. The surface of mercury covered with a paste of mercurous chloride (calomel) and mercury in potassium chloride solution. The electrolyte is also a solution of KCl. This electrode is connected with the help of side tube on the left through a salt bridge with the other electrode, the potential of which is to be determined.

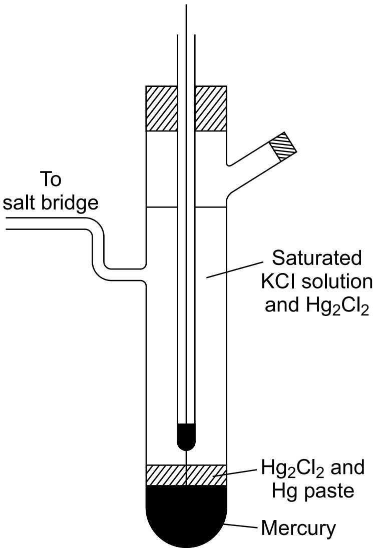


Fig. 1.17 *Calomel electrode*

The potential of Calomel electrode depends upon the concentration of the patassium chloride solution. It has been very accurately determined by connecting it to a standard hydrogen electrode and the results are obtained for reduction potentials of this electrode (Hg/Hg_2Cl_2) for different concentrations of KCl at 24°C are given below:

For 0.1 N KCl solution $E = +0.3338$ V
For 1.0 N KCl solution $E = +0.2800$ V
For saturated KCl solution $E = +0.2415$ V

The positive value indicates that when combined with standard hydrogen electrode, reduction takes place at this electrode.

(c) Silver-Silver Chloride Electrode The silver-silver cloride electrode has recently been employed as a reference electrode in connection with the accurate determination of standard potentials due to reversible and stable, which can be combined with cells containing chlorides without inserting liquid junctions.

For an effective functioning of the electrode, it is necessary that the solution immediate contact with the silver surface is properly saturated by providing a coating of AgCl on the silver. This is done by using the silver electrode as an anode in a chloride solution (KCl or HCl) at a very low current density for about half an hour. The electrode is schematically represented as:

$$Ag \mid AgCl(s), H^+ Cl^- \mid H_2 \text{ (1 atm)}$$

On the hydrogen scale, its standard reduction potential is found to be + 0.2224 volts at 25°C

$$Ag \mid AgCl(s)\ Cl^- (a_{Cl^-} = 1) : E° = +0.2224 \text{ volt at } 25°C$$

1.1.7 Concentration Cells

A concentration cell is a galvanic cell in which electrical energy is produced by the transfer of material from one electrode of higher concentration to another of lower concentration. Concentration cells are of two types:

(a) Concentration cells without transfer
(b) Concentration cells with transfer

Note: *Concentration cells* without transfer may be either electrode concentration cells or electrolyte concentration cells.

(a) Concentration Cells without Transference In these, the EMF arises as a result of two like electrodes at different concentrations dipping in the same solution of the electrolyte. Example of this type of cell consists of two hydrogen electrodes of unequal gas pressures P_1 and P_2 immersed in the same solution of hydrogen ions. The cell is represented as

$$\text{Pt, H}_2\ (\text{PH}_2 = P_1) \mid \text{H}^+ \mid \text{H}_2\ (\text{PH}_2 = P_2)\text{, Pt}$$

If $P_1 > P_2$, oxidation of hydrogen will take place at the left hand electrode and reduction of hydrogen ions at the right hand electrode.

Oxidation reaction	$H_2\ (P_1) \rightarrow 2H^+ + 2e^-$
Reduction reaction	$2H^+ + 2e^- \rightarrow H_2\ (P_2)$
Net reaction	$H_2\ (P_1) \rightarrow H_2\ (P_2)$

From the above, net reaction shows, there is no overall chemical change and there is only a transfer of hydrogen gas from the electrode with pressure P_1, to the electrode with pressure P_2. The EMF in this case depends only on the two pressures and is independent of the concentration of hydrogen ions in which electrodes are immersed.

$$E_{\text{cell}} = \frac{RT}{2F} \log_e = \frac{P_1}{P_2} \quad (\because E^\circ = 0)$$

In the case of amalgam cells which also belong to electrode concentration cells without transference, two amalgams of the same metal at two different concentrations are immersed in the same solution containing the metal ion. Consider two electrodes of zinc amalgam with concentration of zinc equal to C_1 and C_2 immersed in a solution of zinc sulphate.

$$\text{Zn(Hg)}(C_1) \mid \text{Zn}^{2+} \mid \text{Zn(Hg)}(C_2)$$

The overall reaction is

$$\text{Zn(Hg)}(C_1) \rightarrow \text{Zn(Hg)}(C_2)$$

and the cell EMF is given by the expression

$$E_{\text{cell}} = \frac{RT}{2F} \log_e \frac{P_1}{P_2} \quad (\because E^\circ = 0)$$

(b) Concentration Cells with Transference Here, the electrodes are identical but electrolyte solution has two different concentrations. Due to difference in the concentration of electrolyte there occurs corresponding change in the potential of the electrodes dipping in them. The electrical energy in the concentrations cell arises from the transference of substance from the solution of the higher concentration to solution of lower concentration. The two half cells may be joined by a salt bridge. For example, consider the two electrodes of Ag with different concentrations of $AgNO_3$ at C_1 and C_2. The cell is represented as follows:

$$\ominus\ \mathrm{Ag} \left| \begin{array}{l} \mathrm{AgNO_3}(C_1) \\ \text{(dilute)} \end{array} \right\| \begin{array}{l} \mathrm{Ag(NO_3)_2}(C_2) \\ \text{concentrated} \end{array} \Big|\ \mathrm{Ag} \oplus$$

When a metal or electrode is immersed in a solution containing its own ions (M^{2+}), then a potential is generated at the solution and electrode interface, the value of which changes with concentration of ions (C), has Nernst's equation:

$$E = E^\circ + \frac{2.303RT}{nF} \log C$$

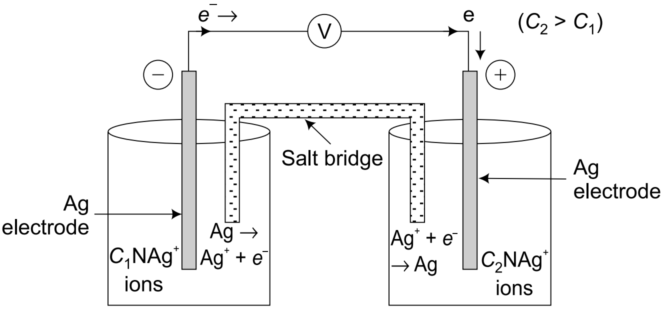


Fig. 1.8 *Concentration cell with transference*

The general concentration cell is represented as

$$^{\ominus}M/M^{n+}\,(C_1M)\;||\;M^{n+}\,(C_2M)/M^{\oplus}$$

where C_1 and C_2 are the concentrations of active metal ions in contact with two electrodes respectively and $C_2 > C_1$.

$$\therefore \qquad \text{EMF of cell} = E_{\text{Right}} - E_{\text{Left}}$$

$$= \left[\left(E^\circ + \frac{0.592\,V}{n}\log C_2\right) - \left(E^\circ + \frac{0.0592\,V}{n}\log C_1\right)\right]$$

$$E_{\text{cell}} = \frac{0.0592\,V}{n}\log(C_2/C_1) \text{ at } 25°\text{C.}$$

and general equation for EMF of the above cell is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF}\log C_2/C_1 \ (\because C_2 > C_1)$$

The following cell reactions occurs for this cell

At the left electrode (Anode): $\mathrm{M} \rightarrow \mathrm{M}^{n+}_{(C_1)} + ne^-$

At the right electrode: $\mathrm{M}^{n+}_{(C_2)} + ne^- \rightarrow \mathrm{M}$

Overall cell reaction: $\mathrm{M}^{n+}(C_2) \rightarrow \mathrm{M}^{n+}\,(C_1)$

It clearly shows the EMF so developed mainly due to transference of metal ions from the solution of higher concentrations (C_2) to the solution of lower concentration (C_1).

1.2

BATTERIES

Electrochemistry has many applications both in science and in our everyday lives. One of the most popular uses of galvanic cells are batteries. A battery is an electrochemical cell or several electrochemical cells connected in 'series' which is a source of direct current at constant voltage. Strictly speaking, cell is a single electrochemical unit consisting of cathode and anode which when connected in series form a battery. Batteries are classified in three types:

1.2.1 Primary Cell or Battery

These cells are not designed to be recharged or cell reaction is not reversible. When the reactants have almost been converted to products, further no more electricity is produced and the battery becomes dead. Hence, discharged batteries cannot be used again.

For example, Voltaic cell (copper and zinc plates dipping in dilute H_2SO_4)

Daniel cell (a negative zinc electrode in $ZnSO_4$ and copper electrode in $CuSO_4$ separated with porous diaphragm).

Dry or Laclanche cell (Anode is zinc can with NH_4 or $ZnCl_2$ and MnO_2 as electrolytes and carbon/graphite rod serve as cathode which is immersed in the centre of electrolyte).

1.2.2 Secondary Cell or Battery

In secondary batteries, the chemical reactions are reversed by passing direct electric current in opposite direction. The cells are designed for repeated use and they are able to be rechargeable.

For example, Ni–Cd storage cell (Ni Cad), Mercury battery, Nickel-Metal hydride lithium batteries.

(i) Nickel–Cadmium Cell The Nickel–cadmium cell or Nicad battery is a secondary cell that produces a potential of about 1.4 V which is slightly lower than that of zinc-carbon cell.

It consists of cadmium anode and a cathode of a paste of $NiO(OH)_2$. The electrode reactions in the cell during discharge are:

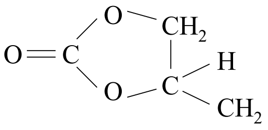
$$\begin{array}{rl} \mathrm{Cd(s)} + 2\mathrm{OH^-(aq)} \rightarrow \mathrm{Cd(OH)_2(s)} + 2e^- & \text{(Anode)} \\ \mathrm{NiO(OH)(s)} + 2\mathrm{H_2O}(l) + 2e^- \rightarrow \mathrm{Ni(OH)_2(s)} + 2\mathrm{OH^-(aq)} & \text{(Cathode)} \\ \hline \mathrm{Cd(s)} + \mathrm{NiO(OH)(s)} + 2\mathrm{H_2O}\ (l) \rightarrow \mathrm{Ni(OH)_2(s)} + \mathrm{Cd(OH)_2(s)} & \text{(Net cell reaction)} \end{array}$$

The cell reactions can be readily reversed since the reaction products $Ni(OH)_2$ and $Cd(OH)_2$ adhere to the electrode surfaces. Like a dry cell, it can be sealed to prevent leakages which is particularly important in electronic devices.

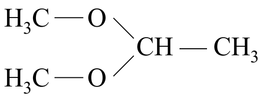
Applications Ni–Cd batteries work well especially in applications such as portable power tools (flash units), CD players, electronic cars, electronic calculators, cordless electronic shavers and transistors. They have high energy density are able to release energy quickly and can be rapidly recharged.

(ii) Lithium Batteries Lithium has the most negative standard reduction potential (–3.05 V) of any metal, so it has lot of appeal as an anode material. Furthermore, lithium is a very light metal, correspondingly lithium employed cell is light in weight. Lithium batteries fall into two categories: (a) primary batteries (can be used once and discarded when fully discharged) and (b) rechargeable cells.

(a) One of the most common lithium primary cell is the lithium manganese dioxide battery. This cell uses a solid lithium anode and a cathode made of heat-treated MnO_2. The electrolyte is a mixture of propylene carbonate and dimethoxy ethane containing dissolved salt such as $LiClO_4$.



Polypropylene carbonate



dimethoxy ethane

The cell reactions are as follows:

$$\begin{array}{rl} \mathrm{Li} \rightarrow \mathrm{Li^+} + e^- & \text{(Anode)} \\ \mathrm{Mn^{IV}O_2} + \mathrm{Li^+} + e^- \rightarrow \mathrm{Mn^{III}O_2(Li)} & \text{(Cathode)} \\ \hline \mathrm{Li} + \mathrm{Mn^{IV}O_2} \rightarrow \mathrm{Mn^{III}O_2(Li)} & \text{(Net cell reaction)} \end{array}$$

This cell produces a voltage of about 3.4 V which is more than twice that of an alkaline dry cell, and because of the light weight of lithium, it produces more than twice as much energy for a given weight.

Applications These cells are used in applications that require a higher current drain or energy pulses (photoflash).

(b) Lithium ion cells (Rechargeable): These cells do not contain metallic lithium hence they are called lithium ion cells and use lithium ions instead. In fact, the cell's operation does not actually involve true oxidation and reduction. But it uses the transport of Li^+ ions through the electrolyte from one electrode to the other accompanied by the transport of electrons through the external circuit to maintain charge balance.

It was discovered that Li^+ ions are able to slip between two layers of atoms in certain crystals such as graphite and $LiCoO_2$. When the cell is constructed, it is in its uncharged state with no Li^+ ions between the layers of carbon atoms in the graphite. When the cell is discharged, Lithium ions leave $LiCoO_2$ and travel through the electrolyte to the graphite (C_6).

Initial charging

$$LiCoO_2 + \text{graphite } (C_6) \rightarrow Li_{1-x}\,CoO_2 + Li_xC_6$$

When the cell spontaneously discharges to provide electrical power, Li^+ ions move back through the electrolyte to the cobalt oxide while the electrons move through external circuit from the graphite electrode to the cobalt oxide electrode. If we represent amount of Li^+ transferring by 'y', the discharge reaction is

Discharge

$$Li_{1-x}CoO_2 + Li_xC_6 \rightarrow Li_{1-x+y}\,CoO_2 + Li_{x-y}C_6$$

Thus, the charging and discharging cycle simply sweep Li^+ ions back and forth between two electrodes with electrons flowing through external circuit to keep the charge balance.

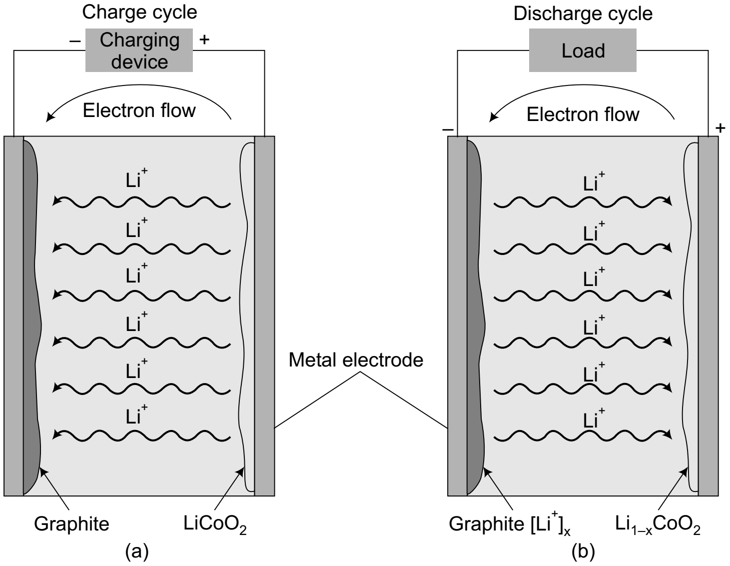


Fig. 1.9 *Lithium ion cell. (a) During the charging cycle, an external voltage forces electrons through the external circuit and causes lithium ions to travel from the $LiCoO_2$ electrode to the graphite electrode. (b) During discharge, the lithium ions spontaneously migrate back to the $LiCoO_2$ electrode, and electrons flow through the external circuit to balance the charge*

1.3

FUEL CELLS

The galvanic cells can only produce electrical energy for a limited time because the electrode reactants are eventually depleted. Fuel cells are different; they are electrochemical cells in which electrode reactants are supplied continuously and are able to operate without theoretical limit as long as the supply of reactants is maintained. This makes fuel cells an attractive source of power where long-term generation of electrical energy is needed.

In a fuel cell, an electrical energy is obtained without combustion from oxygen and a gas that can be oxidised. A fuel cell converts the chemical energy of the fuels directly to electricity.

The important process in the fuel cell is

$$\text{Fuel} + O_2 \rightarrow \text{Oxidation product} + \text{Electricity}$$

1.3.1 Hydrogen–Oxygen Fuel Cell

One of the simplest and successful fuels is hydrogen-oxygen fuel cell. It consists of an electrolyte, a hot (~200°C) concentrated solution of KOH in the centre compartment, is in contact with two porous electrodes that contain catalyst (usually platinum) to facilitate the electrode reactions. Gaseous hydrogen and oxygen under pressure are circulated so as to come in contact with the electrodes. The electrode reactions are as follows:

$$\begin{array}{rll} O_2(g) + 2H_2O + 4e^- \rightarrow & 4OH^-\,(aq) & \text{(Cathode)} \\ H_2(g) + 2OH^-(aq) \rightarrow & 2H_2O\,(l) + 4e^- & \text{(Anode)} \\ \hline 2H_2(g) + O_2(g) \rightarrow & 2H_2O\,(l) & \text{Net cell reaction} \end{array}$$

The standard EMF of the cell is,

$$E° = E°_{ox} + E°_{red} = 0.83\text{ V} + 0.40 = 1.23\text{ V}$$

In actual practice, the EMF of cell is 0.8 to 1.0 V. Generally, large number of these cells are connected in series to make a battery called fuel cell battery or fuel battery.

Hydrogen–oxygen fuel cells are an attractive alternative to gasoline powered engine, particularly because they are pollution free and the only product of the reaction is harmless water. Fuel cells are also thermodynamically efficient, converting as much as 75% of available energy to useful work compared to approximately 25–30% for gasoline and diesel engines.

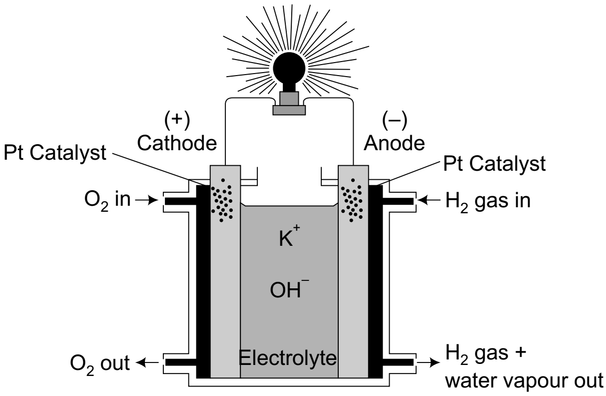


Fig. 1.10 *Hydrogen–oxygen fuel cell*

The major problems associated with fuel cells are (i) energy cost of generating H_2 fuel (ii) problem in providing storage and distribution of highly flammable hydrogen and (iii) availability of alternative fuels.

Applications

1. Hydrogen – oxygen fuel cells are used as auxiliary energy source in space vehicles, submarines, or military vehicles.
2. The weight of fuel battery for 15 days space is about 250 kg.
3. In case of hydrogen–oxygen fuel cells, the product of water proves to be a valuable source of fresh water to the astronauts.

1.3.2 Methanol Fuel Cell

Methanol oxygen is another important fuel cell. It is a sub-category of proton-exchange fuel cells. The direct methanol fuel cell relies upon the oxidation of methanol on catalyst layer to form CO_2. Water is consumed at the anode which is produced at cathode. The positive ions (H^+) are transferred across the proton exchange membrane. Often made from anode to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing power to a connected device. Currently, platinum is used as catalyst in both half-reactions. Methanol and water are absorbed on a catalysts usually made of platinum particles and lose protons until CO_2 is formed.

Methanol or Water mixture is circulated through an anode of cell while O_2 or air is circulated at cathode of the cell as shown in Fig. 1.11.

The half cell reactions are:

Oxidation $CH_3OH\ (l) + H_2O\ (l) \rightarrow CO_2\ (g) + 6H^+\ (aq) + 6e^-$ (Anode)

Reduction $3/2O_2\ (g) + 6H^+(aq) \rightarrow 3H_2O(l)$ (Cathode)

Redox reaction $CH_3OH(l) + 3/2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ Net cell reaction

From the cell reaction, it is observed that for the formation of the final product CO_2, water has to be added. The six electrons pass the load resistance of the outer circuit and are consumed at the cathode together with six protons. For the reaction of one molecule of methanol, $3/2O_2$ molecules will be reduced to $3H_2O$ and at a stationary mode, part of this water has to be introduced at the fuel compartment again. From this, for a six electron charge transfer, a standard cell voltage of 1.21 V and an energy density of 6 kwh/kg methanol is produced.

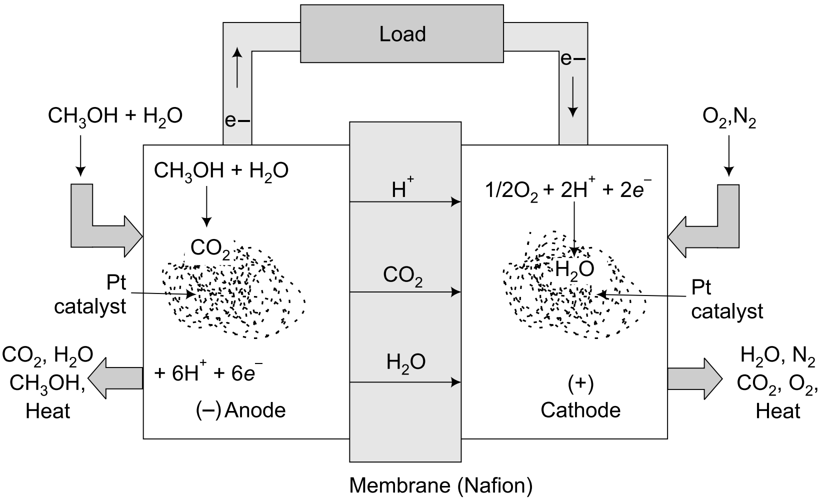


Fig. 1.11 *Methanol fuel cell*

Limitations

1. During the methanol oxidation reaction, CO is formed which is strongly absorbed on to platinum catalyst, reducing the surface area and lowering the performance.
2. Methanol is toxic and flammable. Hence utmost care has to be taken.
3. Limited in the power they produce.
4. The efficiency of current is low due to the high permeation of methanol through membrane material used which is known as methanol cross over.

Advantages

1. Storage of methanol is much easier than H_2 as it does not need high pressure or low temperature since methanol is liquid from –97.0°C to 64.7°C (–142.6°F to 148.5°F).
2. The energy density of methanol (the amount of energy contained in a given volume) is an order of magnitude greater than even highly compressed hydrogen.

1.4

ELECTROCHEMICAL SENSORS

Sensor is a device, which will provides information in respect of the sample continuously, in the form of analytical assay yields information in discrete steps. Electrochemical sensors are the largest group of chemical sensors, representing around 58% of the total available. In addition to this, other types are optical (24%), mass (12%) and thermal (6%). This categorization is based on the general transduction principles ie. How the information is obtained. Electrochemical sensors are electro analytical devices that owe their popularity and success to the discipline of electrochemistry, which provides the strong scientific base on which they stand. Their purpose is to provide information about the chemical environment and the growing need for reliable sources of information guarantees their future.

One of the important applications of electrochemical sensor is a wellknown blood glucose test employed for diabetic patient is an assay (that is, one value per test), while an enzymatic glucose electrode is capable of noticing changes of blood glucose continuously, up and down. Generally, a chemical sensor follows the changes of concentration of some chemical in a predictable and continuous fashion. From and analytical chemistry perspective, the best scope of electrochemistry is the direct conversion of chemical information into an electrical signal, There is no necessity for magnets, light bulbs, lasers, or vacuum pumps.

Schematic Representation of Electrochemical Sensor

The electrochemical sensor mainly consists of outer frame containing an electrolyte gel and three electrodes. At the top of the frame it should have gas permeable membrane. The electrodes are carefully constructed with high sensitivity, long life and allow large surface area. Each cell shall construct with special filter electrodes and electrolytes for high specificity as possible. This will helpful for allowing of larger signal, immediate response and even a smaller volume of electrolyte will provide same response. The block diagram of electrochemical sensor is shown in Figure 1.12.

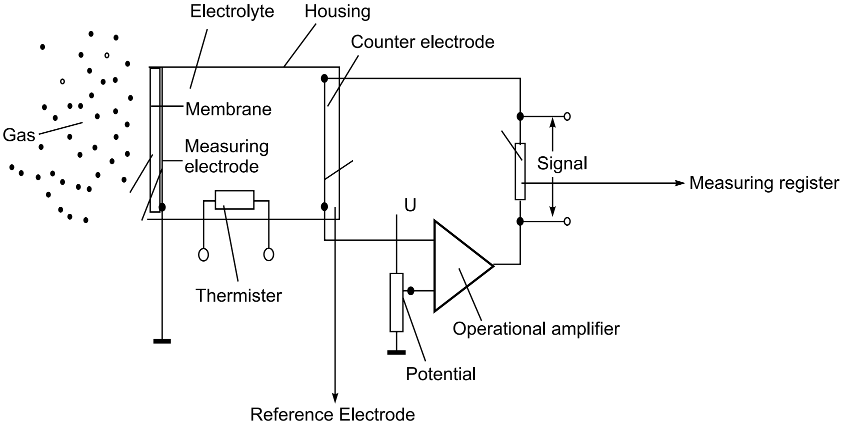


Fig. 1.12 *Block Diagram of Electrochemical sensor*

Classification of Electrochemical Sensor

Electrochemical sensors are devices that evaluate information about sample from measurement of some electrical parameter variations. According to the measures electrical parameter, the Electrochemical Sensors divided into three kinds.

They are:

(i) Potentiometric Sensors if we measure difference of two potentials (in volts)
(ii) Amperometric Sensors if the parameter of interest is current (in amperes) and
(iii) Chemiresistors or Conductometric Sensors if we measure resistance (in ohms) or conductance (the reciprocal of resistance)

These three kinds of sensors are working based on the basic principle of ohm's Law ie. The potential difference in a circuit is equal to the product of the current and the resistance. However, they all have two things in common. First, the measurement must be done with closed electrical circuit, meaning that a hypothetical (test) charge can be passed through the electrical circuit and returned to its origin. Second, electrical neutrality (if it contains electrically charged particles the total sum of negative charges will be equal to the total sum of positive charges if this condition to a solution of electrolytes implies the equality of the total positive ionic charges to the total negative ionic charges. This equality should hold even as we subdivide the solution into smaller and smaller volume elements). That means if, for example, a positive charge is added at one place of the closed circuit another positive charge must be taken out (or a negative charge added) somewhere else. A closed electrochemical circuit used for selective determination of pH is shown in Figure 1.13.

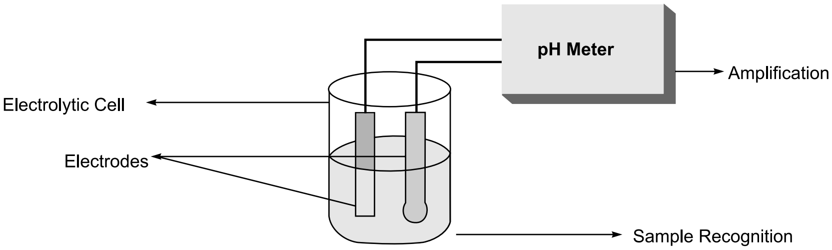


Fig. 1.13 *For electrochemical sensors, closed electrical circuit is a common requirement. The chemical specificity (recognition) comes from the ion selective electrode which is connected to amplifier.*

1.4.1 Potentiometric Sensors

Ion Selective Electrode (ISE) set-up for most true representative Potentiometric Sensor which is shown in Figure 1.14. Ion Selective Electrode is electrode or electrode assembly with a potential that is dependent on the concentration of an ionic species in the test solution and is used for electro analysis. Most common Ion-selective electrodes are often membrane type electrodes. In Ion Selective Electrode, the recognition of hydrogen ion is done by the glass electrode (A membrane electrode with a thin glass membrane (usually in the from of a bulb at the end of a glass tubing) sensing element. It is most often used as a pH electrode, but some glass compositions can also be sensitive to the concentration of other cations (e.g., sodium)), which is coupled with the reference electrode to complete the electrical circuit; and the sensor measures the potential difference between these two electrodes. Since the electrode is "selective for one ion, in preference to other ions". **The "mother of all ion-selective electrodes" is the glass electrode,** which is selectively sensitive to hydrogen ions (pH). It has an astonishing dynamic range of ~36 pH units, it is highly selective and would interfere only few ions. **The greater thing is it is oldest of all electrochemical sensors**. Because it has very high resistance (millions of ohms), due to its thin glass membrane, it requires a high input impedance amplifier for its operation shown in Figure 1.14a, which was introduced by Arnold Beckmann. The analytical potentiometry has flourished ever since.

Working Principle of Potentiometric Sensors: The working principle of glass electrode is similar and common to all ISEs (Ion Selective Electrodes). The glass electrode may be represented as follows:

$$\text{Ag, AgCl/1M HCl/H}^+ \text{ (test solution)}$$

When placed in a solution, the potential of glass electrode depends on the concentration of H+ ions in the solutions. The potential develop across glass membrane as the result of a concentration difference of H^+ ions on the two sides of membrane.

Glass, after it has been exposed to water, adsorbs and develops a very thin hydrated, gel-like layer at its surface. Hydrogen ion available in the solution likes to be in this gel layer, more so than in the solution. Therefore it partitions between the solution and the hydrated glass and establishes a partitioning equilibrium. Because hydrogen ion carries positive charge and because it "likes" the glass more than water, the gel layer becomes positively charged with respect to the solution. In other words, the charges have been separated and when that happens an equilibrium potential is formed. If the concentration (amount of dissolved) material (solute) in a solution) of hydrogen ion changes in the solution, more or less ions are partitioned into the glass, tracking the concentration changes.

The often mentioned pH sensor is the most important and most widely used potentiometric sensor as it measures the acidity/alkalinity of solutions; a parameter important in many practical areas, such as environmental protection, agriculture, biology, medicine, and many chemical processes.

A good sensor may be defined as the ability of a sensor to respond to the species of interest, regardless of the presence of other species, which are called *interferants*. Therefore, if I want to measure concentration of some ion, for example chloride ion, it is much more difficult to measure it in a "dirty" sample, containing many other ions and other chemicals, then in the pure solution containing only dissolved sodium chloride. A good, highly selective sensor will do the job even in the complex sample.

Nernst Equation is defining the equilibrium potential of an electrode. The potential is the sum of the standard electrode potential and a correction term for the deviation from unit concentrations of the reactant and the product of the electrode reaction in the solution: if the "reduced" from is a metal, a pure metal (not alloyed with other metals) is considered to be at unit concentration.

$$E = E^\circ + S \times \log \frac{C_{0x}}{C_{\text{red}}}$$

Basic Requirement of Potentiometric sensor: It requires a stable and reproducible reference shown in Figure. 1.14b. An electrode has a well known and stable equilibrium electrode potential. It is used as a reference point against which the potential of other electrodes (typically that of the working electrode or measuring electrode) can be measured in an electrochemical cell. In practice, there are a few commonly-used electrode assemblies that have an electrode potential independent of the electrolyte used in the cell. Examples: silver-chloride electrode, calomel electrode (0.244 V), and hydrogen electrode (0.0V). The electrode can be used as a measuring electrode in a sensor to determine the hydrogen ion concentration (pH), or it can be used as a reference electrode if all the concentrations are known and constant. It is very importance that exactly 50% of information from the measurement comes from the reference electrrode. In other words, even the best ISE without equally good reference electrode is worthless.

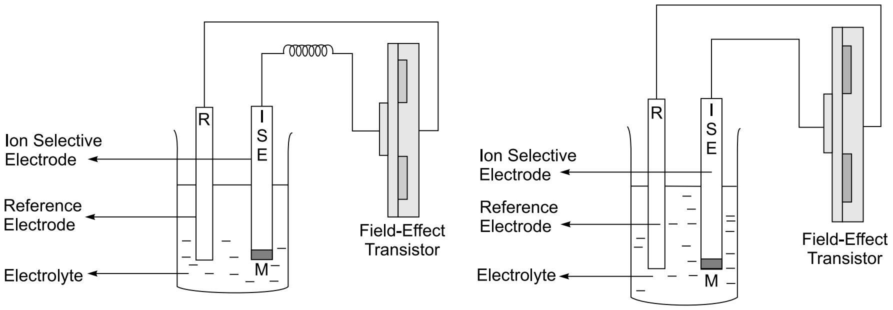


Fig. 1.14 *Potentiometric Sensors. (a) Ion-selective electrode (ISE) with reference electrode wired to the field-effect transistor amplifier. (b) The electrical connection between Ion Selective Electrode and the amplifier in shorter.*

Glucose potentiometric sensor: Glucose is an electrically neutral molecule. Hence, partitioning of glucose, or of any other electrically neutral molecule, to the membrane does not yield a signal. For design of a potentiometric sensor for such molecules one more step has to be made. Initially, the neutral glucose molecule has to be converted into ions, which are then selectively_ detected. Enzymatic oxidation of glucose to gluconic acid and the subsequent measurement of the liberated hydrogen ions.

The electrochemical reactions proceed as follows:

$$\text{D–glucose} + O_2 + H_2O \xrightarrow{\text{glucose oxidase}} \text{D–gluconic acid} + H_2O_2$$

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2\,e^-$$

When glucose dehydrogenase (GDH) was applied, the electrochemical reactions using electron transfer mediator in the glucose sensors are as follows:

$$\text{GDH}_{(OX)} + \text{D–glucose} \rightarrow \text{GDH}_{(red)} + \delta\text{–glucolactone}$$

$$\text{Mediator}_{(OX)} + \text{GDH(red)} \rightarrow \text{Mediator}_{(red)} + \text{GDH}_{(OX)}$$

$$\text{Mediator}_{(red)} \rightarrow \text{Mediator}_{(OX)} + e^-$$

Likewise, hydrolysis of carbon dioxide in water yields carbonic acid, which dissociates to carbonate ion and hydrogen ion, and the lather can be again detected by a pH electrode.

Urine glucose measurement is far inferior to blood glucose measurement, since (i) glucose only appears in the urine when it has exceeded a threshold level in blood, which varies from person to person, and (ii) the urine measurement integrates a glucose value over the time required for the bladder to fill.

1.4.2 Amperometric Sensors (Voltammetric Sensors)

This is second kind of electrochemical sensors. The principle of Amperometry is bases on the measurement of the current between the Working and Counter Electrode which is induced by a redox reaction at the Working Electrode. *The signal or response is with respect to the diffusion current, that is in amperometric sensors*. It is proportional to the concentration of the species, which are being electrochemically transformed (that is, reduced or oxidized) at the electrode. The redox process at the electrode represent charge transfer reactions that can proceed in either direction (oxidation or reduction) each with its own velocity. Some electrochemical reactions proceed very fast in both directions and their charge transfer resistance is very low and called them as reversible. On the other hand some reactions are very slow and their charge transfer resistance is very high, such electrode reactions called as irreversible. The velocities of electrode reactions depends on the applies potential. At more negative potential, the reduction is faster and its charge transfer resistnace becomes small. The same is true for reverse processes i.e., for oxidation.

The size of the electrode plays also a very important role in the performance of amperometric sensor. Electrodes whose diameter is smaller than 20 µm, so called microelectrodes have the best performance as chemical sensors.

The principle of operation of one the most successful amperometric sensor the glucose sensitive electrode. There, the biocatalyst is a highly selective enzyme glucose oxidase. An example of amperometric sensor deriving its selectivity from the mass transport resistance is oxygen sensor.

Usefulness of Amerometric sensors: The above mentioned oxygen sensor (often called the Clark electrode) is an important amperometric sensor, much used in water quality measurements as the dissolved oxygen content of the water is an important environmental factor affecting aquatic life. Many amperometric sensors are used in gas analysis in diverse areas such as the food and beverage industry, and in hazardous materials emergency response to detect dangerous materials like explosive or poisonous gases.

Estimation of Uric Acid (UA)

Uric acid (UA), a major nitrogenous compound in urine, is the product of purine metabolism in the human body and is related to many clinical disorders. One of the major problems in biological determinations of UA comes from electrochemical interferences such as ascorbic acid (AA), which has a similar oxidation potential, $E_{\frac{1}{2}} \approx 200$ mV versus SCE, at graphite electrodes, and is present at high concentration in biological system. There are two methods for thee measurement of UA, enzymatic and non-enzymatic.

The enzymatic procedures using uricase have been developed based on amperometic detection of H_2O_2 produced in the reaction below:

$$\text{Uric acid} + O_2 + 2H_2O \xrightarrow{\text{uricase}} \text{Allantoin} + H_2O_2 + CO_2$$

Othe enzymatic procedures are based on electron transfer mediators, the reactions are as follows:

$$\text{Uric acid} + \text{mediator(ox)} + 2H_2O \xrightarrow{\text{uricase}} \text{Allantoin} + \text{mediator(red)} + CO_2 + 2H^+$$

$$\text{Mediator(red)} \rightarrow \text{Mediator(ox)} + 2\,e^-$$

For the purpose of detecting UA in the presence of AA, differential pulse voltammetry was involved in non-enzymatic Uric acid sensors, because the differential pulse voltammetry peak currents of Uric acid ascorbic acid could be separated in this method and currents correlated with the concentration of uric acid and ascorbic acid.

Advantages

1. When the analyte is not optically active or opacity of the analyte, optical sensors may not be suit. In such conditions, Electrochemical sensors may be the best alternatives.
2. With the advancement in chemically modified sensors in voltammetric and potentiometric techniques, emerge better electrochemical sensors in the analysis of many more inorganic ions.
3. Electrochemical sensor are used in the analysis of electrochemically not active anions with the help of polymer modified electrodes.

Some More Applications

Electrochemical sensors have very wide range of applications in recent times. Few of them are:

1. Detection of oxygen and toxic gases like nitrogen oxideds, sulphur oxides, carbon oxides and hydrogen sulphide.
2. Useful to monitor environmental pollutants from various sources
3. To estimate the concentrations of ionic chemical content in blood, urine and other biological samples
4. For checking the race level concentration of fertilizers, pesticides, drugs and pharmaceuticals etc. from sample matrix.

1.5

SCIENCE OF CORROSION

Most of the metals (except noble metals such as Au, Pt and Ag) occur in nature in combined form of their oxides, hydroxides, sulphides, chlorides, carbonates and silicates. Most metals have a natural tendency to revert back to combined state due to the want of stability. Metals and alloys play an important role in engineering applications and also in day-to-day life.

The natural combined form of metal (i.e., mineral form) is more stable than the other metals. That is why metal after extraction from its ore tends to revert to the stable natural combined form when it comes in contact with other elements in the environment. In other words, deterioration or destruction of the metal starts at the surface when exposed to atmosphere, water or any other reactive liquid medium. This phenomenon is called as 'corrosion'.

$$\boxed{\text{Metal}} \underset{\substack{\text{Metallurgy} \\ \text{(reduction)}}}{\overset{\substack{\text{Corrosion} \\ \text{(oxidation)}}}{\rightleftharpoons}} \boxed{\begin{matrix}\text{Metallic} \\ \text{compound}\end{matrix}} + \text{Energy}$$

Corrosion is reverse processes of metallurgy. Rusting of iron and steel is the most familiar example of corrosion processes. It is estimated that nearly 20% of iron produced annually is used to replace iron objects that have been disposed due to rust damage.

1.5.1 Corrosion

Corrosion may be defined as "the processes of gradual deterioration or disintegration or eating away of metal from its surface by unwanted chemical or electrochemical reaction with its environment."

Formation of a layer of reddish scale of hydrated ferric oxide on the surface of iron is also called 'Rusting of Iron' and formation of green film of basic carbonate on the surface of copper are the most common and familiar examples of corrosion.

$$\text{Metal} + \text{oxygen} \rightarrow \text{Metal oxide}$$

$$2Fe^{2+} + \frac{3}{2}O_2 + 3H_2O \rightarrow Fe_2O_3 \cdot 3H_2O(\text{Rust})$$

$$2Cu^{2+} + \text{moisture} + CO_2 \rightarrow \underset{\text{(Basic cupric carbonate)}}{[CuCO_3 + Cu(OH)_2]}$$

1.5.2 Disadvantages or Consequences of Corrosion

The disadvantages of corrosion briefly are given below:

1. Poor in appearance.
2. The plant may be shut down due to failure.
3. Decrease in production rate and Replacement of equipment is time consuming.
4. Contamination of product.
5. Safety from a fire hazard or explosion or release of toxic product.
6. Health from pollution due to corrosion product or due to escaping of chemical from a corroded equipment.

1.6

TYPES OF CORROSION

On the basis of environment to which it is exposed, corrosion is divided into two types

(a) Chemical or dry corrosion
(b) Electrochemical or wet corrosion.

1.6.1 Chemical or Dry Corrosion

This type of corrosion occurs mainly through direct chemical action of atmospheric gases (O_2, halogen, H_2S, SO_2, N_2, anhydrous inorganic liquids) with metal surface in its immediate proximity.

There are three types of chemical corrosion.

(a) Oxidation corrosion
(b) Corrosion by other gases
(c) Liquid-metal corrosion

(a) Oxidation Corrosion

This is carried out by direct action of oxygen at low or high temperature on metals generally in absence of moisture. At normal temperature, metals are very shortly attacked. Alkali and alkaline earth metals even at low temperature are rapidly oxidised. At high temperatures, except Ag, Au and Pt, all other metals get oxidised.

The reactions involved are

$$2M \rightarrow 2M^{n+} + 2ne^- \qquad \text{Loss of electrons}$$

$$nO_2 + 2ne^- \rightarrow 2nO^{2-} \qquad \text{Gaining of electrons}$$

or

$$2M + nO_2 \rightarrow \underbrace{\underset{\text{Metal ion}}{2M^{n+}} + \underset{\text{Oxide ion}}{2nO^{2-}}}_{\text{Metal oxide}}$$

Mechanism At the surface of the metal, oxidation takes place and resulting metal oxide scale form a barrier which reduce further oxidation. To continue oxidation, either the metal diffuses outward through the scale to the surface or inwards diffusion of oxygen through scale to the underlying metal. Both the cases are possible, but outward diffusion of metal is normally more rapid than inward diffusion of O_2 since metal ion is appreciably smaller than the oxygen ion and hence much of higher mobility of metal ion (see Fig. 1.15)

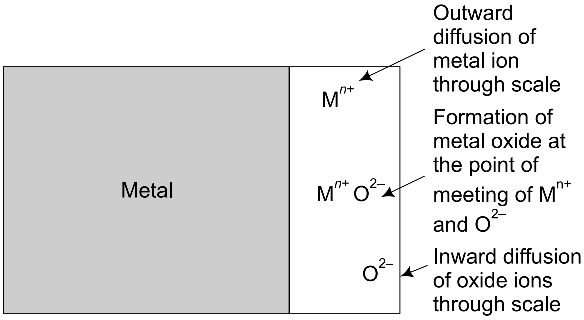


Fig. 1.15 *Mechanism of oxidation corrosion*

The nature of oxide film formed plays an important part at the surface of the metal which decides further action if the film is:

(i) Stable, i.e. impervious and tightly-adhering like oxide film or Cu and Al, it acts as protective coating and hence further corrosion is prevented.

(ii) Unstable, i.e. and decomposes back to metal and oxygen. Hence, oxidation corrosion is not possible in this case. That's why Ag, Al and Pt do not undergo oxidation corrosion.

(iii) Volatile i.e., the moment it is formed, it gets volatilised and metal surface again exposed for further attacking to continue rapid corrosion, e.g.

$$2Mo + 2O_2 \rightarrow \underset{\text{Volatile}}{2MoO_3}$$

This causes Molybdenum undergo excessive corrosion.

(iv) Porous, i.e., atmospheric oxygen passes through poles or cracks of the layer to the underlying metal surface and hence the corrosion continues till the entire metal is converted to metal oxide.

Pilling-Bedworth Rule The Rule states that "an oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed."

$$\text{Specific Ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous through which oxygen can diffuse and further corrosion takes place.

For example, Alkali and Alkaline earth metals (Li, Na, K) formed oxides of volume less than volume of metals, which causes continuous corrosion. Metals like aluminium forms oxide, whose volume is greater than that of metal which causes non-porous layer and consequently retard corrosion.

(b) Corrosion by Other Gases: (SO_2, H_2S, CO_2, F_2, etc.)

The corrosion of this type depends mainly on the chemical affinity between the metal and gas involved. The intensity of attack depends on the formation protective or non-protective films on the metal surface.

(i) If the film is protective or non-porous (AgCl resulting from attack of Cl_2 on Ag), the extent of corrosion decrease due to the formation of AgCl film which protects metal from further attack.

(ii) If the film is non-protective or porous, the metal surface is gradually destroyed, e.g. Formation of volatile $SnCl_4^-$ by the attack of chlorine gas on tin.

(c) Liquid-metal Corrosion

This is due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy. This type of corrosion occurs in devices used for nuclear plant. The corrosion reaction is carried out either by dissolution of solid metal by liquid metal or internal penetration of liquid metal into solid metal. Both reactions lead to weakening of solid metal.

Ex. Coolant (Sodium metal) causes cadmium corrosion in nuclear reactor.

1.6.2 Electrochemical or Wet Corrosion

This type of corrosion mostly takes place: (i) where a conducting liquid is in contact with metal, or (ii) two dissimilar metals, (iii) alloys are either dipped or immersed partially in solution. Electrochemical corrosion involves due to

(i) Existence of separate 'anodic' and 'cathodic' areas/parts between which current flows through conducting medium.

(ii) Oxidation takes place at anodic part which generate metallic ions. *Hence corrosion always occurs at Anodic ions.*

At anode: $$\underset{\text{Metal ions}}{M \rightarrow M^{n+} + ne^-}$$

M^{n+} — Dissolved in solution C

Metal ion — Forms compound such as oxide

(iii) At cathodic part, reduction reaction (electronation) occurs. Generally, cathodic reaction do not affect the cathode since, most metals do not further reduce. Non-metallic ions like OH^- or O^{2-} are formed at cathodic area.

(iv) The metallic and non-metallic ions formed at anode and cathode respectively diffuse each other through conducting medium and form a corrosion product somewhere between anode and cathode.

Mechanism of Electrochemical or Wet Corrosion

Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal as metal ions with the liberation of free electrons

Anodic area $\quad M \rightarrow M^{n+} + ne^-$ (oxidation)

On the other side, the cathodic reaction consumes the electrons with either (a) evolution of hydrogen or (b) absorption of oxygen takes place based on the nature of corrosion environment.

(a) Evolution of Hydrogen

This type of corrosion happens generally in acidic medium when 'Fe' metal is in contact with acidic medium, the anodic reaction is dissolution of Iron as ferrous with the liberation of electrons.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(oxidation)}$$

The released electrons from anode flow through the metal from anode to cathode whereas H^+ ions get reduced to H_2.

$$2H^+ + 2e^- \rightarrow H_2\uparrow \quad \text{(reduction)}$$

The overall reaction is

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$$

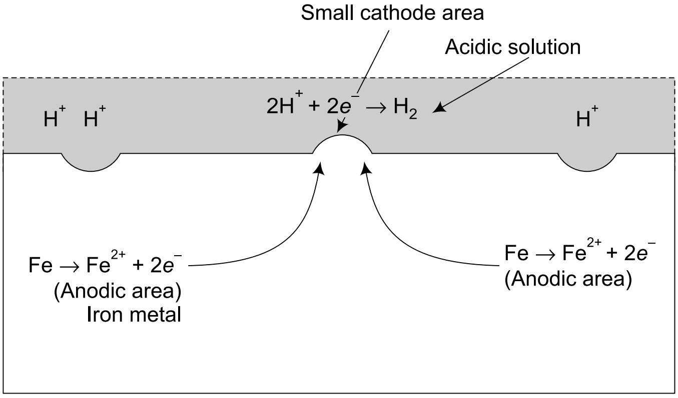


Fig. 1.16 *Mechanism of wet corrosion by hydrogen evolution type*

This type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ion". All the metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous liberation of hydrogen gas. In this type of corrosion, anodes are large areas whereas cathodes are small areas.

(b) Absorption of Oxygen

When metals are in contact with slightly alkaline or neutral solutions (H_2O) with some amount of dissolved oxygen, this type of corrosion takes place. Rusting of Iron in presence of atmospheric oxygen with neutral aqueous electrolyte solution is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, the oxide film develops cracks, anodic area created on the surface while used metal part acts as cathodes. It shows that anodes are small area while rest of metallic part forms large area of cathode.

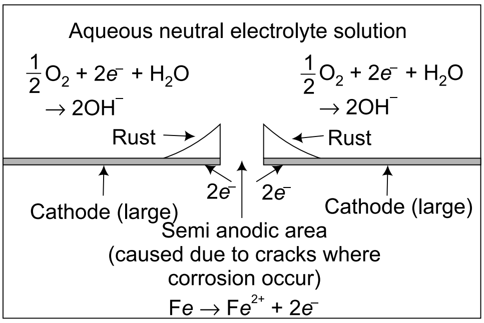


Fig. 1.17 *Mechanism of wet corrosion by O_2 absorption*

At the anode: Iron dissolves as Fe^{2+} with release of electrons.

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (oxidation)}$$

At cathodes: The liberated electrons flow from the anodic to cathodic area through Iron metal where electrons are taken up by dissolved oxygen to form OH^- ions

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

The Fe^{2+} ions at anode and OH^- ions at the cathode react to produce Ferrous hydroxide precipitate.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow$$

(i) If the oxygen is available in excess, Ferrous hydroxide is easily oxidised to Ferric hydroxide

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

The above product called yellow rust corresponds to $Fe_2O_3\ xH_2O$

(ii) If the supply of oxygen is limited, the corrosion product may be black anhydrous magnetite (Fe_3O_4)

(c) Comparison of Chemical and Electrochemical Corrosion

Chemical Corrosion	*Electrochemical/Wet Corrosion*
1. It occurs due to direct chemical attack of metal by environment	1. It occurs due to the formation of large number of anodic and cathodic areas in conducting medium
2. It is explained by absorption mechanism	2. It follows the electrochemical reaction
3. The product of corrosion accumulate on the same spot where corrosion occurs	3. Corrosion occurs at anode while corrosion products gather at cathode
4. It occurs on homogeneous and heterogeneous surfaces.	4. It occurs only on heterogeneous metal surfaces.
5. It is slow process	5. It is a fast process

1.7

THEORIES OF CORROSION

The following theories the tendency and process of corrosion:

(a) ***Direct chemical attack*** This theory is explained on the basis of dry chemical corrosion. Whenever corrosion takes place by direct chemical attack, the film of a solid corrosion product normally formed on the surface of the metal which protects, the metal not to corrode further. However if corrosion product is soluble, then the metal is exposed and further attack corrosion. For example, Chlorine and Iodine attack silver generating a protective film of silver halide. One of the most common ways in which metals are attacked by atmospheric oxygen. Alkali and alkali earth metals suffer extensive oxidation even at low temperature whereas at high temperature all the metals except Pt, Au, Ag are practically oxidised. The intensity of corrosion will depend on the basis of nature of oxide deposit. If it is nonporous, then the metal is protected from oxide film on the metal surface. If it is porous in nature, the oxygen diffuses, inside and further corrosion takes place. For example, Al and chromium form extremely protective oxide layer and hence these metals are normally employed for alloy formation with other more readily attacked metals to provide resistance towards oxidation.

(b) ***The acid theory*** This theory reveals that the presence of acid is essential for corrosion. Rusting of iron is well explained by this theory. Iron reacts with O_2, CO_2 and moisture of surrounding atmosphere results into a soluble Ferrous carbonate which is further oxidised to basic ferric carbonate and finally ferric oxide hydrated.

$$Fe + O + 2CO_2 + H_2O \rightarrow Fe(HCO_3)_2$$

$$2Fe(HCO_3)_2 + H_2O + O \rightarrow 2Fe(OH)CO_3 + 2CO_2 + 2H_2O$$

$$2Fe(OH)CO_3 + 2H_2O \rightarrow 2Fe(OH)_3 + 2CO_2$$

(c) ***Electrochemical Theory*** This theory explains indirect or wet corrosion. The modern electrochemical theory based on Nernst theory states that all metals have a tendency to pass into solution. The tendency of a metal to pass into solution when immersed in a solution of its salt is measured in terms of its electrode potential. If a metal having a higher electrode potential comes into contact with a metal having lower electrode potential, "a galvanic cell" setup and metal at higher electrode potential becomes anode and goes into the solution to a measurable extent. If the surrounding liquid is sufficiently acidic, H_2 gas will be evolved at cathode, while anodic metal dissolves. The greater the difference in potentials of cathode and anode, the greater will be the corrosion. Also, smaller will be the anode area as compared to cathode, the more severe will be the corrosion.

1.8

GALVANIC SERIES

Electrochemical series will give useful information regarding chemical reactivity of metals and may not be able to provide sufficient information in predicting the corrosion behaviour of metal in a particular set of environmental conditions. Passivation makes effective electrode potential of some metals more passive and acts as cathodic and exhibits noble behaviour. This behaviour is exactly opposite to that predicted by electrochemical series. For more practical series called "Galvanic series" (see Table 1.2) have been prepared by studying the corrosion of metals and alloys in a given environment like in sea-water. This series gives real and useful information about corrosion behaviour of metals and alloys in a given environment.

Table 1.2 *Galvanic Series (on the basis of relative oxidation potential of sea water)*

1. Mg	Anodic	14. Brass
2. Mg alloy	↓ ↑	15. Monel
3. Zn		16. Silver solder
4. Al		17. Cu
5. Al alloy		18. Ni
6. Mild steel		19. Cr stainless steel
7. Cast Iron		20. 18–08 Stainless steel
8. High Ni cast Iron		21. 18–8 Mo steel
9. Pb-Sn solder		22. Ag
10. Pb		23. Ti
11. Sn		24. Graphite
12. Iconel		25. Au
13. Ni-Mo-Fe alloy	Cathodic	26. Pt

Galvanic series predicts the corrosion tendency of both metals and non-metals in actual environment whereas electrochemical series predicts the displacement of metals and non-metals in electrolyte. Galvanic series, electrode potentials are measured using calomel electrode as reference electrode whereas in electrochemical series electrode potentials are measured with standard hydrogen electrode as reference electrode.

1.9

GALVANIC CORROSION

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is known as Galvanic corrosion. For example, Zn and Cu; Zn and Ag; Fe and Cu.

In the Zn–Cu Galvanic Cell, Zn acts as anode where oxidation and corrosion occurs and Cu behaves as cathode and is protected.

Mechanism In acidic medium, the corrosion takes place with evolution of hydrogen while in neutral alkaline environment, oxygen absorption occurs. The electron current flows from the anodic metal to the cathodic metal.

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \text{ (Oxidation)}$$

Thus, corrosion occurs at the anodic metal (Zn): while the cathodic part (Cu) is potential from the corrosion.

For example Steel pipe connected to copper plumbing
Steel screw as brass marine hardware
Lead antimony solder around copper wire.

Galvanic corrosion can be regulated by

(a) avoiding galvanic couple and
(b) keeping an insulating material between two metals.

1.10

CONCENTRATION CELL CORROSION OR DIFFERENTIAL AERATION CORROSION

It occurs mainly due to electrochemical attack on the metal surface exposed to an electrolyte of varying concentrations or varying aerations. The most common type of concentration cell corrosion is differential aeration corrosion which occurs when one part of metal is exposed to different air concentration from other part. This causes a difference in potentials between the different areas. Poor oxygenated metallic part becomes anodic and undergoes oxidation and well oxygenated part acts as cathodic in nature.

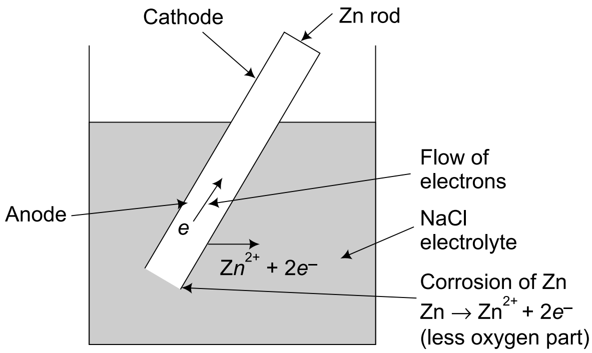


Fig. 1.18 *Concentration cell corrosion*

If a 'Zn' rod is partially immersed in a diluted neutral NaCl solution, the part above and adjacent to the water line are well aerated and hence become cathodic. Whereas parts immersed show poorly oxygenated and become anodic. So a difference of potential is created which causes flow of current between the two differential aerated areas of the same metal. Zinc will dissolve at the anode and oxygen will take up electrons at the cathodic area to form hydroxyl ions.

$$Zn \rightarrow Zn^{2+} + 2e^- \text{ (Oxidation)}$$

$$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ (Reduction)}$$

The following are the facts about differential aeration corrosion:

(i) Less oxygenated area is the anode. Hence cracks serve as foci for corrosion.

(ii) Corrosion is accelerated under accumulation of dirt, scales, water drops or other contaminations. This will restrict the access of oxygen resulting in anode to promote greater accumulation. This result localises corrosion.

(iii) Metals exposed to aqueous media corrode under blocks of wood or glass which restrict the access of oxygen.

1.11

FACTORS INFLUENCING CORROSION

The rate and extent of corrosion depend majorly on: (a) The nature of the metal and (b) The nature of the environment.

1.11.1 Nature of the Metal

Many characteristic properties of metal are responsible for corrosion. These are:

(i) *Position in Galvanic series:* When two metals or alloys are in contact with a conducting medium, then the metal at higher galvanic series is more active towards corrosion. Furthermore apart the two metals in the galvanic series, the faster will be the corrosion of the anodic metal/alloy.

(ii) *Overvoltage:* It can be defined as the difference of potential at which electrolysis actually takes place, and theoretical decomposition potential for the same solution is known as overvoltage. For example, electrolysis of H_2SO_4 with 'Pt' occurs at 1.70 volts whereas its theoretical potential is 1.229 volts. The difference, i.e., 0.471 volt is overvoltage. Reduction in overvoltage of corroding metal/alloy accelerate the corrosion rate.

(iii) *Relative areas of anode and cathode:* Small anodic and large cathodic area causes severe corrosion. When two dissimilar metals/alloys are in contact, the corrosion of anodic part is directly proportional to the ratio of areas of the cathodic part and anodic part.

For example, a small steel pipe fitted in a large copper tank

(iv) *Purity of the metal:* Impurities in a metal cause heterogeneity and turn minute electrochemical cells and anodic part gets corroded. For example, zinc metal containing impurities Pb or Fe, undergoes corrosion of zinc due to the formation of local electrochemical cells. The rate and tendency of corrosion increase with increase in exposure and extent of the impurities. The corrosion of metal is low when its purity is at high.

(v) *Physical state of the metal:* The rate of corrosion is influenced by physical state of metal such as grain size, stress, crystal orientation The smaller the grain size of metal, greater the solubility of the metal and severe is corrosion. Areas under stress, even in pure metal become anode and undergoing corrosion.

(vi) *Nature of surface film:* All the metals except Au, Ag, Pt interact with atmospheric air and form a thin surface film of metal oxide. The ratio of volume of metal oxide to the metal is known as Specific Volume Ratio. Higher the value of SVR, lower will be the corrosion rate. For example, SVR of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively. Hence, we can say that W is least corrosion.

(vii) *Passivity of Metal:* Some metals like Ti, Al, Cr, Ni and Co show passive due to formation of non-porous thin and protective film of self-heating nature. Passivity of metal decrease corrosion rate.

For example, Corrosion resistance of stainless steel is due to passive character of chromium present in steel.

(viii) *Solubility of corrosion product:* In electrochemical corrosions if the corroding metal is dissolved in the contact medium, then the corrosion is rapid. If the corrosion product is insoluble, create physical barrier thereby suppressing further corrosion.

For example, Corrosion of Pb in H_2SO_4 decreases due to formation of insoluble $PbSO_4$.

(ix) *Volatility of corrosion product:* If the corrosion product is volatile, the underlying metal is exposed further and cause severe corrosion.

For example, The oxidation corrosion product of MoO_3 is volatile.

1.12

NATURE OF CORRODING ENVIRONMENT

The process of corrosion will also decide on the basis of environment in which the metal is working.

(i) *Temperature:* The rate of corrosion accelerates when the temperature of environment increases.

(ii) *Humidity of air:* The humidity of air is the deciding factor in atmospheric corrosion. Critical humidity is defined as 'the relative humidity above which atmospheric corrosion rate of metal increases sharply'. The value of critical humidity depends on nature of metal and corrosion product.

In humidity environment, the rates of corrosion is higher due to gases, and vapours present in atmosphere furnish water to the electrolyte, essential to establish an electrochemical corrosion cell. The oxide film formed on the surface of metal has the property to absorb moisture. In the presence of moisturised environment, corrosion rate is enhanced.

(iii) *Presence of impurities in atmosphere:* Presence of corrosive gases such as SO_2, CO_2, H_2S, O_2, etc. in atmosphere increases acidity, and high electrical conductivity, which causes severe corrosion.

(iv) *Presence of suspended particles in atmosphere:* The suspended particles in atmosphere may be chemically active or inactive. If the suspended particles in nature are chemically active, (NaCl, $(NH_4)_2SO_4$), they absorb moisture and thus behave a strong electrolytic medium and scope for severe corrosion.

If the suspended particles in nature are chemically inactive (charcoal), they absorb both sulphur gas and moisture and slowly enhance the corrosion.

(v) *Influence of pH:* The corrosion is higher in acidic media than basic and neutral media. The corrosion rate of Iron in oxygen free water is slow until the pH is < 5.0. The corrosion of metals readily attacked by acid can be reduced by increase of pH of the attacking environment.

For example, Zn rapidly corrodes in weakly acidic solution even in carbonic acid, suffers minimum corrosion at $pH = 11.0$.

(vi) *Conductance of corroding medium:* Conductance of medium is important in the case of underground and submerged structures. Corrosion-conductance of dry-sandy soil is lower than those of mineralised or clayey soils.

Stray currents (from power breakages) will cause more severe damage to the metallic structures, buried under clayey and mineralised soil than those under dry sandy soils.

1.13

CONTROL OF CORROSION

Following are some of the methods for control of corrosion:

1.13.1 Cathodic Protection

The main principle involved in this method is to force the metal to be protected to behave like cathode so that corrosion does not occur. Sacrificial Anodic Protection or Galvanic Protection is the best method in the case of cathodic protection.

In this method, the metal structure to be protected is connected by a wire to a more active metal so that all the corrosion is concentrated at more active metal and saving the metal structure from the corrosion.

The more active metal so used is known as "sacrificial anode". Examples of some of common sacrificial anodes are Mg, Zn, Al and their alloys.

'Zn' is used as sacrificial anode in good electrolytes as sea water. 'Mg' is used in high resistive electrolytes such a soil due to its most negative potential and it can provide highest current output.

Applications Important application of this technique are:

(i) Protection of buried pipelines and underground cables from soil [Fig. 1.19(a)].

(ii) Protection of ships and boats hulls from marine corrosion. Sheets of Mg/Zn are hung around ship hull, these sheets being anodic to Iron and hence Mg/Zn corroded.

(iii) The formation of rusty water is prevented by insertion of Mg sheet/rod into domestic water boiler/Tanks [Fig. 1.19(b)].

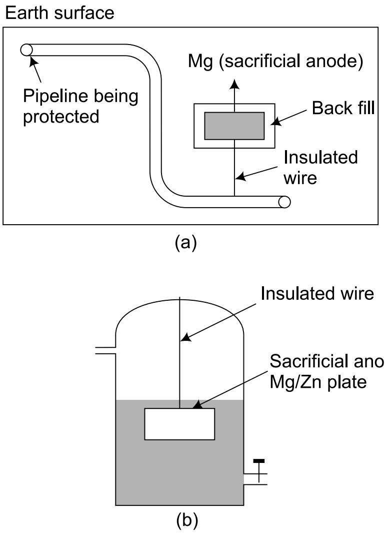


Fig. 1.19 *Galvanic protection using sacrificial anode*

1.13.2 Impressed Current Cathodic Protection

In this method, an impressed current is applied in opposite direction to the corrosion current to nullify and convert the corroding metal from anode to cathode. Once the metal becomes cathodic, it is protected from corrosion. The anode may be either an inert material or one which deteriorates and will have to replace periodically. The commonly used anodic materials are graphite, carbon, steel, high silica iron, scrap iron and platinum. Usually a sufficient d.c. current is applied to an insoluble anode buried in the soil and connected to the metallic structure to be protected. The anode is buried usually in backfil such as gypsum/coke breeze to increase electrical contact with the surrounding soil.

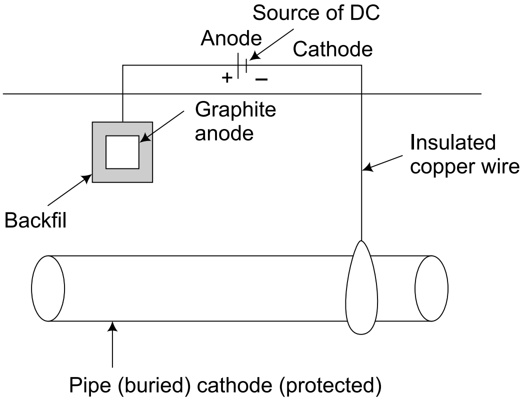


Fig. 1.20 *Impressed current cathodic protection*

Application This protection technique is used when electrolyte resistivity and current requirement are high. It is employed in the case of buried structures such as water tanks, pipe-lines, transmission line towers, laid-up ships.

1.14

USE OF INHIBITORS

A substance which on addition in small quantities to the aqueous corrosive environment decreases the corrosion of metal effectively is called corrosion inhibitor. Corrosion inhibitors are classified into two types. They are:

(i) *Anodic inhibitors:* They are adsorbed on the metal surface forming a protective coating, thereby reducing the rate of corrosion.

For example, Chromate, Phosphates, Tungstates or other ions of transition elements with a high oxygen content.

(ii) *Cathodic Inhibitors:*

(a) In anodic media, the cathodic reaction is evolution of hydrogen.

$$2H^+ (aq.) + 2e^- \rightarrow H_2(g) \uparrow$$

Corrosion may be reduced either by slowing down diffusion of H^+ ions to the cathode or increasing the overvoltage of hydrogen evolution. The diffusion of H^+ ions considerably decreases by organic inhibitors which are capable of adsorbed at metal surface (such as mercaptans, amines heterocyclic nitrogen compounds). Antimony and Arsenic oxides as inhibitors due to they deposit adherent film of metallic arsenic or antimony at cathodic areas thereby increasing hydrogen overvoltage.

(b) In neutral and aqueous medium, the cathodic reaction is

$$H_2O + \frac{1}{2} O_2 + 2e^- \rightleftharpoons 2OH^- \text{ (aq.)}$$

The corrosion can be controlled either by eliminating oxygen from contact medium or by retarding its diffusion to cathodic area. The former is attained by the addition of Na_2SO_3 or by deaeration. The later is carried out by Mg, Zn, or Ni salts which react with OH^- ions forming corresponding insoluble hydroxides which deposit on cathode forming less impermeable barrier.

1.15
ELECTROPLATING

Electroplating is the process of deposition of coating metal in the base metal by passing a direct current through an electrolytic solution which contains the soluble salt of the coating metal. The main objective of electroplating is (i) To increase the resistance of the plated metal, (ii) resistance to chemical attack or (iii) to improve physical appearance and hardness, (iv) for improvement of commercial value and decoration of metal.

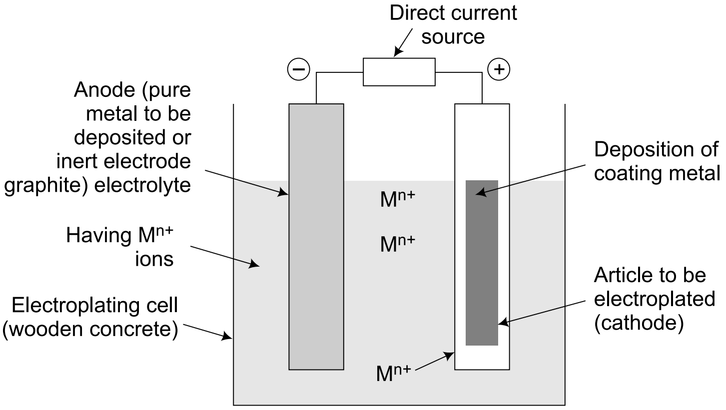


Fig. 1.21 *Electroplating (cathode)*

Oils, greases, etc are removed from the surface of metal to be chloroplated by treatment with organic solvents such as tetrachloroethylene. Surface scales, oxides, etc. are then removed by applying HCl (Nickel or Copper plating) or H_2SO_4 (chromium plating). The cleaned metal is then made cathode of an electrolytic cell. The anode is either an inert material of good electrical conductivity (graphite) or coating metal (pure) itself. Electrolytic is a soluble salt solution of a metal to be coated. The anode and cathode are dipped in electrolytic solution kept in an electroplating cell. When direct current passes through, coating metal ion migrates towards cathode and gets deposited there in the form of thin layer.

1.15.1 Electroplating of Nickel

Nickel plating gives hard, adherent and good wear resistance surface. General nickel plating is used as an undercoat for articles which are finally to be chromium plated.

Requirements for electroplating

1. *Electrolytic bath:* It consists of nickel sulphate (250 g/L), nickel chloride (450 g/L) and boric acid (30 g/L).
2. *pH:* Maintained at 4.0 by boric acid buffer
3. *Operating temperature:* 40–70°C
4. *Current density:* 20–30 mA/cm^2
5. *Additive agent:* Saccharin/coumarin derivatives
6. *Cathode:* Metal article to be plated
7. *Anode:* Nickel pallets/pieces taken in a titanium mesh basket
8. *Current efficiency:* 95%

1.15.2 Electroplating of Chromium

Chromium plating is a porous and non-adherent in which it requires that the article is first given under coat of copper or nickel. Chromium electroplating is carried out in acidic medium by insoluble anode.

1. *Plating bath:* Chromic acid (H_2CrO_4) and H_2SO_4 is 100 : 1 by volume.
2. *Operating temp:* 40–50°C
3. *Catalyst:* SO_4^{2-} ion Cr(IV) convert is to Cr(III) by complex anodic reaction is presence of SO_4^{2-}.
4. *Current density:* 100–200 mA/cm^2
5. *Anode:* Lead and antimony alloy is used for getting insoluble anodes.
6. *Cathode:* Article to be plated and pretreated with organic solvents to remove oils and greases.
7. *Current efficiency:* 10–12%

1.16
ELECTROLESS PLATING

Electroless plating is also a widely used technique to protect the base metal from the corrosion. It is also called displacement plating or Immersion coating/plating. It involves base metal to be immersed in a bath of noble metal salt used for plating. The noble metal ion is displaced from its salt solution by the base metal ion and forms a thin uniform deposit on the base metal article. The better example for electroless plating is nickel plating.

The base metal to be protected from corrosion, is immersed in a bath containing sodium hypophosphate and nickel sulphate at pH 4.5–5.0 and maintain bath temperature of about 100°C. The hypophosphate reduces nickel ion to metal nickel and finally converts into nickel phosphide. An alloy of nickel and nickel phosphide is deposited on the base metal article surface forming a strong adherent non-porous coating with high corrosion resistance.

1.17
SURFACE COATINGS

The application of metallic coating is important method for protecting a metal from the corrosion. The protective coating may be metallic, inorganic non-metallic or organic substances. The protective coatings protect the metal from corrosion by acting as a barrier between the metal and corrosion environment. Before applying of any coating, it is very essential to prepare the metal surface properly. Normally, it involves 3 steps: (i) Removal of grease and other surface contaminants, (ii) Removal of oxide scale rust and corrosion products, and (iii) Etching treatment for better adhesion of coating metal on the surface.

(i) *Removal of oils and greases:* They may be removed by using organic solvents such as acetone, trichloroethylene, CCl_4, xylene, etc.

(ii) *Rust and oxide scales:* These are usually removed by abrasion with the help of grinding, sand blasting, wire brushing or by acid pickling.
For example, 5% H_2SO_4 is used to remove mill scales of iron and steel parts. Brass, bronze articles are pickled by immersion in a mixture of HCl and H_2SO_4 with a little HNO_3 is added.

(iii) *Fine etching:* This is normally employed for better adhesion and improved appearance of the coatings.

1.17.1 Metallic Coatings

These are mostly applied on steel and iron articles since they are cheap and commonly used for various purposes.

Zinc, tin, nickel, copper, chromium, aluminium and lead are commonly used in the metallic coatings.

(a) *Metal spraying*: In this technique, the molten metal is spraying with the help of spraying pistol on the cold surface of the base metal. Spraying is effective provided the surface of the base metal must properly cleaned. After surface cleaning, the spraying as done immediately. The metal thus sprayed adhered to the surface well and protect the metal from the surrounding environment. If the coating is porous or non-adherent, the process is not effective. Examples of coating metals are Zn, Al, Cu, Ni, Sn, etc.

(b) *Hot dipping*: In this technique, the metal to be coated dipped in the molten metal bath used for coating with sufficient time. After some interval, the metal is taken out from the molten bath and a thin layer of protective metal coating is found which prevent the corrosion of base metal. This method is widely used for applying coating of low melting metals and alloys. The coating of metals such as lead, tin and zinc which have low melting points are generally used in hot dipping. The processes of providing a zinc coating on iron is called Galvanising and one providing a tin coating on iron is called Tinning.

(c) *Metal cladding*: Metal cladding is a process in which a dense, homogeneous layer of coating metal is bonded firmly the base metal on one side or both sides to impart corrosion and wear resistance. The choice of cladding material depends on the corrosion resistance required for the given environment. Some of the important corrosion resistant metals like Cu, Pt, Ag, Pb, Ni, etc. and alloys like nickel alloys, copper alloys, stainless steel, etc. are used as cladding materials. Some of the cladding methods include (i) rolling the clean sheets or plates of the two materials together (ii) applying the coating sheet by spot welding or resistance welding and (iii) fusing the cladding material on the surface of the base metal. One of these cladding method is by arranging sheets of coating material and base metal in the form of sandwich, which in turn passed through rollers under the action of heat and pressure (Fig. 1.22).

Applications

- Aluminium clad steel is used in aircraft fuel gauge, in water tanks and gasoline.
- Copper clad steel is used in electrical Industry because of its high strength and good electrical conductivity.

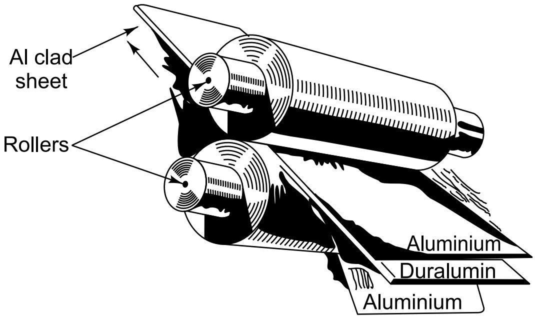


Fig. 1.22 *The metal cladding of duralumin*

(d) *Cementation*: In this technique, the base metal (steel/iron) packed with zinc powder and heated them to a temperature just below the melting temperature of base metal. By diffusion of coating metal, into the base metal, an alloy of two metals is formed. This technique is used for producing an alloying layer on the steel or iron surfaces. If the zinc is made alloy on iron, it is called sheradising, if aluminium is made alloy on iron it is called colourising. A colourised coating is harder and more heat resistant than a zinc coating.

1.17.2 Inorganic Non-metallic Coatings

The coatings of certain inorganic non-metallic substances can be applied on the surfaces of the metals for corrosion protection. These include surface conversion or chemical dip coatings, anodised oxide coatings and vitreous enamel coatings.

(a) *Surface conversion or chemical dip coatings:* In this technique the base metal is immersed in a suitable chemical solution which can react with metal surface forming an adherent coating. These coatings show good protection for the base metal from the corrosive environment and sometimes it act as decorative value. Many of these coatings serve as under coats for the application of enamels, paints and organic coatings. Most common examples for surface conversion coatings are oxide coatings, phosphate coatings and chromate coatings. The oxide coating can be formed by treating the base metal with alkaline oxidising agent. Phosphate coatings can be formed by reacting in base metal with phosphoric acid and phosphate of Zn, Fe (or) Mn in presence of copper salt which act as accelerator. Mg metal and its alloys can be better protected by treating with $Na_2Cr_2O_7$ (or) $Na_2Cr_2O_7$ and HNO_3 followed by painting.

(b) *Anodised coatings:* Anodised coating is normally produced on non-ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process in which base metal is made as anode in an electrolytic bath of definite composition and using direct electric current. The most commonly used electrolytic baths are boric acid, phosphoric acid, Chromic acid, sulphuric acid, oxalic acid or their mixtures. Lead is generally used as cathode.

The anodic oxide film formed on the 'Al' as the above electrolytic bath tends to be porous and provide good adhere for paints. The corrosive resistance and strength of the anodised film is scaled by immersing in boiling water. This helps the changes porous alumina at the surface is to its hydrate ($Al_2O_3 \cdot H_2O$) which occupies more volume thereby the pores are sealed.

(c) *Vitreous enamel coatings:* These coatings are widely used for ferrous materials employed to the equipment in dairy, food, chemical, pharmaceutical industries. Enamelled steel is used for tables, stoves, refrigerators, kitchen utensils, etc. Vitreous (or) porcelain enamels are modified glass-like materials having various compositions which are applied usually on steel and cast iron equipment. The vitreous material for the enamel is called 'frit' which is prepared by fusing acidic retractory with basic fluxes.

High proportions of silica and feldspar and lower proportions of fluxes will give acid resistant enamel. The enamelled metals can't be bent without deformation of coatings. By thermal or the mechanical shock, enamelled articles tend to crack.

Short Answer Questions

1. What is an electrochemical cell? Give an example.

Ans. A device consisting of two electrods, each in contact with a solution of its own ions, transforms the free energy change of redox reaction at electrodes into electrical energy. For Example– Galvanic cell

2. Define the Galvanic cell.

Ans. The energy from a battery produced from a spontaneous redox reaction in which the electron transfer is formed to take place through a wire. The apparatus that provides electricity through redox reaction is called Galvanic cell. It also called a voltaic cell.

3. Define reduction potential.

Ans. The tendency of an electrode to gain electrons, when it is in contact with solution of its own ions.

4. What is oxidation potential?

Ans. The tendency of an electrode to lose electrons when it is in contact with solution of its own ions.

5. What is Nernst equation.

Ans. Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E, from the standard potential E°, and the temperature of the cell. This relation known as Nernst equation.

$$\text{At } 25°\text{C} \quad E_{celu} = E^{o}_{cell} + \frac{2.303\,RT}{nF} \log K$$

where E^{o} = Standard electrode potential
R = gas constion
T = Kelvin temperature
n = Number of elections transferred in the half–reaction
F = Faraday of electricity
K = equalisation constant

6. The emf of cell, Mg/Mg^{+2} 00.01M||Cu^{2+}(M)|Cu is found to 2.78 V at 300 K. The Standard electrode potential of Mg electrode –2.371V. What is the electrode potential of copper electrode?

Ans. The electrode potential of 'Mg' is (according to Nernest equation)

$$E_{Mg} = E^{o}_{Mg^{2+}/Mg} + \frac{0.0591}{n} \log[Mg^{2+}]$$

$$= -2.37 + \frac{0.0591}{2} \log (0.01)$$

$$= -2.37 - 0.0591$$

$$= -2.4290 \text{ V}$$

$$\therefore \quad E_{Cell} = E_{Cu} - E_{Mg}$$

$$2.78 = F_{Cu} - (-2.4290)$$

$$E_{cu} = 2.78 - 2.4290$$

$$= 0.3509 \text{ V}$$

7. Calculate the standard electrode potential $E^o_{Cu^{2+}/Cu}$ of copper its electrode potential E, at 25°C is 0.296 V when the concentration of Cu^{2+} ion 0.015 m

Ans. The Nernst equation for single electrode potential is

$$E = E^o + \frac{0.0591}{n} 10g_{10}[Cu^{2+}]$$

Given: $E = 0.296 \text{ V}$

$$E = E^o_{Cu^{2+}/Cu} + \frac{0.0591}{2} 10g_{10}[0.015]$$

Therefore, $E^o_{Cu^{2+}/Cu} = 0.296 - \frac{0.0591}{2} 10g_{10}[0.015]$

$$= 0.296 + 0.0540$$

$$= 0.35 \text{ V}$$

8. What is primary battery? Give an example?

Ans. These cells are not designed to be recharged or cell-reaction is not reversible are called primary battery. When the reactants have almost been converted to product further no more electricity is produced and battery becomes dead for example–voltaic cell, Daniel cell, carbon– zinc battery.

9. What is secondary battery? Give an example

Ans. In secondary batteries, the chemical reactions are reversed by passing direct current in opposite direction. The cells are designed for repeated use and they are able to be recharge able. For Example: Nickel – Cadmium cell, Lithium Batteries

10. What is a fuel cell? Give an example.

Ans. A fuel cell is an electrochemical cell in which the chemical energy of fuel–oxidant system is directly converted into electrical energy.

11. What are the Limitations of methanol fuel cell?

Ans. During the methanol oxidation reaction, CO is formed which is strongly absorbed on to platinum catalyst, reducing the surface are and lowering the performance.

→ Methanol is toxic and flammable.

→ Limited in the power they produce.

12. What is meant by Sensor?

Ans. Sensor is a device which is able to detect a change in physical/chemical quantity and produce an electrical signal suitable for a computer.

13. What are the different kinds of electrochemical sensors.

Ans. Electrochemical sensors are three types

1. Potentiometric sensors
2. Amperometric sensors
3. Chemiresistors sensors

14. What is meant by corrosion?

Ans. Any process of deterioration and consequent loss of solid metallic materials through an unwanted chemical or electrochemical attack by its environment, starting at its surface is called corrosion.

15. What is dry corrosion?

Ans. Corrosion caused by direct chemical action of atmospheric gases such as oxygen, halogen, sulphur dioxide with metal surface in immediate proximity.

16. What is pilling-Bed worth rule?

Ans. An oxide film is protective (or non-porous) if the volume of the oxide is at-least as great as the volume of the metal from which it is formed on the other hand, if the volume of the oxide film is less than the volume of the metal, then the oxide film is porous and non-protective

$$\text{Specific Ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

17. Write short note on cathodic protection.

Ans. In this technique, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal and thus saving the metal structure from corrosion.

18. Why is coating of zinc on Iron is called sacrificed anode?

Ans. Zinc acts as an anode with resect to iron so zinc is go into solution and iron is protected. Hence zinc is 'Sacrificed' instead iron.

19. What is chemical formula of rust?

Ans. $Fe_2O_3 . x\, H_2O$

20. Define Electroplating.

Ans. Electroplating or Electro deposition is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolyte solution, containing the soluble salt of the coating metal.

Review Question

Short Type question

1. Define Electrochemical Cell
2. Derive Nernst Equation
3. What is significance of electrochemical series.
4. Differentiate between the primary and Secondary Batteries
5. Write short note on a Methanol fuel Cell
6. What are the applications of Electrochemical Sensors?

7. How one can analyse Glucose by Electrochemical Sensors?
8. What is oxidation Corrosion? Give an example?
9. Explain the various factors which influence Corrosion?
10. What is meant by electrochemical theory of corrosion?
11. Distinguish between Wet and Dry Corrosion
12. Write basic principle of Galvanic cell.
13. Explain the principle involved in Fuel cells.
14. What is meant by sacrificial anodic protection?
15. Define electrochemical sensor? Give suitable Examples
16. Explain the significance of pilling Bedworth rule to explain the corrosion?

Essay Type Questions

1. (a) Describe the cathodic protection of corrosion control.
   (b) Write a note on electroplating.
2. Write down the equation for the hydrogen evolution in an electrochemical corrosion reaction.
3. Give an account of the various factors influencing corrosion by giving suitable examples.
4. (a) What is corrosion? How is it different from erosion? Explain the term 'passivity' with suitable examples.
   (b) Give an account of oxidation corrosion with relevant chemical equations involved.
5. Explain the mechanism of corrosion when
   (a) Two dissimilar metals are connected and exposed to electrolyte
   (b) A metal is exposed to varying aeration.
6. How do the following factors influence the rate of corrosion?
   (a) passive character of the metal (b) overvoltage
   (c) volatility of corrosion products
7. Explain the effect of the following factors on the rate of corrosion.
   (a) Nature of corrosion product (b) Temperature
   (c) pH (d) Anodic and Cathodic areas.
8. (a) Give reasons for the following:
   (i) Pin holes on tin coated iron are more prone to corrosion of iron than those on Zinc coated iron.
   (ii) Use of dissimilar metals should be avoided.
   (iii) Iron corrodes faster than aluminium though aluminium is above iron in emf series.
   (iv) Corrosion of a specimen can be controlled by using impressed current. [8]
9. (b) Explain why stainless steel is resistant to atmospheric corrosion.
   (c) Distinguish between differential aeration corrosion and differential metal corrosion. [6+5]
10. What is meant by cathodic and anodic inhibitors?

11. Explain sacrificial anode method in detail.

12. Differentiate galvanic series and electrochemical series with suitable examples.

13. Explain how corrosion control can be brought about by the following methods.

14. Explain the process of wet corrosion by evolution of hydrogen and absorption of oxygen. [16]

15. (a) What is oxidation corrosion and how does it take place? Describe the mechanism of oxidation corrosion?
   (b) Describe the various factors influencing the rate of chemical corrosion. [8+8]

16. (a) Elucidate the various steps that can be taken to minimise corrosion.
   (b) Give suitable reasons:
      (i) Zn plate fixed below the ship made of iron
      (ii) Metal under water drop undergoes accelerated corrosion. [8+8]

17. (a) Why chromium anodes are not used in chromium plating?
   (b) Distinguish between galvanising and sheradising.
   (c) Discuss the role of following factors on the nature of electrodeposit:
      (i) Current Density (ii) pH

18. (a) Explain the corrosion phenomenon involving oxide film growth law.
   (b) How design and material selection help in controlling metallic corrosion? [8+8]

19. Explain in detail the various methods of chemical conversion coatings. [16]

20. (a) Explain the following factors influencing the rate of corrosion.
      (i) Nature of corrosion product (ii) Position in electrochemical series
      (iii) pH.
   (b) Differentiate between dry corrosion and wet corrosion. [8+8]

21. (a) List the differences between anodic coating and cathodic coating.
   (b) How zinc coated on iron prevents corrosion?
   (c) Explain sand blasting method of surface preparation.

22. (a) What is Pilling-Bedworth rule? [8]
   (b) Give an account of the corrosion by other gases and liquid metal corrosion.[8]

23. What happens and why does it happen for the following:
   (a) When a zinc plate is fixed below the ship
   (b) When an iron pole is partly buried under the earth. [8+8]

24. (a) What is corrosion? What are the units in which it is expressed? How is it different from erosion?
   (b) Explain the mechanism of electrochemical corrosion. [8+8]

25. Write short notes on:
   (a) Overvoltage (b) Cathodic-protection [8+8]

26. Explain what happens and why does it happen?
   (a) When a zinc article is under strain [4]
   (b) When iron sheets are riveted with copper rivets [4]
   (c) When an iron pole is partly buried under soil [4]
   (d) When a metallic structure is buried under mineralised soils [4]

27. Explain what happens and why does it happen [4×4=16]
   (a) When a zinc plate is attached below a ship.
   (b) When steel is alloyed with chromium homogeneously.
   (c) When there are crevices between the adjacent parts of the structure.
   (d) When there is no uniform flow of a corrosion liquid.

28. (a) What are electrochemical series and galvanic series? [5]
   (b) How do you differentiate the electrochemical series from galvanic series? [6]
   (c) Explain why the rate of corrosion accelerates with reduction in the overvoltage of the corroding metal?

29. Explain how corrosion control can be brought by the following methods.
   (a) Proper designing [5]
   (b) Modifying the environment [5]
   (c) Use of inhibitors [5]

30. Justify the following statements with suitable examples.
   (a) The rate of corrosion is dependent on the nature of the corroding environment. [8]
   (b) A pipe half buried in water undergoes corrosion fastly. [8]

31. Define corrosion of metals and explain the mechanism of electrochemical corrosion?

32. Explain various factors influence the corrosion of metals.

33. Explain the theory and mechanism of corrosion.

34. (a) Explain the differential aeration corrosion.
   (b) Galvanisation process.

35. (a) Write a note on various types of gaseous dielectrics.
   (b) Write a note on electrical insulators.

36. (a) Differentiate between the different types of insulating materials.
   (b) Explain the use of silicone fluids as insulating materials.

37. Summarise the important applications of thermal insulators.

38. What is meant by specific conductance and equivalent conductance? What are its units?

39. Equivalent conductance of an electrolyte increases, whereas specific conductance decreases.

40. Explain the relationship between cell constant, conductivity and conductance?

41. Define the specific resistance of a solution? Explain the specific conductance with diagrammatic illustrate of specifc conductivity. What are its units?

42. Define the cell constant of a conductivity cell? Explain how it is measured? What are its units?

43. The resistance of N/2 solution of an electrolyte in a cell was found to be 50 ohm. Calculate the equivalent conductance of the solution, if the electrode in cell are 2.2 cm apart and with an area of 3.8 sq cm.

44. Discuss the titration curves obtain in conductometric titrations of weak acid and strong base?

45. What are the limitations of conductometric titrations?

46. (a) Define the terms ‘specific conductance’ and ‘equivalent conductance’.
   (b) Describe with a neat diagram, the experimental determination of equivalent conductance of a solution.

47. (a) Specific conductance of an electrolyte decreases; whereas equivalent conductance increases on dilution. Explain.
   (b) State the relationship between cell constant, conductivity and conductance.

48. (a) What is meant by cell constant of a conductivity cell? How is it measured? What are its units?
   (b) Give an account of various applications of conductance measurements.

49. (a) Define the term ‘molecular conductance’. What is the relationship between specific conductance, equivalent conductance and molecular conductance?
   (b) Define the specific resistance of a solution. Mention its units.

50. (a) Discuss the principle involved in conductometric titrations.
   (b) Discuss the titration curve obtained in the titration of strong acid and strong base by this method.
   (c) What are the advantages of conductometric titrations.

51. Discuss the titration curves obtained in conductometric titrations of
   (i) Strong acid with weak base (ii) $AgNO_3$ with KCl
   (iii) weak acid with strong base (iv) $MgSO_4$ with $Ba(OH)_2$
   (v) complex metric titrations.

52. Discuss all types of Conductometric titrations. Explain the nature of the graphs between conductance and volume of titrant used.

53. (a) What is an electrochemical series? Explain its different uses.
   (b) Describe the construction and working of hydrogen-oxygen fuel cell.

54. (a) Write short notes on
      (i) Concentration cells (ii) Significance of standard electrode potentials.
   (b) Explain the various applications of EMF series.
   (c) What are concentration cells? Explain electrolyte concentration cell and its applications.

55. (a) What are secondary cells? Describe the construction, of Ni–Cd cell. Write cell reactions and what are its applications?
   (b) Write a short note on fuel cells.

56. Define electromotive force. How is it measured by potentiometric method?

57. (a) What is galvanic cell and how does it differ from electrochemical cell?
   (b) State two applications of concentration cells.

58. Justify the following statements with your answers.
   (a) The direction of current in back EMF is opposite to that of electrolysis.
   (b) Standard electrode potential of zinc is negative; while that of copper is positive.
   (c) Conductivity titrations do not require indicators.

59. Distinguish between concentrations cell and Galvanic cell.

60. (a) Explain the principle involved in fuel cell. Describe the construction and working of methanol – oxygen fuel cell.
   (b) Explain the advantages of fuel cells over electrochemical cells.

61. Describe the construction, working and applications of Ni – Cd cell.

62. What are fuel cells? Indicate the advantage of fuel cells. Explain methanol–oxygen fuel cell with reaction involved.

63. What is a fuel cell? How does it differ from the commercial galvanic cells?

64. Describe the construction working of methanol – oxygen fuel cell.

65. Write a note on hydrogen – oxygen fuel cell.

66. Calculate the emf of a concentration cell at 30ºC consisting of two zinc electrodes dipped in Zn^{2+} solution of 0.1 N and 0.01 N concentrations. [0.0296 V]

67. What is a salt bridge? Explain its function in the construction of a cell.

68. Define reference electrode. Explain standard Hydrogen electrode.

69. Explain the Nernst equation for electrode potential.

70. What are the reference electrodes? Describe the construction of Calomel electrode.

71. Differentiate between the characteristics of Galvanic cell and Electrolytic cell.

72. What is meant by standard electrode potential? How can it be measured?

73. Derive Nernst equation for a single electrode potential and explain the terms involved in it. What are its applications?

74. State and explain Kohlrausch’s law of independent mobilities of ions.

75. Define Kohlrausch’s law? Discuss its applications in the determination of equivalent conductance of weak electrolytes at infinite dilution.

76. State and explain Kohlrausch’s law. Discuss its significance and applications.

77. Describe a simple Galvanic cell. Explain the cell reaction.

78. Distinguish between “single electrode potential” and “standard electrode potential. Draw a neat sketch of a saturated Calomel electrode and label its parts.

79. Describe a hydrogen electrode and answer the following:
   (i) Why is this electrode coated with a layer of platinum black?
   (ii) What is the concentration of HCl and pressure of the hydrogen gas taken in normal hydrogen electrode.
   (iii) What reaction takes place at this electrode?

80. Define corrosion? Explain the factors which influence corrosion.

81. Explain the theory and mechanism of electrochemical corrosion.

82. What is meant by corrosion? What are the consequences of corrosion?

83. What are the different types of corrosion? Explain dry corrosion.

84. Write the mechanism of oxidation corrosion.

85. Differentiate between chemical and electrochemical corrosion with suitable examples.

86. What is meant by Galvanic corrosion? Explain in detail.

87. What is differential aeration corrosion? Explain with suitable examples.

88. What are cathodic and anodic protections? Discuss their merits and demerits.

89. What are the causes for metal corrosion? Explain the mechanism of chemical corrosion?

90. Write short notes on (a) use of inhibitors (b) Galvanic series

91. Account for the following:

(a) Iron bolt in copper vessel are undesirable.

(b) Though aluminium is with lower electrode potential than iron, it has higher corrosion resistance than iron in oxidising environment.

(c) Zn in contact with Ag undergoes faster corrosion than Zn in contact with copper.

(d) Metal under water drop undergoes accelerated corrosion.

(e) Part of the nail inside the frame undergoes corrosion but the exposed part does not.

92. What happens and when?

(a) Zinc plate is fixed in below the ship

(b) Iron sheet is rivetted with copper rivets

(c) An iron pole is partly buried under earth

93. Explain the rusting of iron using electrochemical theory of corrosion.

94. Explain important parameters involved in electroplating.

95. Explain how the metal ion concentration and current density influence electrodeposition.

96. What are the good requisites for electrodeposit? Explain the factors influencing the nature of electrodeposition?

97. What is meant by chromium plating? Discuss its principal objectives and applications. Chromium plating has nickel under coat. Explain why?

98. Explain briefly electroless plating with a suitable example.

99. Distinguish between Galvanic series and electrochemical series.

100. (a) Small anodic area provides intense corrosion. Give reasons.

(b) What is the effect of CO_2 in electrochemical corrosion?

101. Distinguish between galvanising and tinning.

102. Briefly explain the following:

(a) Acid pickling (b) Sherardising (c) Cementation (d) Colourising

103. What is meant by metal cladding? Explain by taking suitable example.

104. Give an account of galvanising and tinning.

105. What are metallic coatings? Explain briefly.

106. Explain the mechanism of inihibitor action in corrosion control.

107. What are different protective coatings? How do protective coatings help in controlling corrosion.

Multiple Choice Questions

1. Electrolyte can conduct electricity since ________

(a) their molecules contain unpaired electrons, which are mobile

(b) their molecules contain loosely held electrons which become free under the influence of voltage

(c) with applied voltage, the molecules ionise into ions

(d) when the electrolyte is dissolved in the solvent, the molecules are broken into ions.

2. Which of the following is an electrolyte?

(a) CH_3Cl_3 (b) C_6H_6

(c) NaCN (d) C_6H_5Cl

3. Ionisation of an electrolyte in an aqueous solution is due to ________

(a) hydrolysis of electrolyte

(b) instability of the compound in aqueous medium

(c) increase in the electrostatic forces of attraction between the ions

(d) decrease in the electrostatic forces of attraction between oppositely charged ions.

4. With increase in dilution, conductivity of a solution ________

(a) decreases

(b) does not change

(c) increases

(d) increases first and then decreases.

5. Equivalent conductivity of an electrolytic solution ________

(a) is independent of dilution

(b) increases with dilution

(c) decreases with dilution

(d) no effect on dilution.

6. The units of equivalent conductivity is ________

(a) $ohm^{-1}\ cm^2\ eq^{-1}$

(b) $ohm^{-1}\ cm^{-2}\ eq^{-1}$

(c) $ohm^{-2}\ cm^{-2}\ eq^{-1}$

(d) $ohm^{-2}\ cm^{-2}\ eq^{-1}$.

7. The resistance of a conductor is 5×10^{-2} ohms. Conductance is equal to ________.

(a) 200 mhos (b) 20 mhos

(c) 500 mhos (d) 50 mhos.

8. Cell constant of a conductometric cell ________

(a) increases with dilution

(b) depends on the nature of the electrolyte

(c) decreases with dilution

(d) is independent of the nature of the electrolyte.

9. The equivalent conductance of a strong electrolyte at infinite dilution ________

(a) tends to a finite value at higher concentrations

(b) tends to zero

(c) tends to an infinite value

(d) tends to finite value which is below that at higher concentrations.

10. Specific conductance is the conductance of a solution of volume ________

(a) 10 cm^3 (b) 1 cm^3

(c) 1,000 cm^3 (d) 100 cm^3.

11. The relationship between specific conductivity and equivalent conductance is

(a) $\lambda_{eq} = \kappa \times C/1{,}000$

(b) $\lambda_{eq} = C \times 100/\kappa$

(c) $\lambda_{eq} = C \times 1{,}000/\kappa$

(d) $\lambda_{eq} = \kappa \times 1{,}000/C$.

12. Units of specific conductance is ________

(a) ohm cm^2 (b) ohm cm

(c) mhos cm^{-1} (d) $mhos^{-1}$ cm.

13. Conductivity of a solution is directly proportional to

(a) number of ions

(b) dilution

(c) volume of the solution

(d) current density.

14. Pure water does not conduct electricity because it is ________

(a) almost not ionised

(b) decomposed easily

(c) low boiling

(d) neutral.

15. The potential of the standard hydrogen electrode is ________

(a) 1 volt (b) 0 volt

(c) 10 volts (d) 0.5 volt.

16. The electrode potential is the tendency of metal ________.

(a) to lose electron

(b) to gain electrons

(c) to either lose or gain electrons

(d) none of these.

17. The potential of two metal electrodes used in a cell are 0.35 V and 0.25 V. The EMF of the cell formed by connecting them is ________

(a) 0.5 V (b) 1.20 V

(c) – 0.5 V (d) none of these.

18. In the electrochemical series, elements are arranged in the ________.

(a) increasing order of SRP

(b) decreasing order of SRP

(c) increasing order of equivalent weights

(d) increasing order of oxidation potential.

19. In the cell: $Cu/Cu^{2+} \| Ag^{+}/Ag$

(a) 'Ag' electrode is the negative electrode

(b) copper electrode is the negative electrode

(c) Ag^{+} is reduced to Ag

(d) Cu is oxidised to Cu^{2+}.

20. A galvanic cell converts ________.

(a) chemical energy into electrical energy

(b) electrical energy into chemical energy

(c) chemical energy into heat energy

(d) electrical energy into heat energy.

21. One of the most popular uses of galvanic cells are ________

(a) Battery

(b) Electrolyte preparation

(c) Potentiostat

(d) none of these

22. Which of the folowing is a primary cell

(a) Mercury battery

(b) Lithium battery

(c) Daniel cell

(d) Nicad

23. ________ is a secondary cells or battery

(a) Nicad

(d) Daniel cell

(c) Voltaic cell

(d) Laclanche cell

24. Which of the following is proton exchange fuel cells

(a) H_2–O_2 fuel cell
(b)Methanol–O_2 fuel cell

(c) Phosphoric acid fuel cell

(d) Solid polymer electrode fuel cell.

25. H_2–O_2 fuel cells are used as auxiliary energy source in ________

(a) Trains

(b) Aeroplanes

(c) Space vehicle

(d) Automobile engines.

26. If the oxidation potential of 'Zn' metal is 0.76 V, the E_{cell} for the redox reaction $Zn + 2H^{+}$ (aq, 1M) → $Zn^{2+} + H_2$ (1 atm) is

(a) –0.76 (b) 0.76

(c) –0.38 (d) + 0.38.

27. Standard reduction potential of zinc and silver electrodes are –0.76 V and +0.80 V respectively. If the cell is constructed by coupling the two electrodes then ________.

(a) Silver acts as anode

(b) 'Ag' loses electrons

(c) Zinc acts as anode
(d) zinc gains electrons.

28. Given: $E°_{Ag+/Ag}$ = 0.799 V and $E°Zn^{2+}/Zn$ = – 0.763V, then

(a) Ag can oxidise H_2 to H^+
(b) Ag^+ can be reduced by $H_2(g)$
(c) Ag can reduce Zn^{2+}
(d) Zn^{2+} can be reduced by H_2.

29. When iron/zinc is added to $CuSO_4$ solution, copper is precipitated. It is due to ________

(a) oxidation of Cu^{2+}
(b) hydrolysis of $CuSO_4$
(c) ionisation of $CuSO_4$
(d)reduction of Cu^{2+}.

30. The potential of cell: Pt; $H_2(g)$/ $H^+(10^{-8}$ M) || H^+ (0.001 M)/$H_2(g)$; Pt is ________

(a) – 0.0592 V (b) 0.0275 V
(c) 0.0592 V (d) 0.296 V.

31. When copper turnings are added to silver nitrate solution, a blue coloured solution is formed after some time. It is because copper ________

(a) is oxidised to Cu^{2+}
(b) displaces silver from the solution
(c) is reduced to Cu^{2+}
(d) forms a blue complex with $AgNO_3$.

32. What is the voltage produced by the H_2–O_2 fuel cell, operating under standard conditions?

(a) 1.0 V (b) 1.23 V
(c) 2.0 V (d) 0.5 V.

33. Give an example where use of small-size and low mass battery are the most important considerations.

(a) cell phones
(b) pacemakers
(c) radios
(d) electronic equipment.

34. Which of the following is an example for secondary cell?

(a) dry cell
(b) alkaline battery
(c) nickel-cadmium
(d) none of these.

35. Which of the following is not true in the case of fuel-cells?

(a) they store chemical energy
(b) they do not store chemical energy
(c) efficiency is twice that of conventional power plants
(d) reactants are supplied constantly.

36. The electrical conductance of solutions has been well explained by ________

(a) Ostwald (b) Arrhenius
(c) Maxwell (d) Newton

37. The charged particles are called ________

(a) atoms (b) molecules
(c) ions (d) free radicals

38. The fraction of total number of molecules present in a solution as ions is known as ________

(a) molality (b) free radicals
(c) mole fraction (d) ionisation

39. The reciprocal of the resistance is called________

(a) equivalent conductance
(b) specific conductance
(c) conductance
(d) none of these.

40. In conductometric titrations, the concentration of the titrant must be ________ times as the solution being titrated.

(a) four (b) two
(c) three (d) ten

41. Which of the following not effectively conducted in conductometric titrations

(a) acid-base

(b) strong acid-weak base
(c) precipitation
(d) none of these

42. The difference of potential which causes the flow of current from one electrode to another electrode is called ________

(a) oxidation
(b) reduction
(c) neutralisation
(d) electromotive force

43. Kohlrausch's law is related to ______

(a) equivalent conductance
(b) molar conductance
(c) molar conductance at infinite dilution
(d) specific conductance

44. The effect of dilution on the molar conductivity of a weak electrolyte is ________

(a) decrease (b) increase
(c) unchanged (d) not expected

45. In conductometric titrations _______ energy source used

(a) A.C (b) D.C
(c) A.C and D.C (d) none of these

46. An aqueous solution of $CuSO_4$ is acidic in nature mainly due to ________

(a) oxidation (b) reduction
(c) hydrolysis (d) neutralisation

47. The tendency of an electrode to loose (or) gain electrons when it is in contact with its own ions is called ________

(a) hydration
(b) oxidation
(c) reduction
(d) electrode potential

48. When does a cell formulation represent a non-spontaneous activity of a galvanic cell

(a) emf is negative
(b) emf is positive
(c) emf is zero
(d) none of these

49. Which of the following is a primary reference electrode

(a) Calomel electrode
(b) hydrogen electrode
(c) glass electrode
(d) none of these

50. The main purpose of salt bridge in the voltaic cell is ________

(a) to maintain flow of electrons
(b) to maintain charge neutrality of solution
(c) barrier for electron transfer
(d) none of these

51. ________ is the voltage generated by the H_2–O_2 fuel cell under standard conditions

(a) 0.8 V (b) 1.12 V
(c) 1.23 V (d) 1.75 V

52. Salt bridge represented in electrochemical cell is ________

(a) one vertical line
(b) two vertical lines
(c) dash
(d) none of these

53. ________ converts the chemical energy of the fuel directly to electricity

(a) Galvanic cell
(b) Daniel cell
(c) fuel cell
(d) leaded cell.

54. The emf of concentration cell decrease mainly, due to________

(a) oxidation
(b) reduction
(c) transfer of metallic ions from higher concentration to lower concentration
(d) can't explain

55. Nernst equation is mainly useful to calculate ________

(a) redox system
(b) emf of cell
(c) polarisation
(d) none of these

56. One of the most popular uses of galvanic cells are ________
(a) battery
(b) electrolyte preparation
(c) potentiostat
(d) none of these

57. Which of the following is a primary cell ________
(a) Mercury battery
(b) Lithium battery
(c) Daniel cell
(d) Ni Cad

58. ________ is a secondary cell (or) battery
(a) Ni Cad
(b) Daniel cell
(c) Voltaic cell
(d) Laclanche cell

59. Which of the following proton exchange fuel cell
(a) H_2–O_2 fuel cell
(b) methanol–O_2 fuel cell
(c) phosphoric acid fuel cell
(d) solid polymer electrolyte fuel cell

60. H_2–O_2 fuel cell are used as auxilary energy source in ________
(a) trains
(b) aeroplains
(c) space vehicles
(d)automobile engines

61. Corrosion is an example of
(a) reduction (b) oxidation
(c) corrosion (d) electrolysis.

62. The rusting of iron is catalysed by which of the following
(a) O_2 (b) Zn
(c) H^+ (d) Fe.

63. The corrosion will be rapid when
(a) pH = 7 (b) pH > 7
(c) pH < 7 (d) none of them.

64. Rusting of iron is
(a) prevented on coating with Zn
(b) reduced in the presence of dissolved salts
(c) protected if the article is connected with a Mg wire
(d) enhanced by wet air.

65. The rate of corrosion of iron in atmosphere depends on
(a) frequency of rainfall
(b) humidity of air
(c) intensity of atmosphere pollution
(d) all the above.

66. Electrochemical corrosion can occur only when
(a) air is in contact with metal
(b) liquid medium is in contact with metal
(c) oxygen is in contact with metal.

67. Metal at the top in the electrochemical gases is
(a) most noble (b) most active
(c) most stable (d) least active.

68. Chemical corrosion always takes place in
(a) Anodic and cathodic area
(b) anodic area
(c) cathodic area
(d) the interior of metal.

69. During Galvanic corrosion, the most noble metal acts as
(a) anode as well as cathode
(b) cathode
(c) anode
(d) corroding metal.

70. Iron corrodes faster than aluminium due to
(a) Al reacts with medium
(b) Al forms protective oxide film
(c) Al is lighter than Fe
(d) none of these.

71. Electrochemical corrosion in acidic environment is carried with

(a) oxygen evolution
(b) oxygen absorption
(c) hydrogen evolution
(d) hydrogen absorption.

72. In oxygen concentration type corrosion, the corrosion occurs at

(a) less oxygenated part
(b) uniform throughout
(c) cathode part
(d) more oxygenated part.

73. In which of the following electroplating is porous and non-adherent?

(a) Ni (b) Zn
(c) Cr (d) Pt.

74. Which of the following are anodic inhibitors?

(a) Mercaptans
(b) amines
(c) heterocyclic nitrogen compounds
(d) Chromates.

75. ________ is the cathodic inhibitor.

(a) Chromates (b) Tungstates
(c) Mercaptans (d) Phosphates.

76. Iron corrodes under the drop of salt solution due to

(a) Galvanic corrosion
(b) stress corrosion
(c) pitting corrosion
(d) differential aeration corrosion.

77. The rusting of iron is faster in saline water than ordinary water mainly due to

(a) increased conductivity of water due to NaCl
(b) decrease in the conductivity of water due to salts
(c) localise corrosion
(d) none of these.

78. A steel screw in a brass marine hardware corrodes due to

(a) pitting corrosion
(b) stress corrosion
(c) Galvanic corrosion
(d) soil corrosion.

79. Bolt and nut made up of the same metal is preferred mainly due to

(a) non-permit galvanic corrosion
(b) increase in the corrosion
(c) for decorative /good appearance
(d) none of these.

80. Which of the following metal oxide film is protective from corrosion?

(a) porous (b) non-porous
(c) volatile (d) unstable.

81. In cathodic potassium, the iron article is made cathode by connecting it with more metal

(a) Pt (b) Sn
(c) Zn (d) Ti.

82. The chemical formula of rust

(a) Fe_2O_3 (b) $Fe_2O_3\ xH_2O$
(c) $Fe_2O_3\ 2H_2O$ (d) Fe_2O_4.

83. When zinc and copper alloy is placed in moisture environment, then undergo corrosion.

(a) Cu (b) Zn
(c) Zn–Cu (d) none of these.

84. Which type of the metal oxide film causes rapid and continuous corrosion?

(a) non-porous and adherent
(b) stable and non-porous
(c) porous or volatile
(d) none of these.

85. Impure metal corrodes faster than pure metal due to

(a) homogeneity
(b) heterogeneity
(c) both
(d) none of these.

86. Tinning is done by ________

(a) Electroplating
(b) Spraying

(c) Hot dipping
(d) Cementation

87. The process of providing a zinc coating on the base metal is called ________
(a) Tinning
(b) Galvanising
(c) Electroplating
(d) Sheardising

88. Duralumin is prepared by ________ method.
(a) Metal coating
(b) Cementation
(c) Hot dipping
(d) Metal cladding

89. Cementation is also called ________
(a) Diffusion coating
(b) Hot dipping
(c) Galvanisation
(d) Tinning

90. ________ are used to spray on the base metal
(a) High melting metals
(b) Non-metals
(c) Low melting metal
(d) None of these.

91. In the phosphate coatings, the base metal is treated with ________
(a) HPO_4 (b) H_3PO_4
(c) H_2SO_4 (d) $Na_2Cr_2O_7$

92. In the cementation, producing an alloy layer on steel or iron with Zn is called ________
(a) chromising (b) Galvanising
(c) sheardising (d) colourising

93. Diffusion of 'Al' coating on steel through cementation is called ______
(a) colorising (b) Galvanising
(c) sheardising (d) siliconising

94. ________ coatings are widely used for ferrous materials used for equipment in the industry.
(a) oxide coatings
(b) vitreous enamel
(c) organic
(d) surface coatings

95. The vitreous material for the enamel is called ________
(a) frit
(b) alloy
(c) coating material
(d) none of these

96. Phosphate coatings are generally ________ in colour.
(a) Brown (b) Reddish
(c) Grey (d) Brick red

97. The main cause for high oxidation resistance of an oxide film are:
(a) high electrical conductivity
(b) continuous oxide film
(c) porous oxide film
(d) high dipole moment

98. Which of the following is valatile oxidation corrosion product of a metal
(a) CuO (b) Fe_2O_3
(c) MoO_3 (d) PbO

99. Which of the following utensils normally used for strong food stuffs
(a) galvanised (b) tinned
(c) colourised (d) cemented

100. In galvanised articles, which metal protect the base metal
(a) Fe (b) Cu
(c) Zn (d) Pb

101. In 'Alclad' sheet, a plat of duralumin is sandwiched between two layers of ________
(a) Zinc (b) Iron
(c) Aluminium (d) Copper.

102. If the corrosion product is volatile, then the rate of corrosion of base metal will be ________
(a) decrease (b) increase
(c) unchanged (d) not expected.

103. The corrosive resistance of stainless steel is mainly due to passive nature of ________ metal.

(a) Zinc (b) Tin

(c) Iron (d) Chromium.

104. In electrochemical corrosion, if the corrosion product is insoluble in the medium then the corrosion rate further ________

(a) increase

(b) decrease

(c) no change

(d) none of these

105. When the two metals or alloys are electrically contact in presence of electrolyte________ suffer corrosion

(a) less active metal

(b) moderate active metal

(c) more active metal

(d) none of these

Answers

1. (d)	**2.** (c)	**3.** (d)	**4.** (a)	**5.** (b)
6. (a)	**7.** (b)	**8.** (a)	**9.** (a)	**10.** (b)
11. (d)	**12.** (c)	**13.** (a)	**14.** (a)	**15.** (b)
16. (c)	**17.** (a)	**18.** (a)	**19.** (b)	**20.** (a)
21. (a)	**22.** (c)	**23.** (a)	**24.** (b)	**25.** (c)
26. (b)	**27.** (c)	**28.** (b)	**29.** (d)	**30.** (d)
31. (c)	**32.** (b)	**33.** (b)	**34.** (c)	**35.** (a)
36. (b)	**37.** (c)	**38.** (d)	**39.** (c)	**40.** (d)
41. (c)	**42.** (d)	**43.** (c)	**44.** (b)	**45.** (a)
46. (c)	**47.** (d)	**48.** (a)	**49.** (b)	**50.** (b)
51. (c)	**52.** (b)	**53.** (c)	**54.** (c)	**55.** (b)
56. (a)	**57.** (c)	**58.** (a)	**59.** (b)	**60.** (c)
61. (b)	**62.** (c)	**63.** (c)	**64.** (c)	**65.** (d)
66. (b)	**67.** (b)	**68.** (b)	**69.** (b)	**70.** (b)
71. (c)	**72.** (a)	**73.** (c)	**74.** (d)	**75.** (c)
76. (d)	**77.** (a)	**78.** (c)	**89.** (a)	**80.** (b)
81. (c)	**82.** (b)	**83.** (b)	**84.** (c)	**85.** (b)
86. (c)	**87.** (b)	**88.** (d)	**89.** (a)	**90.** (c)
91. (b)	**92.** (c)	**93.** (a)	**94.** (b)	**95.** (a)
96. (c)	**97.** (b)	**98.** (c)	**99.** (b)	**100.** (c)
101. (c)	**102.** (b)	**103.** (d)	**104.** (b)	**105.** (c)

Fill Up the Blanks Questions

1. A substance which allows electric current to pass through it is called ________.
2. ________ is the conductivity of one cm^3 of solution.
3. The conductance of all the ions present in one mole of electrolyte in the solution is called ________.
4. What would be the value of degree of ionisation for a strong electrolyte is _______.
5. The tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25°C is called ________.

6. The salt bridge is indicated by ________.
7. In the electrochemical cell, anode is written on ________.
8. The positive value of E_{cell} indicates that the cell reaction is ________.
9. The emf measurement are accurately determined through ________.
10. The materials which are used for charge storage is the main function, they are called ________.
11. Fuel cells are thermodynamically efficient, convert as much as ________ to useful work.
12. In methanol, oxygen fuel cell, ________ transfer takes place.
13. ________ is alternative to gasoline powered engine, because they are pollution free.
14. ________ is used as electrolyte in H_2–O_2 fuel cell.
15. Iron corrodes under drops of salt solution manually due to ________.
16. Wire mesh corrodes faster of joints due to ________.
17. The rusting of iron is quicker in saline water than in ordinary water. This may be mainly due to ________.
18. In electrochemical corrosion always takes place at ________.
19. The chemical formula of rust is ________.
20. A process of rendering the surface of steel resistant to oxidation by heating the base metal with aluminium and aluminium oxide at 800–1000°C is called ________.
21. The ability plating system to produce even deposit on an irregular object is called ________.
22. In cathodic protection, the more active metal act as ________.
23. Impressed current cathodic protection, convert the corroding metal from ________.
24. In differential aeration corrosion, the corrosion always taken place-at ________.

Answers

1. conductor
2. specific conductivity
3. molar conductivity
4. Nearly one
5. Electrode potential of a metal
6. two vertical lines
7. left hand side
8. feasible
9. potentiometer
10. Dielectrics
11. 75% of available energy
12. six electron charge
13. Hydrogen-oxygen fuel cell
14. Conc. KOH solution
15. Differential aeration corrosion
16. More stress at joints (due to welding)
17. In salt water conductivity is more than ordinary water
18. Anodic areas
19. $Fe_2O_3\, x\, H_2O$
20. Colourising
21. Throwing power of a bath
22. Sacrificial anode
23. Anode to cathode
24. Poor oxygenated area

2

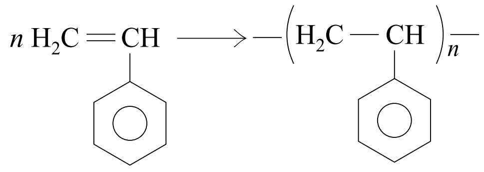
Polymers

2.1 INTRODUCTION

Every matter is composed of many small units called molecules. Molecules are in different sizes and shapes and associated with atoms. They are generally too small to be observed under a powerful microscope. But polymers are giants or macromolecules. They play a vital role in our daily life. These materials provide the basic needs of our lives (food, clothing and shelter). The major developments in polymer science and technology took place since 1920 and this lead to the production of plastics, fibres, elastomers and biopolymers.

The word polymer was derived from the Greek word ‘Poly’ = many and ‘mers’ = parts or units. A polymer may be defined as a high molecular weight compound (macromolecule or giant molecule) made by the combination of a large number of small molecules (monomers). The repeating units in a polymer are called monomers.

e.g., 1. Polystyrene is a polymer of styrene



Styrene (monomer) Polystyrene (polymer)

2. Polythene or Polyethylene is a polymer of ethylene

$$n\,H_2C{=}CH_2 \longrightarrow -\left(H_2C-CH_2\right)_n-$$

Ethylene (monomer) Polyethylene (Polymer)

The number of repeating units in a polymer chain is called degree of polymerisation (DP). The properties of polymers are different from those of its monomers.

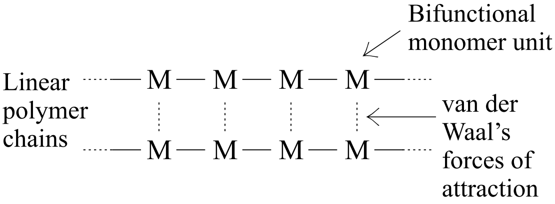
Molecular weight of polymer = Molecular weight of monomer × DP

Polymers with high DP are called high polymers while the polymers with low DP are called oligopolymers. The molecular weight of high polymers ranges from 10,000–10,00,000. Polymers may be natural (e.g. cellulose, proteins, natural rubber, wool and silk) or synthetic (e.g. polythene, PVC, teflon, nylon and bakelite).

2.2
BASIC CONCEPTS

(i) Functionality The number of bonding sites or reactive sites present in a monomer is called as its functionality. Every monomer must have minimum two bonding sites for polymerisation process.

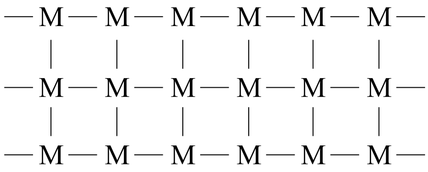
(a) If the functionality of monomer is two (bifunctional), i.e. two reactive groups attach side by side to each other, linear or straight chain polymers are formed.



e.g. Ethylene, styrene and vinyl chloride.

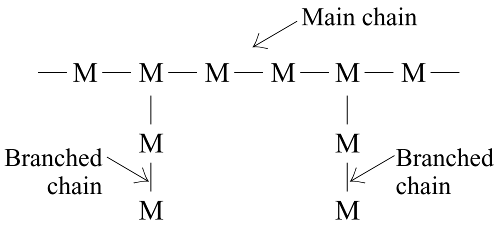
(b) If the functionality of monomer is three (trifunctional), cross-linked three-dimensional network polymers are formed.

The monomer molecules are joined to each other by covalent bonds and the movement of individual molecules is totally restricted.



e.g. Bakelite

(c) Mixture of bifunctional and trifunctional polymers give branched chain polymers.

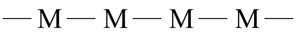


(ii) Nomenclature of Polymers

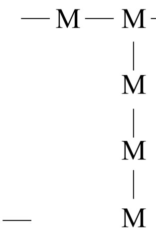
(a) *Homopolymers* Polymers obtained from same type of monomers are called homopolymers.

e.g., PVC, polythene and teflon.

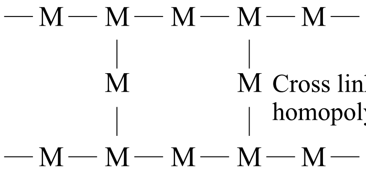
They may be linear branched or cross linked.



Linear homopolymer



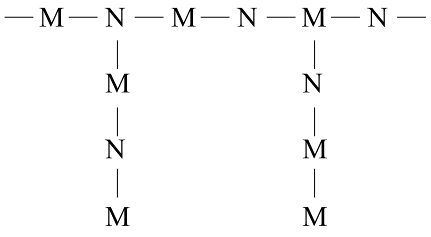
Branched homopolymer



Cross linked homopolymer

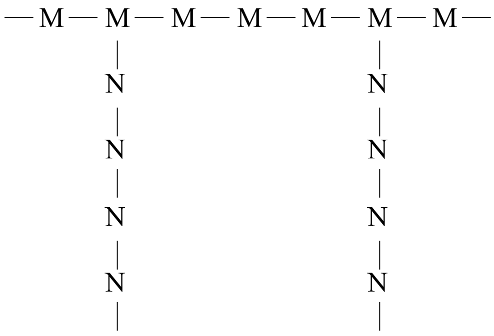
(b) *Heteropolymers or Copolymers* Polymers obtained from different type of monomers are called copolymers. They may be generally linear or branched.

Linear copolymer



Branched co-polymer

Graft copolymers are branched structures in which the monomer units on the branches and main chain are different.



$$\begin{array}{ccccccccccccccc} — & M & — & M & — & M & — & M & — & M & — & M & — & M & — \\ & & & | & & & & & & & & | & & & \\ & & & N & & & & & & & & N & & & \\ & & & | & & & & & & & & | & & & \\ & & & N & & & & & & & & N & & & \\ & & & | & & & & & & & & | & & & \\ & & & N & & & & & & & & N & & & \\ & & & | & & & & & & & & | & & & \\ & & & N & & & & & & & & N & & & \\ & & & | & & & & & & & & | & & & \end{array}$$

(c) *Homo Chain Polymers* If the main chain is formed with same atoms, the polymer is called homo chain polymer.

$$—C—C—C—C—C—$$

e.g. PVC, Polythene, etc.

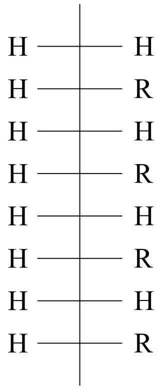
(d) *Hetero Chain Polymers* If the main chain is formed with different atoms, the polymer is called hetero chain polymer.

$$—C—O—C—O—C—O—C—$$

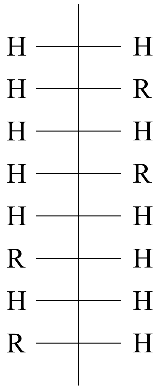
e.g. Nylon 6, 6.

(iii) Tacticity The difference in configuration because of orientation of functional groups in polymer in an orderly or disorderly manner with respect to the main chain is called tacticity.

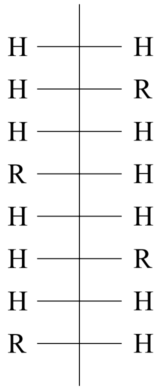
(a) *Isotactic Polymer* If the functional groups are arranged on the same side of the chain, it is called isotactic polymer.



(b) *Atactic Polymer* If the functional groups are arranged at random around the chain, it is called atactic polymer.



(c) *Syndiotactic Polymer* If the functional groups are arranged in alternative fashion with respect to the main chain, it is called syndiotactic polymer.



2.3
POLYMERISATION

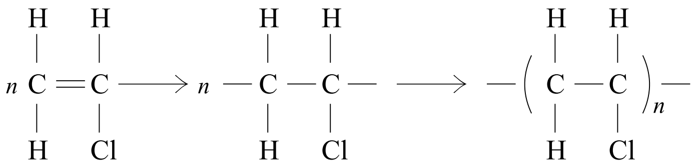
The chemical reaction by which the monomers are combined to form polymers is called polymerisation.

Types of Polymerisation

(i) Addition polymerisation
(ii) Condensation polymerisation
(iii) Co-polymerisation

(i) Addition Polymerisation (or) Chain Polymerisation In addition polymerisation, several bifunctional monomers combine to form polymers by addition reaction without the elimination of any byproducts. The monomers containing double bonds generally undergoes addition polymerisation and produce linear polymers. The produced polymer contains the same elemental composition as that of the monomer. The molecular weight of polymer is an integral multiple of the monomer.

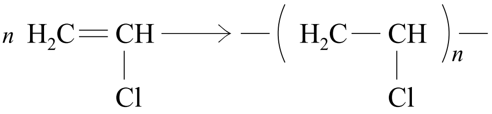
e.g. 1. Polymerisation of vinyl chloride



$$n\,\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}=\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}} \longrightarrow n\,-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}- \longrightarrow -\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_n-$$

Vinyl chloride   Bifunctional species   Polyvinyl chloride (PVC)

or



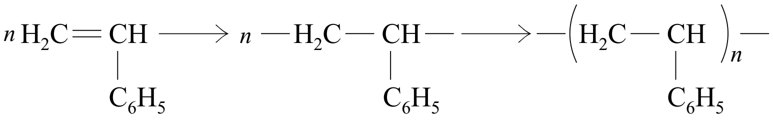
$$n\ \mathrm{H_2C{=}}\underset{\mathrm{Cl}}{\mathrm{CH}} \longrightarrow -\left(\mathrm{H_2C-}\underset{\mathrm{Cl}}{\mathrm{CH}}\right)_n-$$

2. Polymerisation of ethylene

$$n\mathrm{H_2C{=}CH_2} \longrightarrow \underline{n}\ -\mathrm{H_2C-CH_2}- \longrightarrow -\left(\mathrm{H_2C-CH_2}\right)_n-$$

Ethylene   Bifunctional species   Polythene

3. Polymerisation of styrene

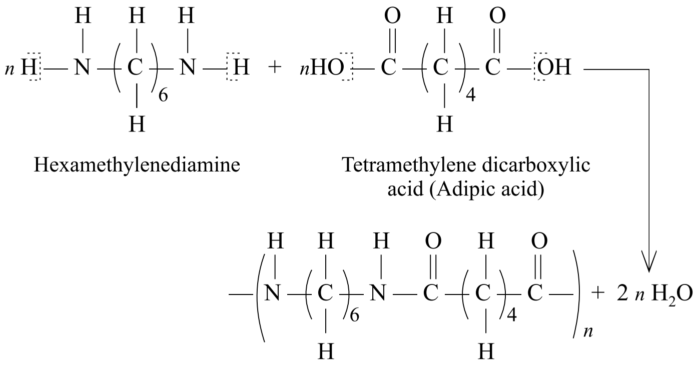


$$n\mathrm{H_2C{=}}\underset{\mathrm{C_6H_5}}{\mathrm{CH}} \longrightarrow n\ -\mathrm{H_2C-}\underset{\mathrm{C_6H_5}}{\mathrm{CH}}- \longrightarrow -\left(\mathrm{H_2C-}\underset{\mathrm{C_6H_5}}{\mathrm{CH}}\right)_n-$$

Styrene   Bifunctional species   Polystyrene

(ii) Condensation Polymerisation (or) Stepwise Polymerisation In condensation polymerisation, the polymer is formed by stepwise reaction between the same or different polar groups containing monomers with the elimination of small molecules like H_2O, HCl and NH_3. Polymerisation proceeds through intermolecular condensation and forms linear or cross linked polymers. The molecular weight of a polymer is not an integral multiple of the molecular weight of monomers.

e.g. 1. Nylon-6, 6



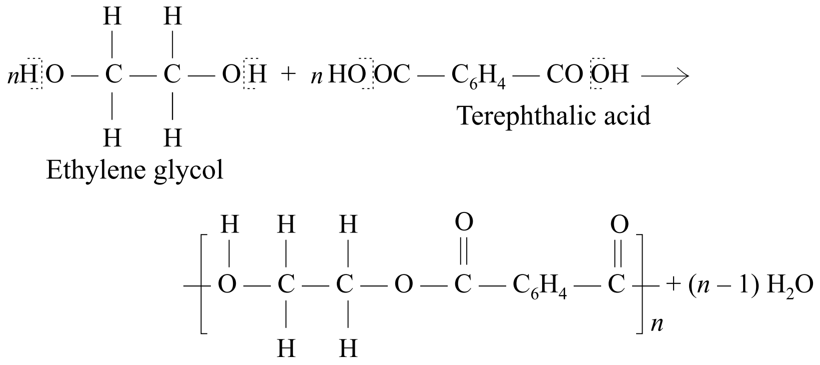
$$n\,\mathrm{H}-\overset{\mathrm{H}}{\mathrm{N}}-\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_6-\overset{\mathrm{H}}{\mathrm{N}}-\mathrm{H} + n\mathrm{HO}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

Hexamethylenediamine   Tetramethylene dicarboxylic acid (Adipic acid)

$$\longrightarrow -\left(\overset{\mathrm{H}}{\mathrm{N}}-\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_6-\overset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\left(\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}\right)_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right)_n + 2\,n\,\mathrm{H_2O}$$

Nylon-6, 6

2. Polyester



$$n\,H\,O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-O\,H + n\,HO\,OC-C_6H_4-CO\,OH \longrightarrow$$

$$\left[-\overset{\overset{H}{|}}{O}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-O-\overset{\overset{O}{\|}}{C}-C_6H_4-\overset{\overset{O}{\|}}{C}-\right]_n + (n-1)\,H_2O$$

(iii) Copolymerisation When two or more different types of monomers undergo simultaneous polymerisation, it is called copolymerisation. The properties of copolymer are different from those of individual monomers. The copolymers may be alternating, random block and graft copolymers.
e.g. *GRS-rubber* or *Styrene Butadiene Rubber (SBR)*

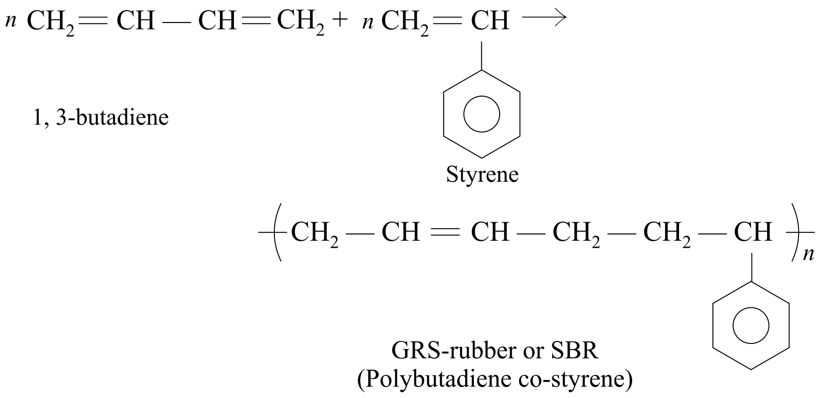


Table 2.1 *Differences between Addition polymerisation and Condensation Polymerisation*

Addition polymerisation	*Condensation polymerisation*
1. Reaction proceeds in a fast manner under favourable conditions.	1. Reaction proceeds comparatively slow.
2. Proceeds by chain growth mechanism.	2. Proceeds by a step growth mechanism.
3. No by-product is formed.	3. By-products are formed.
4. Monomers with carbon–carbon unsaturation $\left(\underset{\vert}{\overset{\vert}{C}} = \underset{\vert}{\overset{\vert}{C}}\ \text{(or)} - C \equiv C -\right)$ are involved.	4. Monomers with reactive functional groups are involved.
5. Number of monomers decreases throughout the course of the reaction	5. Concentration of Monomers decreases much faster in the early stages of the reaction.

2.4

MECHANISM OF ADDITION POLYMERIZATION

During chain or addition polymerization, three different types of active centres have been found to be formed. These are free radicals, carboniumions and carbanions.

(a) Free radical addition polymerization:

The mechanism involves the following three steps

(i) Initiation: This involves the dissociation of an initiator in to two free radicals.

$$\underset{\text{(initiator)}}{R-R} \longrightarrow \underset{\text{(free radicals)}}{2\dot{R}}$$

Then the free radical so formed adds to the first monomer molecule (H)

$$\dot{R} + M \rightarrow R - \dot{M}$$

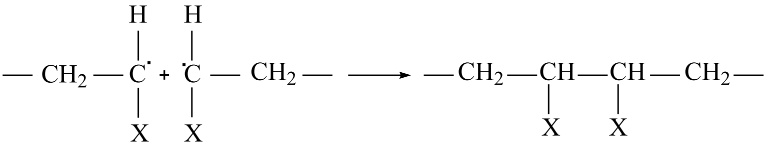
(ii) Propagation: This involves the growth of polymer chain by successive addition of monomeric units resulting in the formation of polymeric chain with free radical centre

$$R - \dot{M} + M \rightarrow R - M - \dot{M} \rightarrow R\,.\,.\,.\,.\,.\,\dot{M}$$

(iii) Termination: This can be takes place either of two

(a) Coupling termination: This involves collision between the active ends of two chains.

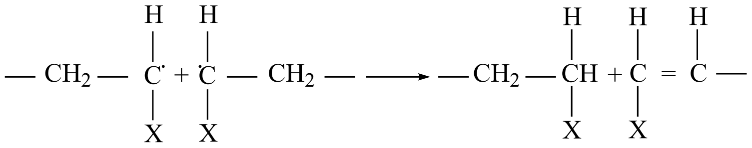
eg:



$$-CH_2-\overset{H}{\underset{X}{C^{\bullet}}} + \overset{H}{\underset{X}{\dot{C}}} - CH_2- \longrightarrow -CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-$$

(b) Disproportionation termination: This involves the transfer of a hydrogen atom of one radical centre to another radical centre, resulting in the formation of two polymer units one saturated and another unsaturated.

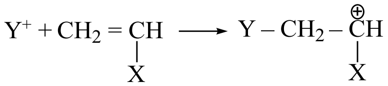
eg:



$$-CH_2-\overset{H}{\underset{X}{C^{\bullet}}} + \overset{H}{\underset{X}{\dot{C}}} - CH_2- \longrightarrow -CH_2-\overset{H}{\underset{X}{CH}} + \overset{H}{\underset{X}{C}} = \overset{H}{C}-$$

(b) Cationic addition polymerization: This involves the following three steps.

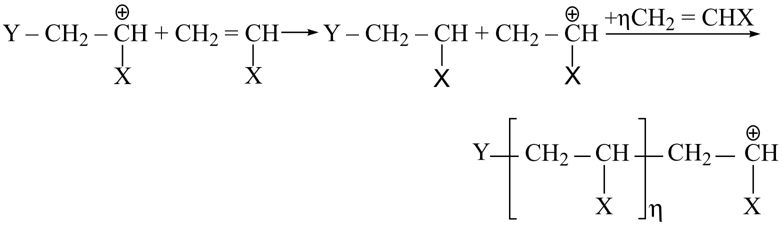
(i) Initiation: In this step formation of carboniumion takes place, usually by transfer of a proton.



$$Y^{+} + \underset{\displaystyle X}{CH_2 = \overset{}{CH}} \longrightarrow Y - CH_2 - \underset{\displaystyle X}{\overset{\oplus}{CH}}$$

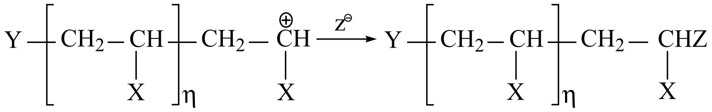
(cation) (monomer) (Carboniumion)

(ii) Propagation:



$$Y - CH_2 - \underset{\displaystyle X}{\overset{\oplus}{CH}} + CH_2 = \underset{\displaystyle X}{CH} \rightarrow Y - CH_2 - \underset{\displaystyle X}{CH} + CH_2 - \underset{\displaystyle X}{\overset{\oplus}{CH}} \xrightarrow{+\eta CH_2 = CHX} Y \left[CH_2 - \underset{\displaystyle X}{CH} \right]_{\eta} CH_2 - \underset{\displaystyle X}{\overset{\oplus}{CH}}$$

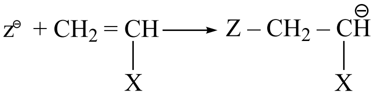
(iii) Termination:



$$Y \left[CH_2 - \underset{\displaystyle X}{CH} \right]_{\eta} CH_2 - \underset{\displaystyle X}{\overset{\oplus}{CH}} \xrightarrow{Z^{\ominus}} Y \left[CH_2 - \underset{\displaystyle X}{CH} \right]_{\eta} CH_2 - \underset{\displaystyle X}{CHZ}$$

(c) Anionic addition polymerization: This mechanism involves the following three steps:

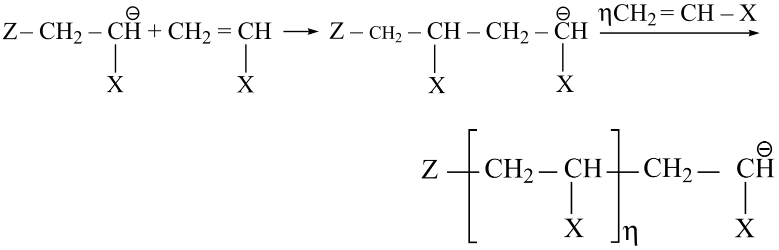
(i) Initiation: In this step formation of carbanion takesplace



$$Z^{\ominus} + CH_2 = \underset{\displaystyle X}{CH} \longrightarrow Z - CH_2 - \underset{\displaystyle X}{\overset{\ominus}{CH}}$$

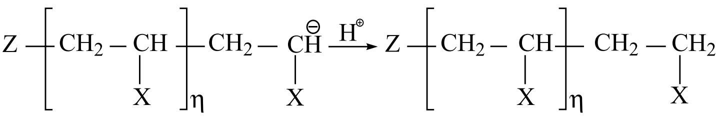
(anion) (monomer) (carbanion)

(ii) Propagation:



$$Z - CH_2 - \underset{\displaystyle X}{\overset{\ominus}{CH}} + CH_2 = \underset{\displaystyle X}{CH} \rightarrow Z - CH_2 - \underset{\displaystyle X}{CH} - CH_2 - \underset{\displaystyle X}{\overset{\ominus}{CH}} \xrightarrow{\eta CH_2 = CH - X} Z \left[CH_2 - \underset{\displaystyle X}{CH} \right]_{\eta} CH_2 - \underset{\displaystyle X}{\overset{\ominus}{CH}}$$

(iii) Temination:



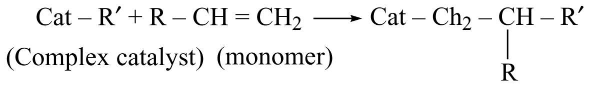
$$Z \left[CH_2 - \underset{\displaystyle X}{CH} \right]_{\eta} CH_2 - \underset{\displaystyle X}{\overset{\ominus}{CH}} \xrightarrow{H^{\oplus}} Z \left[CH_2 - \underset{\displaystyle X}{CH} \right]_{\eta} CH_2 - \underset{\displaystyle X}{CH_2}$$

Polymer

(d) Co-ordination or zieglar–Natta polymerization:

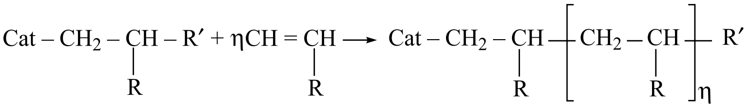
Zieglar and Natta discovered that in the presence of transition metal halide like $Ticl_4$ with an organometallic compound, triethyl aluminium (zieglar-Natta catalyst), stereo specific polymerization can be effected. Polymerization occurs due to insertion of alkane monomer molecules between the Ti-c bond. Mechanism of co-ordination polymerization involves the following three steps:

(i) Initiation:



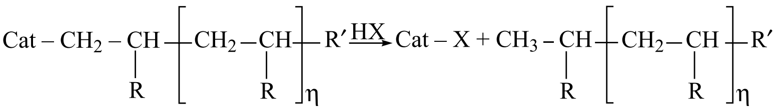
$$\underset{\text{(Complex catalyst)}}{\text{Cat}-\text{R}'} + \underset{\text{(monomer)}}{\text{R}-\text{CH}=\text{CH}_2} \longrightarrow \text{Cat}-\text{Ch}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}-\text{R}'$$

(ii) Propagation:



$$\text{Cat}-\text{CH}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}-\text{R}' + \eta\text{CH}=\underset{\text{R}}{\underset{|}{\text{CH}}} \longrightarrow \text{Cat}-\text{CH}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}-\left[\text{CH}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}\right]_{\eta}-\text{R}'$$

(iii) Termination:



$$\text{Cat}-\text{CH}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}-\left[\text{CH}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}\right]_{\eta}-\text{R}' \xrightarrow{\text{HX}} \text{Cat}-\text{X}+\text{CH}_3-\underset{\text{R}}{\underset{|}{\text{CH}}}-\left[\text{CH}_2-\underset{\text{R}}{\underset{|}{\text{CH}}}\right]_{\eta}-\text{R}'$$

2.5

MECHANISM OF CONDENSATION POLYMERIZATION

Condensation reaction is rather slow and proceeds stepwise, such polymerization is often called step polymerization. It involves condensation reaction of two or more reactive functional groups of monomers with elimination of by products like H_2O, HCl, NH_3 etc.

The main features of condensation polymerization are:

(a) the monomers having two or more reactive functional groups can undergo condensation polymerization
(b) There is continuous elimination of by products.
(c) The polymer chain build up is slow and stepwise.
(d) Linear or Cross linked polymers are produced.
(e) Polymerization is catalyzed by acids or alkali.

Two types of poly condensation are possible.

(i) AA–BB type poly condensation: When a pair of bifunctional monomers under goes poly condensation. One of the monomer is trifunctional the polymer obtained is a three dimensional network polymer

$$\eta A - A + \eta B - B \rightarrow A \left(AB \right)_{\eta} B + (2\eta - 1) \text{ by product}$$

(ii) A – B type poly condensation: when a single bifunctional monomer undergoes self condensation.

$$\eta A - B \rightarrow B \left(AB \right)_{\eta} A + (\eta - 1) \text{ by product}$$

2.6

PLASTOMERS

Plastics are high polymers which can be moulded into any desired form by application of heat and pressure in presence of a catalyst. There is no chemical change during the moulding process. Resins are basic binding materials, which form a major part of the plastics and these two terms are used synonymously. Plastics have very important position as engineering materials. Some important uses of plastics are for making electrical goods, handles for tools, paints, table tops, wind screens, radio and T.V. parts, overhead water tanks and floor tiles.

2.6.1 Properties of Plastics

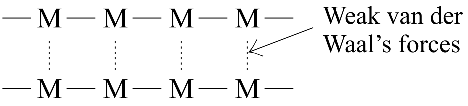
Nowadays, plastics have attained great importance in everyday life because of their certain unique properties like: (i) light in weight (ii) good thermal and electrical insulation (iii) low fabrication cost (iv) easy moulding (v) insect resistant (vi) chemical inertness (vii) low maintenance cost (viii) high resistance to abrasion (ix) good dimensional stability (x) corrosion resistance (xi) easy workability (xii) high refractive index, and so on.

2.6.2 Classifications of Plastics

Plastics are classified into two types:

(i) Thermoplastics
(ii) Thermosetting plastics

(i) Thermoplastics or Thermoplastic Resins These are the polymers which become soft on heating and hard on cooling. On reheating, they become soft again and can be remoulded to any desired shape. They are formed by addition polymerisation and have linear long chain polymeric structure. The chemical structure is not changed during heating or moulding operations. The weak, secondary van der Waal's forces act between the thermoplastic resin chains.

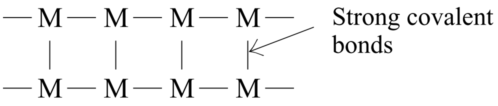


Thermoplastics

During the heating, only secondary van der Waal's forces are broken while on cooling, these secondary bonds are reestablished.

e.g., Polythene, PVC, teflon and polystyrene.

(ii) Thermosetting Plastics (or) Thermosetting Resins These are the polymers which are fusible on initial heating, but on further heating become set insoluble, infusible, rigid, hard and three dimensional network product, i.e. once they are set on heating, they cannot be reformed.



Thermosetting plastics

They are formed by condensation polymerisation.

e.g. Bakelite, polyesters, urea formaldehyde resin, etc.

Table 2.2 *Differences between Thermoplastics and Thermosetting Plastics*

Thermoplastics	*Thermosetting plastics*
(i) These are formed by addition polymerisation.	(i) These are formed by condensation polymerisation.
(ii) They are soft, weak and less brittle.	(ii) They are hard, strong and more brittle.
(iii) They soften on heating and harden on cooling.	(iii) They are fusible on initial heating, but become hard, rigid and infusible products on further heating.
(iv) They consist of linear long chain polymers.	(iv) They consist of three-dimensional network joined by strong covalent bonds.
(v) They are usually soluble in some of the organic solvents.	(v) They are insoluble in almost all organic solvents.
(vi) They can be reclaimed from wastes.	(vi) They cannot be reclaimed from wastes.
(vii) There is no change in chemical composition and structure during moulding process.	(vii) They undergo chemical changes such as further polymerisation and cross links during moulding process.

Fabrication or moulding of plastics into articles Different methods of fabrication are used to give required shapes to plastics. The important methods are

(i) Compression moulding
(ii) Injection moulding
(iii) Transfer moulding
(iv) Extrusion moulding

(i) *Compression moulding:* This method can be adopted to both thermoplastic and thermosetting plastics. The raw materials (resin, filler and other ingredients) are placed in a mould and mould is closed under pressure (Fig. 2.1). The mould is heated, the gap between the projected part and the cavity decides the shape of the moulded article. In case of thermoplastic curing is done by cooling while in thermosetting plastics curing is done by heating. After the setting the moulded article can be taken out by opening the mould parts.

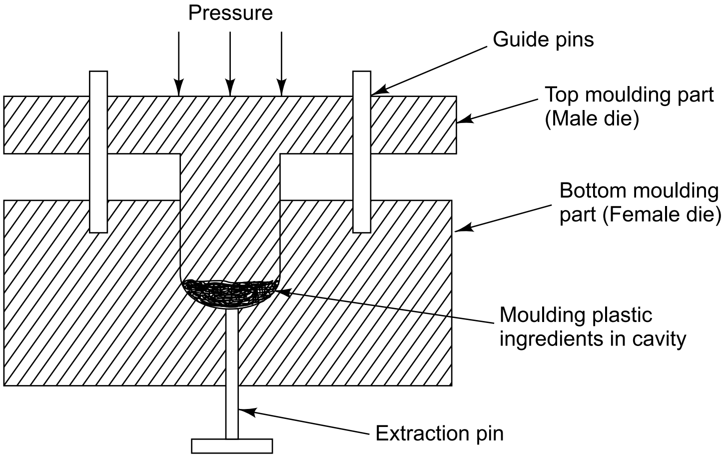


Fig. 2.1 *Compression moulding of plastics*

(ii) *Injection moulding:* This method is adopted to the thermoplastic resins. The thermoplastic material is softened by heating and then the hot softened plastic is injected into a mould by means of a screw (Fig. 2.2), where it sets by cooling. After sufficient curing the article is ejected.

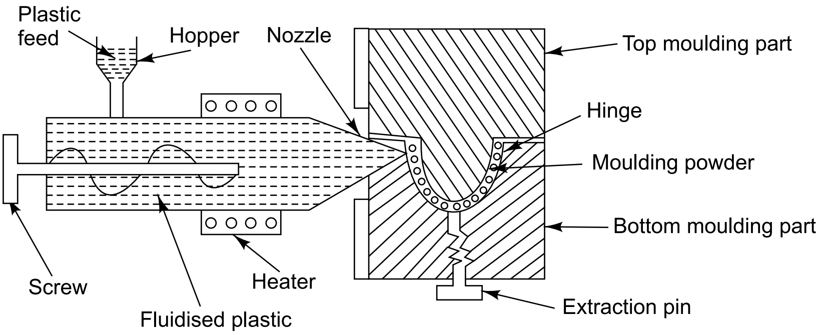


Fig. 2.2 *Injection moulding of plastics*

(iii) *Transfer moulding:* This is a modified form of injection moulding applicable for thermosetting resins.The raw materials (resin, filler and other ingredients) are heated in a chamber (just begins to become plastic) and then transferred through an orifice into the hot mould by plunger (Fig. 2.3). Afer the proper setting, the moulded article is ejected.

(iv) *Extrusion moulding:* This method is used for continuous moulding of thermoplastic materials into articles of uniform cross section like tubes, rods, insulated electric cables, etc. The plastic material is softened by heating and pushed into a die using a revolving screw (Fig. 2.4). The finished product coming out from the die is cooled by spraying of water.

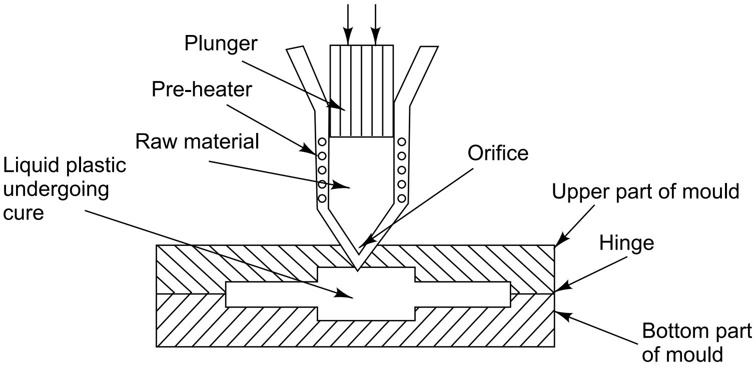


Fig. 2.3 *Transfer moulding of plastics*

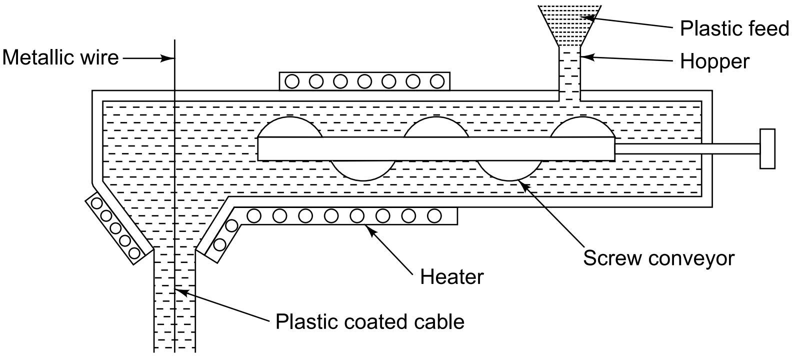


Fig. 2.4 *Extrusion moulding*

2.6.3 Some Important Polymers

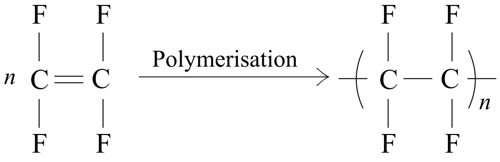
(i) Teflon (or) Polytetrafluoro Ethylene (PTFE) or Fluon

Preparation Teflon is obtained by the polymerisation of water-emulsion of tetrafluoro ethylene under pressure in the presence of benzoyl peroxide as catalyst. The monomer, tetrafluoro ethylene (TFE) is obtained by the following reactions.

$$\underset{\text{Chloroform}}{CHCl_3} + 2HF \rightarrow \underset{\text{Chlorodifluoro methane}}{CHClF_2} + 2HCl$$

$$2CHClF_2 \xrightarrow{\text{Pyrolysis}} \underset{\text{TFE}}{F_2C = CF_2} + 2HCl$$

TFE undergoes polymerisation, PTFE is obtained



$$n\,CF_2{=}CF_2 \xrightarrow{\text{Polymerisation}} \left(CF_2-CF_2\right)_n$$

TFE PTFE

Properties Teflon is a thermoplastic resin and has the following properties:

(a) Highly crystalline (93–98%)
(b) High melting point, 330°C
(c) Not soluble in any solvent
(d) High density, 2.3 g/cm^3
(e) Good electrical and mechanical properties
(f) Excellent thermal stability

Uses It is used

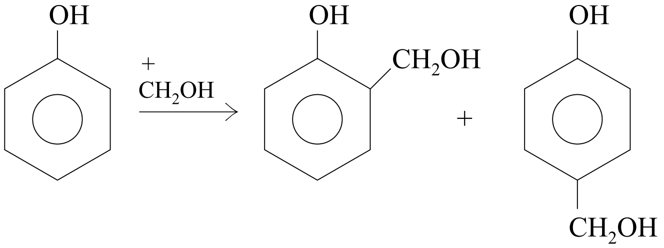
(a) for insulation of motors, generators, capacitors, transformers, etc.
(b) in making stopcocks for burettes, non-lubricating bearings, chemical carrying pipes, etc.
(c) for coating on articles like bakery trays, frying pans, etc.

(ii) Bakelite (or) Phenol-Formaldehyde resin or Phenolic resin (or) Pheno plasts

Preparation Bakelite is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of an acid or alkali catalyst. The following steps are involved:

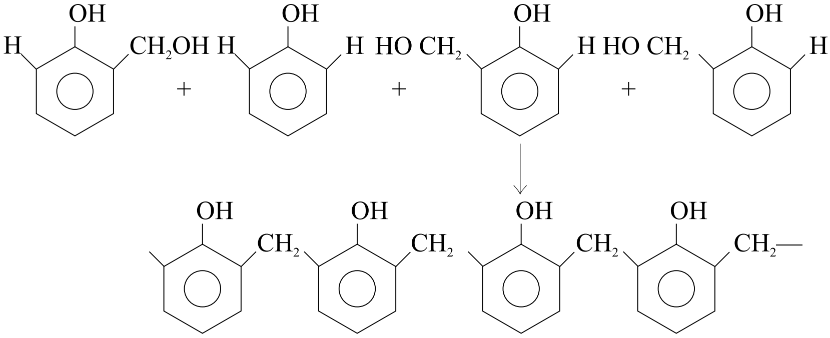
(a) In the first step, phenol reacts with formaldehyde to form *o*-hydroxymethyl phenol and *p*-hydroxymethyl phenol.

$$HCHO \xrightarrow{H^+} \overset{+}{C}H_2OH$$



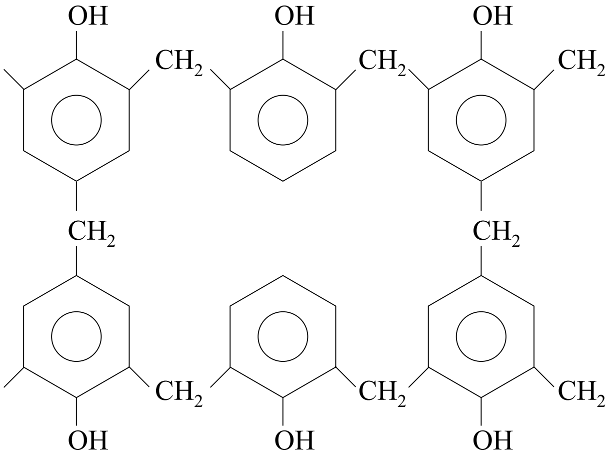
o-hydroxymethyl phenol *p*-hydroxymethyl phenol

(b) In the second step, condensation between hydroxymethyl phenol and phenol occurs to give linear polymer (Novolac).



Novolac

(c) In the third step a small amount of hexamethylene tetramine is added. It produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible novolac into a hard, infusible solid of cross-linked three-dimensional polymer called Bakelite while ammonia neutralizes the acid.



Bakelite

Properties

(a) Bakelite is a rigid, hard, scratch resistant, infusible solid substance.

(b) It is resistant to acids, salts and most organic solvents but attacked by alkali (because of presence of —OH groups).

(c) It possesses excellent electrical insulating character.

Uses It is used

(a) for making electrical equipments like switches, plugs, holders, switch boards, heater handles, etc.

(b) for making telephone parts, radio and T.V. cabinets.

(c) in paints and varnishes.

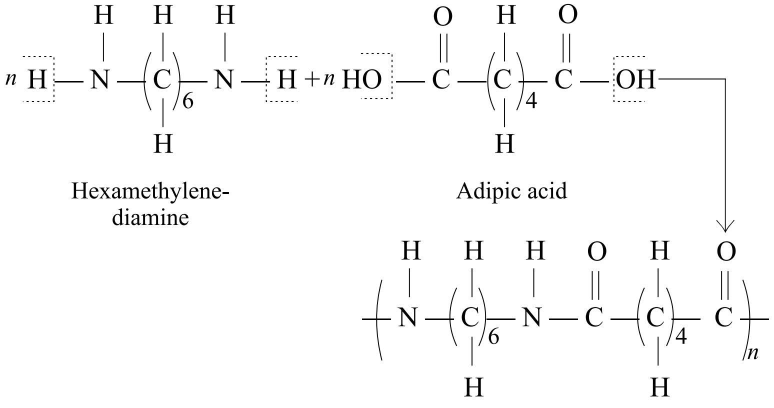
(d) for making bearings, propeller shafts for paper industry and rolling mills.

(e) in the production of ion-exchange resins.

(iii) Nylon (Polyamides) The nylons have been named on the basis of the number of carbon atoms in the monomer chain.

(a) Nylon-6, 6

Preparation It is obtained by the polymerisation of adipic acid with hexamethylenediamine.



$$n\,\text{H}-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{H} + n\,\text{HO}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{OH} \longrightarrow \left[\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}\right]_n + 2n\,\text{H}_2\text{O}$$

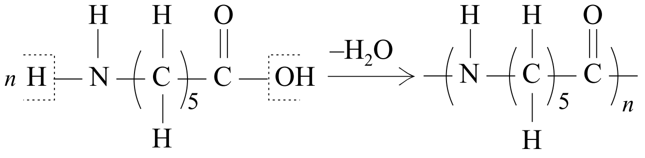
Hexamethylene-diamine

Adipic acid

Nylon 6, 6
(Poly hexamethylene adipate)

(b) Nylon-6

Preparation It is produced by the self-condensation of α-aminocaproic acid

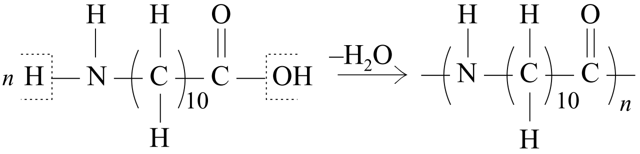


$$n\,\text{H}-\text{NH}-(\text{CH}_2)_5-\text{CO}-\text{OH} \xrightarrow{-\text{H}_2\text{O}} \left[\text{NH}-(\text{CH}_2)_5-\text{CO}\right]_n$$

Nylon-6

(c) Nylon-11

Preparation It is obtained by the self condensation of W-amino undecanoic acid



$$n\,\text{H}-\text{NH}-(\text{CH}_2)_{10}-\text{CO}-\text{OH} \xrightarrow{-\text{H}_2\text{O}} \left[\text{NH}-(\text{CH}_2)_{10}-\text{CO}\right]_n$$

Nylon-II

Properties

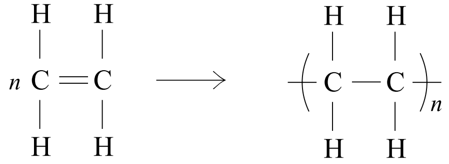
1. Nylons show plastic and fibre property.
2. They possess good mechanical properties.
3. They are insoluble in common organic solvents and soluble in formic acid and phenol.
4. They have high strength and abrasive resistance.

Uses

1. Nylon-6, 6 is used as fibres for making socks, dresses, carpets, undergarments, etc.
2. Nylon-6 and Nylon-11 are used for moulding purposes for gears, bearings, etc.
3. They are also used for making filaments, films, bristles for tooth-brushes, etc.

(iv) Polyethylene (or) Polythene

Preparation Polyethylene is obtained by the addition polymerisation of ethylene under high pressure (1500 atmosphere) and temperature range of 180–250°C and in the presence of oxygen.



$$n\,\mathrm{CH_2{=}CH_2} \longrightarrow \left(\mathrm{CH_2{-}CH_2}\right)_n$$

Ethylene Polyethylene (PE)

There are two kinds of polyethylene

(a) Low density polyethylene (LDPE)
(b) High density polyethylene (HDPE)

HDPE is formed by using ionic catalyst like Zeigler-Natta catalyst or chromium or molybdenum oxides.

Properties

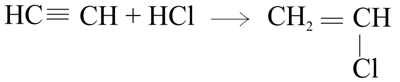
(i) Polyethylene is a rigid, waxy, white, translucent material.
(ii) It crystallises very easily.
(iii) It has high chemical resistance to acids, alkalies and salt solutions at room temperature.
(iv) LDPE melts at 110–125°C while HDPE melts at about 144–150°C.
(v) HDPE is completely linear in structure.

Uses

(i) LDPE is used for packing purposes in the form of films, sheets, bags, etc.
(ii) HDPE is used in the manufacture of pipes, bottles, toys, industrial cloths, household articles, etc.

(v) Polyvinyl Chloride (PVC)

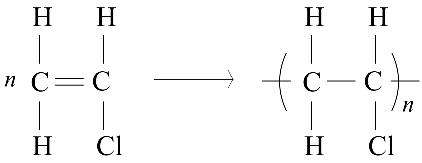
Preparation Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepard by reacting acetylene with hydrogen chloride at 100–150°C in the presence of metal salt catalyst



$$HC \equiv CH + HCl \longrightarrow \underset{\displaystyle Cl}{CH_2 = \overset{}{CH}}$$

Vinyl chloride

PVC is prepared by heating a water-emulsion of vinyl chloride in presence of benzoyl peroxide or hydrogen peroxide in a autoclave under pressure.



Vinyl chloride PVC

Properties

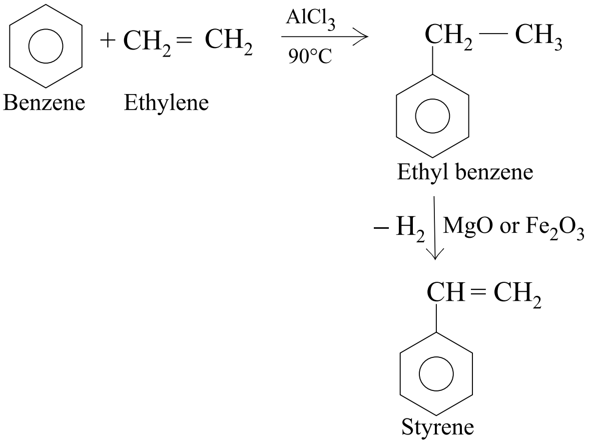
(i) PVC is a colourless and odourless powder.
(ii) It is non-inflammable and chemically inert.
(iii) It is soluble in chlorinated hydrocarbons like ethyle chloride, etc. and ketones.
(iv) It has high resistance to light, inorganic acids, alkalis and atmospheric oxygen.

Uses

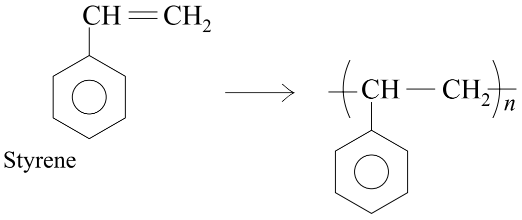
(i) Plasticised PVC is used for making table cloths, raincoats, coatings for electric wire and cables, toilet articles, radio, T.V. components, pipes, coupling, valves, etc.
(ii) Unplasticised PVC or rigid PVC is used for making refrigerators components, cycle and motor cycle mudguards, tubes, pipes, etc.

(vi) Polystyrene (PS)

The monomer styrene is obtained from benzene and eltylene under pressure at 90°C, in presence of a catalyst and the resulting ethyl benzene is dehydrogenated to styrene in presence of iron oxide or magnesium oxide.



Polystyrene is obtained by polymerisation of styrene in presence of benzoyl peroxide catalyst.



Polystyrene (PS)

Properties

(i) Polystyrene is light, transparent and resistant to alkalis, oxidising agents, etc.
(ii) It is chemically inert.
(iii) It is a good electrical insulator.

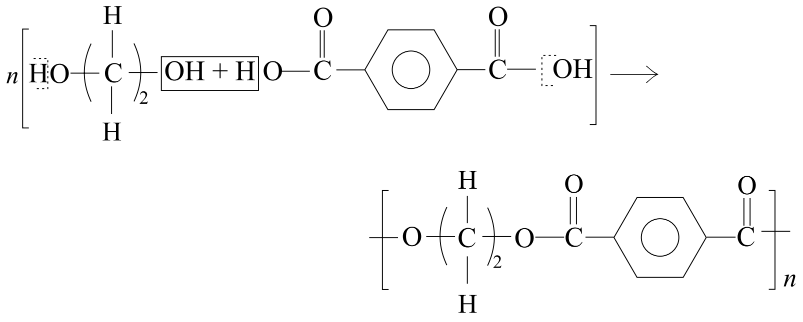
Uses Polystyrene is used in the manufacture of moulded articles like toys, jars, bottles, radio and TV parts, high frequency insulators, etc.

(vii) Polyester Resins

Polyester resin is the condensed product of dicarboxylic acids with dihydroxy alcohols.

(viii) Terylene or Dacron or Polyester or Polyethylene Tetraphthalate (PET)

Terylene is obtained by condensation of ethylene glycol and terephthalic acid.



Polyester (or) terylene (or) Dacron (or) PET

Properties

(i) It is highly resistant to mineral and organic acids but is less resistant to alkalies.
(ii) It possesses high melting point due to presence of aromatic ring.
(iii) It is chemically inert.
(iv) It has good mechanical strength.

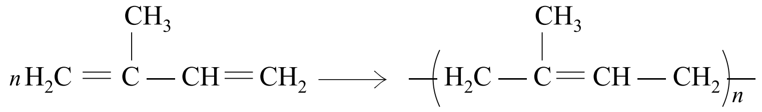
Uses It is used

(i) for making synthetic fibres, modern garments blended with cotton, etc.
(ii) as a glass reinforcing material in battery boxes, aircrafts, etc.

2.7

ELASTOMERS

The main source of natural rubber is the species of tree known as Haveabrasiliensis. It is a polymeric material having elastic character. India ranks 5th and produces about 2.7% of the total world production. Most of the Indian production comes from Kerala. Natural rubber is the polymer of isoprene.



$$n\,H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2 \longrightarrow -\!\left(H_2C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2\right)_{n}\!-$$

2-methyl, 1, 3-butadiene
(isoprene)

Polyisoprene
(Natural rubber)

X-ray diffraction studies have shown that isoprene units are arranged in natural rubber in cis-form.

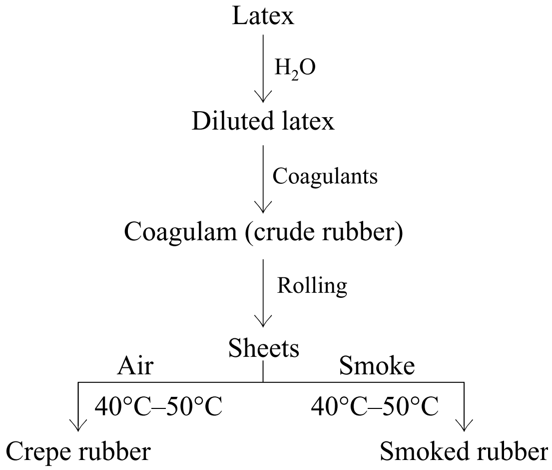
2.7.1 Processing of Natural Rubber

The milk of rubber trees is called latex. It is a colloidal emulsion containing about 25–40% of rubber. The latex is collected by cutting the bark of the rubber trees. The latex is diluted with water and filtered to eliminate dirt present in it. The latex then coagulates by the addition of dilute acetic acid or formic acid. The coagulated rubber hydrocarbon is called crude rubber. It is then rolled out into sheets.

Crepe Rubber To the crude rubber, a small amount of sodium bisulphite is added to bleach the colour and passed into rollers which produce 1 mm or more thickness sheets resembling crepe paper and dried in air about 40–50°C.

Smoked Rubber The crepe rubber sheets are placed inside smoke rooms maintaining a temperature 40–50°C for 4 days. The dried rubber sheets are called smoked rubber and are sent to rubber factories for further processing.

Flow chart of processing of Natural Rubber



2.7.2 Drawbacks of Crude Rubber or Raw Rubber

Crude rubber obtained from the latex contain the following drawbacks.

(i) It becomes soft at high temperature and is brittle at low temperature.
(ii) It shows large water absorption capacity.
(iii) It shows little durability.
(iv) It shows high elasticity.
(v) It attacks easily by oxidising agents.
(vi) It swells in organic solvents.
(vii) It possesses tackiness.
(viii) It shows low tensile strength.

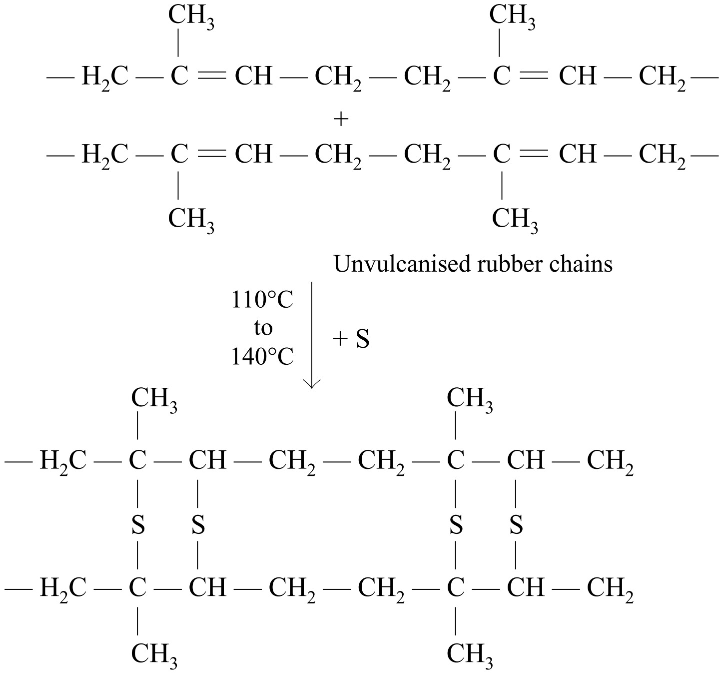
All the above drawbacks of raw rubber can be rectified by the process of vulcanisation.

2.7.3 Vulcanisation

The vulcanisation process was discovered by Charles Good Year in 1839.

'The process by which sulphur is added to raw rubber at 110°C–140°C to improve the quality of rubber is called vulcanisation'. The added sulphur combines chemically at the double bonds of rubber chains and cross links of the linear polymer chains, resulting in a three-dimensional network structure. Thus, the rubber loses plastic state and acquires an elastic state. The stiffness of vulcanised rubber depends on the amount of sulphur added.

e.g., A flexible tyre rubber contains about 3–5% of sulphur whereas hard rubber (ebonite) contains about 32% of sulphur.



$$-H_2C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

$$+$$

$$-H_2C-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

Unvulcanised rubber chains

$$\xrightarrow[140^\circ C]{110^\circ C \text{ to}} \quad + S$$

$$\begin{array}{l} -H_2C-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH-CH_2 \\ \qquad\quad\;\; |\quad\;\; |\qquad\qquad\qquad\qquad\quad\;\; |\quad\;\; | \\ \qquad\quad\;\; S\quad\; S\qquad\qquad\qquad\qquad\quad\; S\quad\; S \\ \qquad\quad\;\; |\quad\;\; |\qquad\qquad\qquad\qquad\quad\;\; |\quad\;\; | \\ -H_2C-\underset{\underset{\displaystyle CH_3}{|}}{C}-CH-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}-CH-CH_2 \end{array}$$

Vulcanised rubber

Other vulcanising agents used are hydrogen peroxide, sulphur monochloride, benzoyl peroxide, benzoyl chloride, etc.

Advantages of Vulcanisation

Vulcanisation process brings excellent changes in the properties of rubber, i.e., vulcanised rubber has

(i) good tensile strength.
(ii) low water absorption tendency.
(iii) higher resistance to oxidation.
(iv) high stiffness.
(v) slight tackiness.
(vi) good durability.
(vii) good resistance to change in temperature.
(viii) good resistance to swelling in organic solvents, etc.

2.7.4 Compounding of Rubber

Compounding is mixing of raw rubber (synthetic or natural) with different substances to impart special properties to an application.

Some of the substances (ingredients) mixed with raw rubber are given below:

(i) Softeners and Plasticisers These are added to give greater plasticity and flexibility and to reduce the brittleness of the products. e.g., waxes, stearic acid and vegetable oils.

(ii) Vulcanising Agents When rubber is heated with sulphur, its tensile strength, elasticity and resistance to swelling are increased. The sulphur atoms chemically bond with double bonded carbons of rubber chains and bring about excellent changes in their properties. The percentage of sulphur added varies from 0.15 to 32%. S_2Cl_2, H_2S, H_2O_2 benzoyl chloride, etc. are other vulcanising agents.

(iii) Antioxidants Natural rubber has tendency for oxidation. Antioxidants like phenylnaphthyl-amine and phosphites are added for preventing the oxidation of rubber.

(iv) Accelerators These shorten the time required for vulcanisation and give toughness to the rubber. For example, 2-Mercaptol and Benzothiozole.

(v) Fillers These are added to give rigidity and strength to the rubber.
For example, Carbon black, zinc oxide and calcium carbonate.

(vi) Colouring matter These materials provide pleasing colour to the rubber product.

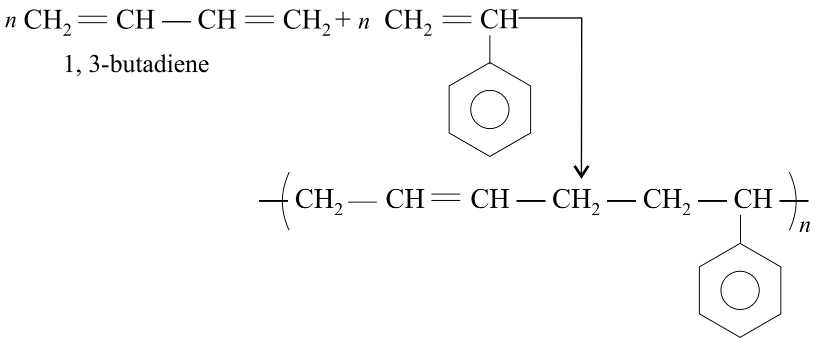
For example,
Titanium oxide – White
Ferric oxide – Red
Lead chromate – Yellow
Antimony oxide – Crimson
Chromic oxide – Green

2.8

SYNTHETIC RUBBERS OR ELASTOMERS

(i) Buna–S or Styrene Rubber (or) GR-S Rubber

Preparation The Buna-S rubber contains 1,3-butadiene (75%) and styrene (25%). It is produced by co-polymerisation of butadiene and styrene.



Buna-S rubber (Polybutadiene co-styrene)

Properties

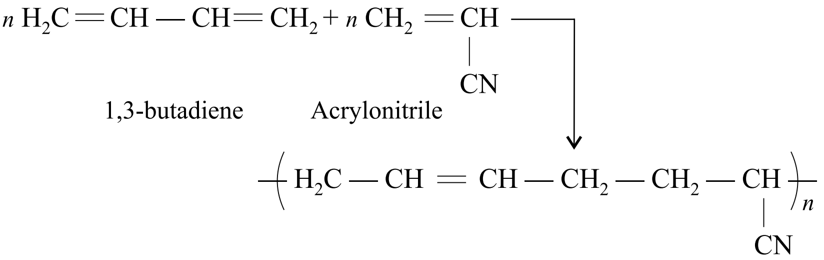
- (a) It possesses high abrasion resistance and high load bearing capacity.
- (b) It easily oxidises in presence of ozone atmosphere.
- (c) It swells oils and solvents.
- (d) It can be vulcanised in the same way as natural rubber.

Uses

- (a) It is mainly used for manufacture of tyres.
- (b) It is also used for floor tiles, shoe soles, gaskets, wire and cable insulations, adhesives, tank linings, etc.

(ii) Buna-N (or) Nitrile Rubber (or) GR-A Rubber

Preparation It is prepared by co-polymerisation of 1, 3-butadiene and acrylonitrile.



$$n\,H_2C{=}CH{-}CH{=}CH_2 + n\,CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \longrightarrow \left(H_2C{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}\right)_n$$

Polybutadiene-co-acrylonitrile
(Nitrile rubber)

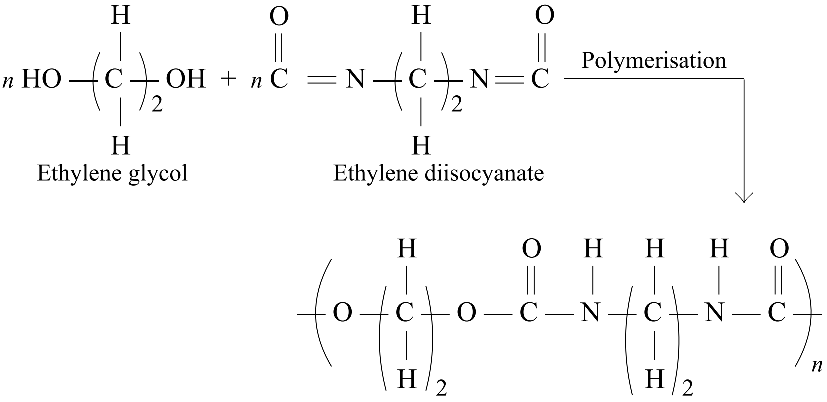
Properties

(a) It can be vulcanised in the same way as natural rubber.
(b) It has good oil resistance, heat resistance and abrasion resistance.
(c) It is attacked by alkalis due to presence of cyanogroups (–CN)

Uses Nitrile rubber is used for making aircraft components, conveyor belts, tank linings, gaskets, hoses, printing rollers, automobile parts, etc.

(iii) Polyurethane Rubber or Isocyanate Rubber

Preparation It is obtained by reacting polyalcohols (e.g., ethylene glycol) with diisocyanates (e.g., ethylene diisocyanate).



$$n\,\mathrm{HO}-\left(\overset{\mathrm{H}}{\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}}\right)_2-\mathrm{OH} + n\,\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}=\mathrm{N}-\left(\overset{\mathrm{H}}{\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}}\right)_2-\mathrm{N}=\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \xrightarrow{\text{Polymerisation}} \left(-\mathrm{O}-\left(\overset{\mathrm{H}}{\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}}\right)_2-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\left(\overset{\mathrm{H}}{\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}}\right)_2-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right)_n$$

Polyurethane rubber

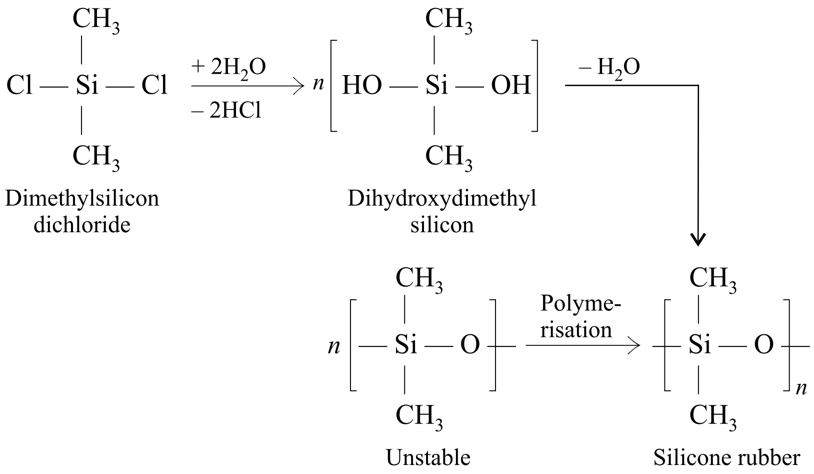
Properties

(a) They are highly resistant to organic solvents but are attacked by acids and alkalis.
(b) They also show good resistance to oxidation because of their saturation character.
(c) Their forms are light, tough and resistant to heat, weathering, chemicals and abrasion.

Uses They are used for surface coatings, manufacture of foams and spandex fibres.

(iv) Silicone Rubber

Preparation It is obtained by the polymerisation of Dihydroxy dimethyl silicon. In first step, Dihydroxydimethyl silicon (monomer) is produced by hydrolysis of Dimethyl silicon dichloride which on dehydration is followed by polymerisation in the presence of peroxide and inorganic fillers like TiO_2, SiO_2, etc. to form silicon rubber.



Properties

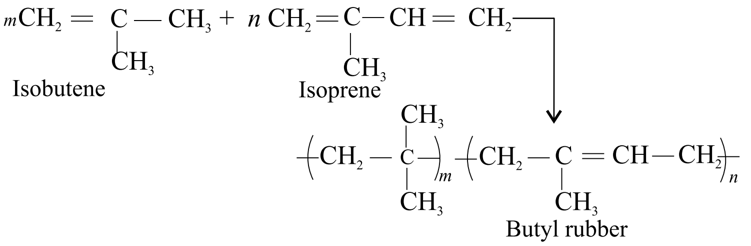
(a) It has good resistance to sunlight, oils, dilute acids and alkalies.
(b) It retains rubber properties over a much wider temperature range.
(c) It is also resistant to air and ozone at high temperature range.

Uses

(a) It is used in making lubricants, paints, etc.
(b) For making artificial heart valves, transfusion tubings, for special boots to be used at low temperature, etc.

(v) Butyl Rubber (or) GR–I

Preparation Butyl rubber is obtained by co-polymerisation of isobutene with small amount of isoprene.



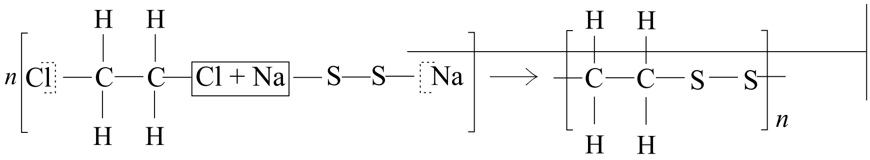
Properties

(i) It is resistant to sunlight, air, heat, mineral acids, polar solvents, etc.
(ii) It is non-resistant to flame and oil

Uses It is used in manufacture of cycle and automobile tubes, hoses, conveyor belts, etc.

(vi) Polysulphide Rubber (or) Thiokol (or) GR-P

Preparation Thiokol is produced by condensation between sodium polysulphide (Na_2S_2) and 1, 2-dichloroethane



Ethylene dichloride (1, 2-dichloroethane) Sodium polysulphide Thiokol

Properties

- (i) It is resistant to mineral oils oxygen, ozone, sunlight, etc.
- (ii) It does not form hard rubber because it cannot be vulcanised.
- (iii) It has poor abrasion resistance.

Uses It is used for making hoses, gaskets, printing rollers, tank linings, etc.

2.9

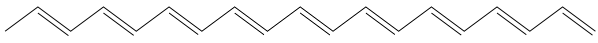
CONDUCTING POLYMERS

Polymers are poor conductors of electricity and generally used as electrical insulators and dielectric materials. However, there are polymers with improved electrical conductivity prepared by the addition of some additives such as conducting metals like copper and silver or other materials.

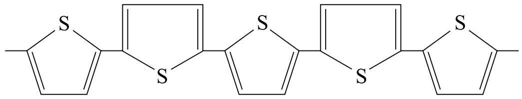
'An organic polymer with highly delocalised Pi-electron system, having electrical conductance on par with metallic conductor is called a conducting polymer.'

For example, Polyacetylene, polythiophene, polyphenylene, polyphenylene sulphide and polyaniline.

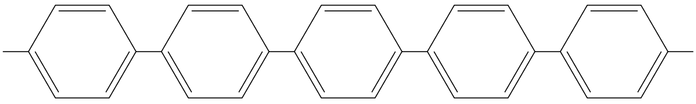
Chemical Structures



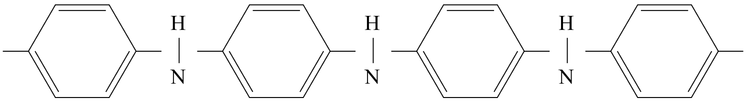
Polyacetylene



Polythiophene



Polyphenylene



Polyaniline

2.9.1 Classification

(i) *π-electrons conducting polymers:* The polymer whose backbone is made up of molecules that contain conjugated π-electrons which extend the entire polymer and made it conducting.

(ii) *Conducting element filled polymer:* This type of polymers acts as a binder, i.e., which binds the conducting elements such as metal oxides, metallic fibres and carbon black.

(iii) *Doped-conducting polymer:* It is obtained by exposing a polymer to a charge transfer agent in gas or solution phase.

(iv) *Blended conducting polymer:* It is made by blending a conventional polymer with a conducting polymer.

(v) *Inorganic or coordination conducting polymer:* It is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand.

2.9.2 Synthesis

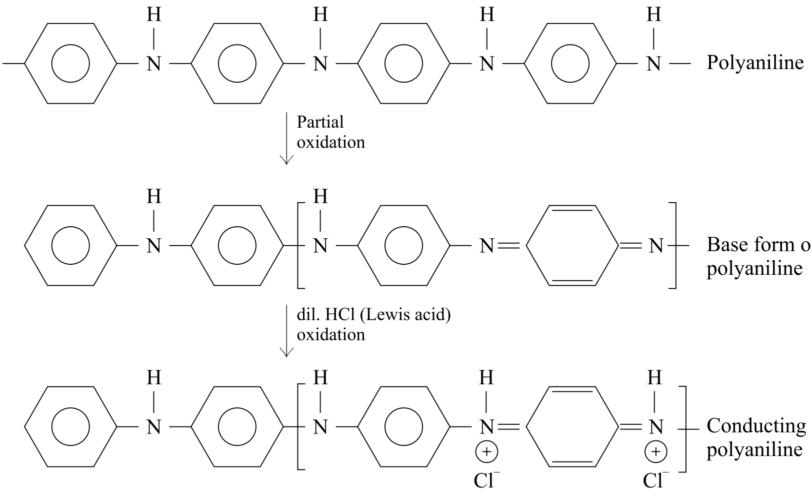
The conducting polymers like polyacetylene and polyaniline can be synthesised by doping in which charged species are introduced in organic polymers having π-electron backbone.

(i) *P-doping:* In this process, an intrinsically conducting polymer or conjugated π-electron conducting polymer is treating with Lewis acid. Thereby, oxidation takes place and creates positively charged sites on polymer backbone, which are current carriers for conduction. Some of the general P-dopant used are I_2, Br_2, ASF_3, etc.

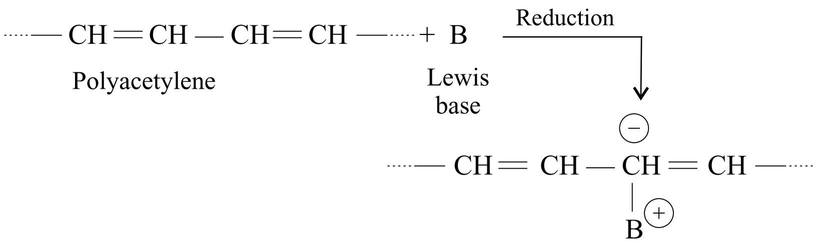
(a) $\underset{\text{Polyacetylene}}{(C_2H_2)_n} + 2FeCl_3 \rightarrow (C_2H_2)_n^+ FeCl_4^- + FeCl_2$

$$2\,(C_2H_2)_n + 3I_2 \rightarrow 2[(C_2H_2)_n^+ I_3^-]$$

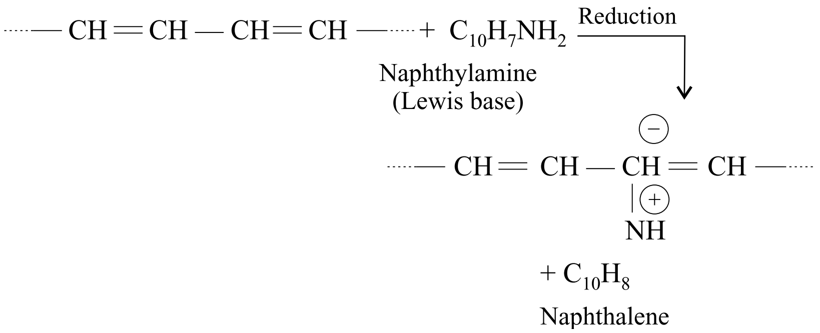
(b)



(ii) *n-doping:* In this process, conjugated π-electron are treating with Lewis base. Thereby, reduction takes place and creates negatively charged sites on polymer backbone, which are responsible for the conduction. Some of the general *n*-dopant used are Li, Na, Ca and tetrabutyl ammonium.



$$\cdots\text{—CH=CH—CH=CH—}\cdots + \underset{\text{Lewis base}}{\text{B}} \xrightarrow{\text{Reduction}} \cdots\text{—CH=CH—}\overset{\ominus}{\underset{\overset{|}{\text{B}^{\oplus}}}{\text{CH}}}\text{=CH—}\cdots$$



$$\cdots\text{—CH=CH—CH=CH—}\cdots + \underset{\substack{\text{Naphthylamine}\\\text{(Lewis base)}}}{C_{10}H_7NH_2} \xrightarrow{\text{Reduction}} \cdots\text{—CH=CH—}\overset{\ominus}{\underset{\overset{|\oplus}{\text{NH}}}{\text{CH}}}\text{=CH—}\cdots + \underset{\text{Naphthalene}}{C_{10}H_8}$$

2.9.3 Applications

Some of the important applications of conducting polymers are:

(i) In solar cells
(ii) In photovoltaic devices.
(iii) In non-linear optical materials.
(iv) In telecommunication systems.
(v) As electrode material for commercial rechargeable batteries.
(vi) In antistatic coatings for clothing.
(vii) As film membranes for gas separations.
(viii) In wiring in aircrafts and aerospace components.
(ix) In fuel cells as the electrocatalytic materials.

2.10

LIQUID CRYSTALS

In general, crystalline solids melt at a certain temperature and there is a sharp transition to liquid state and then to gaseous state with the collapse of the lattice, i.e. the free rotation and movement of the particles takes place. In certain crystalline solids, the sharp transition of solid to liquid does not takes place and intermediate stages may be identified which are called mesomorphic.

There are two mesomorphic states like plastic crystals and liquid crystals. A mesomorphic substance exhibits four states, i.e. solid, liquid crystal, liquid and gas, e.g., Cholesterol benzene melts at 145°C into a liquid having turbid appearance. At 179°C, the liquid becomes clear. The colour of the liquid changes from red to blue. On cooling, the reverse occurs.

2.10.1 Classification of Liquid Crystals

Liquid crystals are classified into two types:

(a) *Thermotropic liquid crystals* (which exhibit liquid crystal phases due to change of temperature).

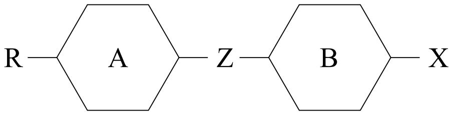
For example, P-Azoxy anisole, P-Methoxy benzylidene, *p′*-*n*-butylaniline and *p*-*n*-Hexyl-*p′*-cyano-biphenyl.

(b) *Lyotrophic liquid crystals* (which change into liquid crystal phases with change of concentration in a solution).

For example, Kevlar, Poly-P-benzamide and Polybenzyl-L-glutamate.

2.10.2 Chemical Structure of Liquid Crystals

Chemical structure of many liquid crystals can be represented as given below:



where R = Side chain group
A and B = Aromatic rings
Z = Linking group
X = Terminal group

2.10.3 Structural Forms of Liquid Crystals

There are three states or structural forms of liquid crystals.

(i) Smectic state
(ii) Nematic state
(iii) Cholesteric state

The rigid units of the polymer are called mesogens. The arrangement of mesogens in liquid crystal polymers are shown in Fig. 2.5.

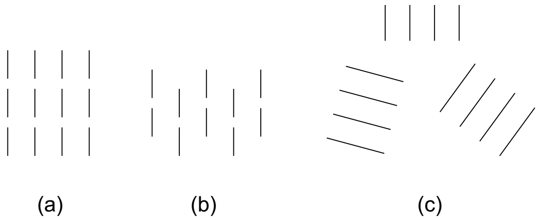


Fig. 2.5 *(a) Smectic (b) Nematic (c) Cholesteric states of a liquid crystal*

2.10.4 Properties of Liquid Crystals

(i) Thermotropic polymers such as vectra and vectex have high thermal stability, strength, good dimensional strength, low thermal expansion, low water absorption, low smoke emission, etc.

(ii) These are easy to process by injection moulding, extrusion moulding, etc.

2.10.5 Applications

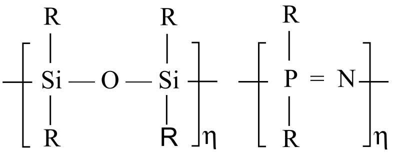
Liquid crystals have been used in flat panel displays, temperature sensors display for watches and calculators, improving the separation efficiency of chromatographic columns, data storage discs, fibre optic cables, etc.

2.11

INORGANIC POLYMERS

The Polymer chain back bone made with out carbon-carbon Links is called inorganic polymer. Atoms in these polymers are linked together mainly by covalent bonds.

eg:



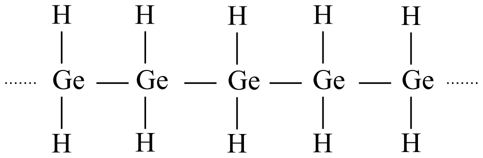
$$\left[-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\underset{R}{\overset{R}{\mathrm{Si}}}-\right]_{\eta}\qquad\left[-\underset{R}{\overset{R}{\mathrm{P}}}=\mathrm{N}-\right]_{\eta}$$

etc.

Silicone Poly phosphazine

A polymer with the chain back bone made entirely of the same type of atoms atoms is called a homochain polymer

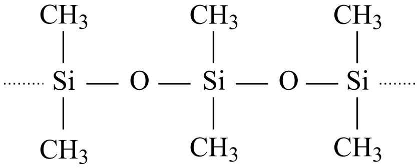
eg: Polygermanes



$$\cdots\underset{H}{\overset{H}{\mathrm{Ge}}}-\underset{H}{\overset{H}{\mathrm{Ge}}}-\underset{H}{\overset{H}{\mathrm{Ge}}}-\underset{H}{\overset{H}{\mathrm{Ge}}}-\underset{H}{\overset{H}{\mathrm{Ge}}}\cdots$$

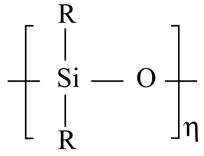
A polymer with the chain back bone made of different types of atoms is called a hetero chain polymer.

eg: Silicone rubber



$$\cdots\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\cdots$$

Silicones: Silicones have alternate silicon-oxygen bonds and organic radicals attached to the silicon atoms. Silicon is capable of forming long chains like carbon and in these chains silicon is always combined with oxygen.



$$\left[-\overset{R}{\underset{R}{Si}}-O-\right]_\eta$$

R = alkyl or phenyl radical.

Preparation:

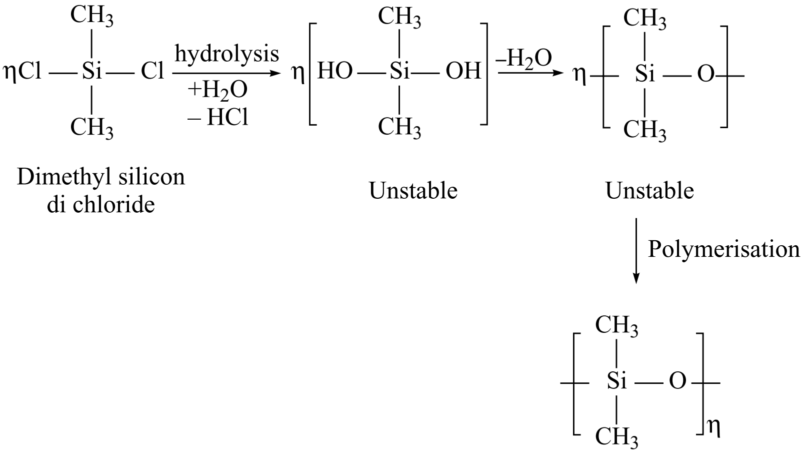
The monomers for silicone polymer are produced by the hydrolysis of chlorosilanes. The unstable monomers condense to yield silicon polymer.

Silicon with alkyl halide (or) Silicon halide with Grignard reagent gives organo silicon halides (chloro silanes)

$2Rel + Si \rightarrow R_2\ Sicl_2$

$Sicl_4 + RMgcl \rightarrow R\ Sicl_3 + Mgcl_2$.

(a) Dimethyl silicon dichloride is bifunctional which gives linear polymer



$$\eta Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow[+H_2O,\ -HCl]{hydrolysis} \eta\left[HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH\right] \xrightarrow{-H_2O} \eta\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right] \xrightarrow{Polymerisation} \left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right]_\eta$$

Dimethyl silicon di chloride

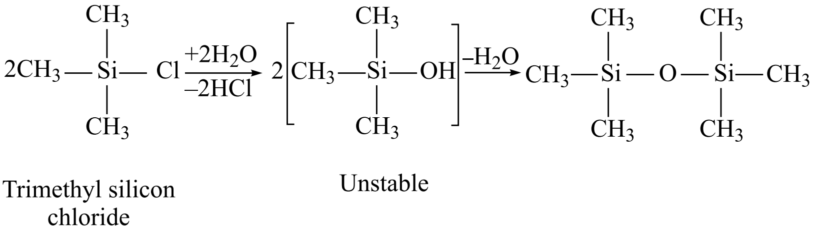
Unstable

Unstable

Polymerisation

Silicon rubber

(b) Trimethyl silicon chloride is mono functional which gives polymer of limited chain length.

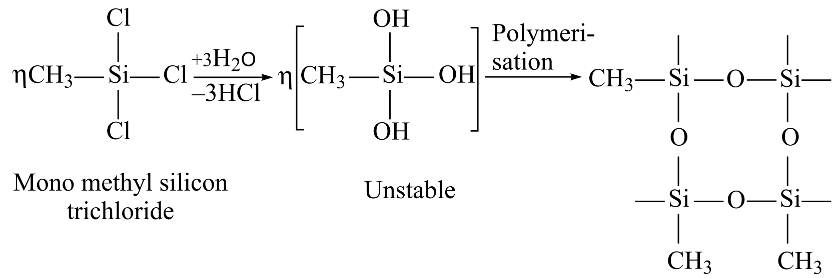


$$2CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow[-2HCl]{+2H_2O} 2\left[CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-OH\right] \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Trimethyl silicon chloride

Unstable

(c) Monomethyl silicon chloride is tri functional and gives cross linking to the product.



Mono methyl silicon trichloride

Unstable

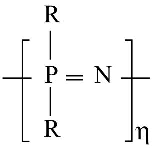
Properties:

(i) Silicones may be liquid, viscous liquid, semisolid, rubber like and solids
(ii) Their physical properties are much less effected by variation in temperatures
(iii) They are non-toxic in nature
(iv) They exhibit good water resistance, good oxidation stability and poor chemical resistance.

Uses:

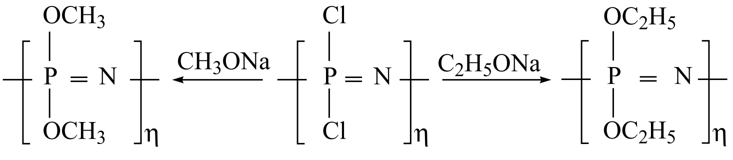
(i) Silicone fluids are used as high temperature Lubricants, anti foaming agent for paper and textile treatment. Silicon fluids are modified and used as silicone greases and silicone compounds.
(ii) Silicone rubbers are used is making Lubricants, paints, artificial heart valves, for special boots to be used at low temperature etc.
(iii) Solid silicone resins are used for making high voltage insulators, high temperature insulating foams etc.

Poly Phosphazines: These are inorganic polymers containing phosphorus atoms. Their general formula is given below eg: polymethoxy phosphazines and polydimethoxy phosphazines:



$$\left[-\overset{R}{\underset{R}{P}}=N- \right]_{\eta}$$

These are prepared by treating phosphonitrile chloride with sodium methoxide (CH_3ONa) and sodium elthoxide (C_2H_5ONa) respectively



Poly methoxy Phosphazine

Poly dimethoxy phosphazine

They are colorless, transparent and film forming Thermoplastics. On heating above 100°C, they can slowly form cyclic polymers.

Short Answer Question

1. Write Short note on Polymer and Monomer.

   Polymer: A high Molecular Weight Compound (Macro molecule or giant molecule) Made by the Combination of a large number of Small Molecules.

   Monomer: The repeating units in a polymer are called monomers.

2. What is polymerisation? How many types?

   Ans. The Chemical reaction by which the monomers are combined to form polymers is called polymerisation

   Polymerisation process 3 Types:

   (i) Addition Polymerisation
   (ii) Condensation Polymerisation
   (iii)Co-Polymerisation

3. Define the degree of Polymerisation.

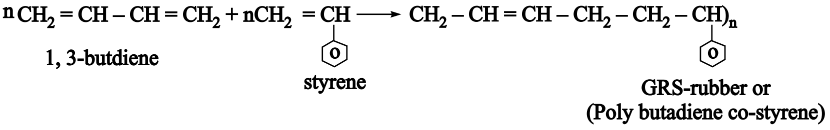
   Ans. The number of repeating units in a polymers chain is called degree of polymerisation (DP).

   Molecular weight of polymer = Molecular weight of Monomer × DP

   Polymers with high DP are called high polymers while the polymers with low DP are called oligo polymers.

4. Write short note on Co-Polymerisation.

   Ans. When two are more different types of Monomers undergo Simultaneous Polymerisation, it is called Co-polymerisation



5. What is an elastomer?

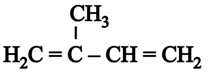
   Ans. Any rubber line elastic polymer, which can be stretched to at least three times, but it returns to its original shape and size as soon as stretching force is removed.

6. What is natural rubber?

   Ans. It consist of long-coiled chains of polymers isoprene.

7. Write the for mula of isoprene unit

   Ans.



$$H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$

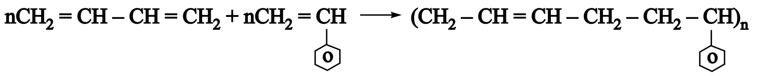
   2-Methyl, 1, 3-butadiene (Isoprene)

8. Why does natural rubber need compounding?

   Ans. Natural rubber possesses many draw backs. In order to improve the characteristics and to impart desired colour, raw rubber is compounded with many ingredients like plasticizer, vulcanizing agent, antioxidant etc.

9. Describe the preparation of Buna-S rubber

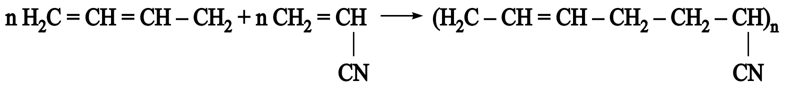
   Ans. Preparation: The Buna-S rubber contains 1, 3 butadiene (75%) and styrene (25%). it is produced by Co-Polymerisation of butadiene and styrene



Buna-s-rubber
(Poly butadiene-co-Styrene)

10. Give the preparation and structure of Buna-N rubber

Ans. Preparation it is prepared by Co-Polymerisation of 1, 3 butadiene and acryloritrile



$$n\,H_2C=CH=CH-CH_2+n\,CH_2=\underset{\displaystyle CN}{\underset{|}{CH}}\longrightarrow(H_2C-CH=CH-CH_2-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}})_n$$

1, 3 butadiene **Acrylonitrile** **Poly butadiene-co-acrylontrile**
(Nitrile rubber)

11. Define the plastics?

Ans. Plastics are high polymers which can be moulded into any desired form by application of heat and pressure in presence of a catalyst.

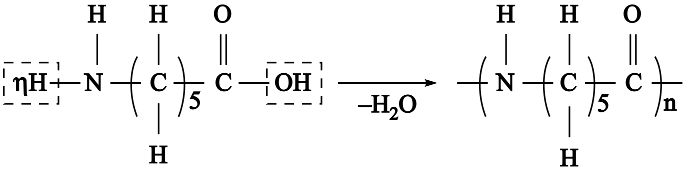
12. Why can not thermosetting plastic be reused and reshaped?

Ans. The molecules of monomers in thermosetting plastics are held together by strong covalent bonds, and these bonds retain their strength, even on heating. Thus, they can not be softened by heating and can not be reshaped or reused How ever, on very strong heating they burn and undergo total destruction.

13. Which Nylons are obtained by self condensation

Ans. Nylon-6, **Nylon**-11, obtained by self-condensation

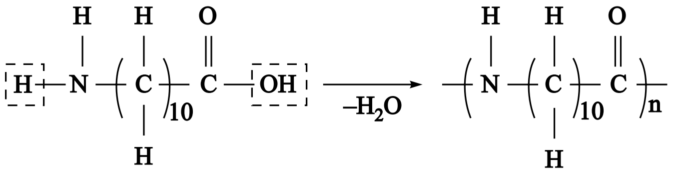
Nylon-6: **Preparation:** it is produced by the self-condensation of α-amino caproic acid



Nylon-6

Nylon-11:

Preparation: it is obtained by self-condensation of w-amino undecanoic acid



Nylon-11

14. What are the conducting polymers?

Ans. An organic polymer with highly delocalised Pi-electron (πe^-) system having electrical conductance on par with metallic conductor is called a conducting polymer.

15. Write about classification of conduction polymers.

Ans. The conducting polymers are classified into 5 types

(i) π-electrons conducting polymers

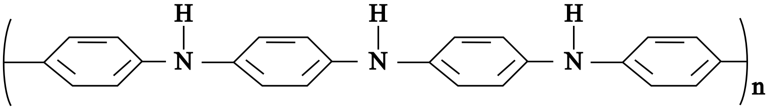
(ii) Conducting element filled polymer

(iii) Doped-conducting polymer

(iv) Blended conducting polymer

(v) Inorganic or Co-ordination conducting polymer

16. Write the structure of poly aniline



17. Write the classification of Liquid Crystals:

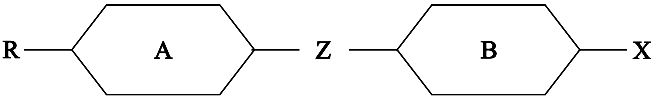
Ans. Liquid crystals are classified into two types.

(a) Thermo tropic liquid crystals: which exhibit liquid crystal phases due to change of temperature

(b) Lyotrophic hyotrophic liquid crystals: which change into liquid crystals phases with change of concentration in a solution.

18. Write the chemical formula of liquid crystal

Ans. The chemical structure of many liquid crystals can be represented as given below.



where R = Side Chain group

A and B = Aromatic ring

Z = Linking group

X = Terminal group

19. What are the application of conducting polymers

Ans. Some of the important applications of conducting polymers

(i) In solar cells

(ii) In photo voltaic devices

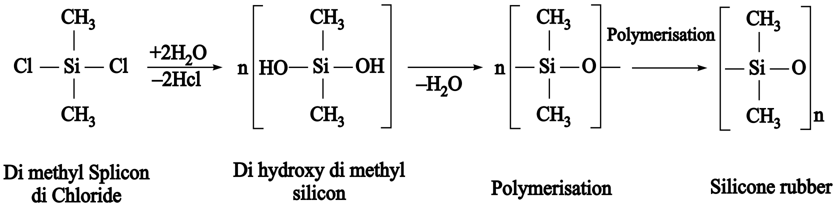
(iii) In non-linear optical Materials

(iv)In tele communication systems.

(v) In antistatic coatings for clothing

20. Write a method of preparation of Silicone rubber.

Ans. Preparation: it is obtained by polymerisation of dihydroxy dimethyl Silicon. In first step dihydroxy dimethyl Silicon (Monomer) is produced by hydrolysis of dimethyl silicon dichloride which on dehydration is followed by polymerisation in presence of peroxide and inorganic fillers like TiO_2, SiO_2. etc., to form silicon rubber.



Review Question

Short Type Question

1. What is polymerization process?
2. What kind of compounds is used in Addition polymerization?
3. Differentiate between Natural rubber and Synthetic rubber
4. Write short note on compounding of RUBBER.
5. Give the cationic Mechanism in polymerization
6. What are the engineering applications of Buna-S, Buna-N Rubber
7. Distinguish between Thermoplastic and Thermosetting plastics
8. How do you prepare the Bakelite?
9. What is self condensation polymerization? Give one Example
10. What are liquid crystals? Give few applications.
11. Write the formula of lsoprene unit
12. Write classification of liquid crystals.
13. What are conducting polymers? How are they classified?
14. What are the important applications of liquid polymers?
15. What are the monomers of nylon 6,6?
16. Write short note on co-polymerization
17. What is functionality of monomer?
18. Write short note on condensation polymerization
19. What is meant by tacticity?

Essay Type Questions

1. Explain the differences between thermoplastics and thermosetting plastics?
2. (a) What is a homochain polymer? Give examples.
   (b) What is polymerisation? Explain the different types of polymerisation with examples.
3. Write a note on
   (a) Teflon (b) Silicone rubber.
4. (a) What is bakelite? How is it manufactured? Mention its properties and uses?
   (b) Write the merits and demerits of using plastics in place of metals.
5. (a) Distinguish between addition and condensation polymerisation.
   (b) What is meant by degree of polymerisation?

6. Write brief notes on
   (a) Vulcanisation
   (b) Compounding of rubber.

7. Describe the preparation, properties and uses of
   (a) Buna-S rubber
   (b) Buna-N rubber
   (c) Polyurethane rubber.

8. (a) Explain the procedures used in the processing of natural rubber.
   (b) Differentiate the natural polymers and synthetic polymers.

9. (a) What are the drawbacks of raw rubber?
   (b) Explain preparation, properties and uses of nylons.

10. What are liquid crystal polymers? How are they produced? Explain the characteristics and applications (uses) of liquid crystals.

11. Define liquid crystal polymers? Write the classification and structural forms of liquid crystal polymers?

12. What are conducting polymers? How are they classified? Write important engineering applications?

13. Give an account of preparation, properties and uses of the following.
   (a) Polyethylene
   (b) PVC
   (c) Polystyrene

14. Describe the preparation, properties and uses of the following
   (a) Butyl rubber
   (b) thiokol
   (c) polyester resins

15. Describe the moulding methods of plastics?

Multiple Choice Questions

1. Phenol-formaldehyde resin is comm-ercially known as
   (a) nylon (b) PVC
   (c) bakelite (d) teflon.

2. Tetrafluoroethylene is the monomer of
   (a) PVC (b) nylon-6, 6
   (c) Polythene (d) teflon.

3. Molecular mass of polymer is
   (a) large (b) small
   (c) negligible (d) very small.

4. Which of the following is thermosetting plastic?
   (a) PVC (b) polystyrene
   (c) bakelite (d) teflon.

5. The repeating units in a polymer chain are known as
   (a) monomers (b) dimers
   (c) polymer (d) tetramers.

6. The number of repeating units in a polymer is called
   (a) functionality
   (b) degree of polymerisation
   (c) tacticity
   (d) graft polymer.

7. An example of co-polymer is
   (a) PVC (b) polythene
   (c) Buna-S rubber (d) teflon.

8. Vulcanisation of rubber is mainly done by the addition of
   (a) oxygen gas
   (b) magnesium oxide
   (c) sulphur
   (d) zinc oxide.

9. Buna-S rubber is made up of the monomers
(a) butadiene and styrene
(b) butadiene and phenol
(c) butadiene and acrylonitrile
(d) styrene and phenol.

10. An example of thermoplastic is
(a) polythene (b) polystyrene
(c) PVC (d) all of these.

11. A good example of condensation polymer is
(a) teflon
(b) polythene
(c) bakelite
(d) polypropylene.

12. Natural rubber is a polymer of
(a) isoprene (b) ethylene
(c) vinyl chloride (d) styrene.

13. Fluorine atoms are present in
(a) nylon (b) styrene
(c) polythene (d) teflon.

14. Nylon is a
(a) polyester (b) polyamide
(c) vinyl polymer (d) PVC.

15. Ebonite is
(a) highly vulcanised rubber
(b) synthetic rubber
(c) PVC
(d) polystyrene.

16. A plastic which can be softened on heating and hardened on cooling is called
(a) thermite (b) thermoplastic
(c) thermosetting (d) bakelite.

17. The number of bonding sites in a monomer is known as
(a) degree of polymerisation
(b) tacticity
(c) functionality
(d) silicones.

18. Nitrogen atoms are present in
(a) teflon (b) polythene
(c) nylon (d) PVC.

19. Buna-N rubber is made up of the monomers
(a) butadiene and acrylonitrile
(b) butadiene and styrene
(c) butadiene and formaldehyde
(d) butadiene and phenol.

20. Polyurethane rubber is made up of the monomers
(a) phenol + formaldehyde
(b) phenol + styrene
(c) ethylene glycol + ethylene disocyanate
(d) ethylene glycol + styrene.

21. Which of the following is a synthetic polymer?
(a) nucleic acids (b) polythene
(c) proteins (d) cellulose.

22. Vinyl chloride is the monomer of
(a) polythene (b) PVC
(c) polystyrene (d) bakelite.

23. The process of vulcanisation makes rubber
(a) soft (b) hard
(c) elastic (d) swells oils.

24. If the arrangement of functional groups are at random around the main chain of polymer it is called
(a) isotactic polymer
(b) syndiotactic polymer
(c) atactic polymer
(d) none of these.

25. Which of the following has cross-links?
(a) phenol-formaldehyde resin
(b) polythene
(c) PVC
(d) polystyrene.

Answers

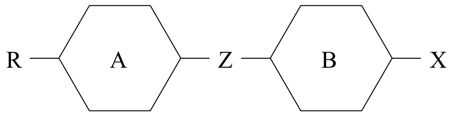
1. (c)
2. (d)
3. (a)
4. (c)
5. (a)
6. (b)
7. (c)
8. (c)
9. (a)
10. (d)
11. (c)
12. (a)
13. (d)
14. (b)
15. (a)
16. (b)
17. (c)
18. (c)
19. (a)
20. (c)
21. (b)
22. (b)
23. (b)
24. (c)
25. (a)

Fill Up the Blanks Questions

1. HDPE has a ________ melting point than LDPE.
2. Polythene is made up of the monomer________.
3. Transfer moulding is mainly used for ________ plastics.
4. Compression moulding is used for ________ and ________.
5. Latex is the dispersed mixture of ________ molecules.
6. The percentage of sulphur present in ebonite rubber is about ________.
7. A good example of condensation polymerisation is ________.
8. A good example of thermosetting plastics is ________.
9. PVC is made up of the monomer________.
10. Thiokol rubber is made by the reaction berween ________and ________.
11. Polymerisation in which two or more chemically different monomers take part is called ________.
12. It the arrangement of functional groups are all on the same side of the main chain of polymer it is called ________ polymer.
13. Chemical structure of many liquid crystals can be represented as ________.
14. An organic polymer with highly delocalised pi-electron system, having electrical conductance on par with metallic conductor is called ________.
15. A good example of conducting polymers is ________.
16. Number of structural forms of liquid crystals are ________.

Answers

1. high
2. elthylene
3. thermosetting
4. thermoplastics, thermosetting plastics
5. isoprene
6. 32%
7. Nylon 6,6
8. bakelite
9. Vinyl chloride
10. Ethylene dichloride, sodium polysulphide
11. Copolymerisation
12. Isotactic
13.



14. Conducting polymer
15. Polyacetylene
16. Three

3

Fuel Technology

3.1

INTRODUCTION

With rapid growth in world population during the past few decades, the energy requirements have also increased at an even larger rate. Heat energy is one of the main sources of power that is produced by burning of fuels. *A fuel is a combustible substance which on proper burning in presence of oxygen or air gives large amount of heat energy* that can be used economically for domestic and industrial purposes. The main elements of any fuel are carbon and hydrogen. During the process of combustion of a fuel, these elements combine with oxygen to produce CO_2 and H_2O with the liberation of heat. This energy liberation is due to the rearrangement of valency electrons of these atoms. The energy released in combustion process is the difference in the energy of the reactants and that of the products formed.

$$\text{Fuel} + O_2 \rightarrow \underset{(CO_2,\, H_2O)}{\text{Products}} + \text{Heat}$$

e.g. coal, wood, kerosene, petrol, diesel, producer gas and oil gas.

The stored fuels available (coal, petroleum, natural gas) in earth's crust are called fossil fuels.

3.2

CLASSIFICATION OF FUELS

Fuels are classified according to occurrence and state of aggregation.

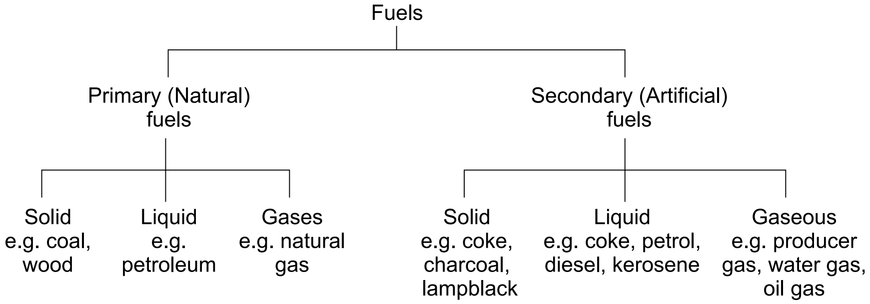
(A) According to occurrence

  (i) Primary fuels: Fuels which occur in nature as such are called primary fuels, e.g., coal, petroleum and natural gas.

 (ii) Secondary fuels: Fuels which are derived from the primary fuels, e.g. coke, petrol, diesel and water gas are called secondary fuels.

(B) According to state of aggregation

 (i) Solid fuels: e.g. wood, coke and coal.
 (ii) Liquid fuels: e.g. petroleum, petrol and diesel.
 (iii) Gaseous fuels: e.g. natural gas, producer gas and water gas.



3.3
CHARACTERISTICS OF A GOOD FUEL

A good fuel should possess the following characteristics for its selection for a particular purpose.

 (i) It should have less moisture and ash.
 (ii) It should possess high calorific value.
 (iii) The velocity of the combustion should be moderate.
 (iv) It should be cheap and readily available.
 (v) It must be easy to handle, store and transport at minimum cost.
 (vi) Combustion of the fuel should be easily controlled.
 (vii) It should have higher carbon content.
 (viii) It should not produce undesirable products or objectionable toxic gases.

3.4
SOLID FUELS

Advantages

 (i) They are easy to transport.
 (ii) They are convenient to store without any risk.
 (iii) They possess moderate ignition temperature.
 (iv) Their cost of production is less.

Disadvantages

(i) They contain high ash content.
(ii) Excess of air is required for complete combustion.
(iii) Calorific value is less when compared to liquid or gaseous fuels.
(iv) Cannot be used as internal combustion engine fuels.
(v) Combustion operations cannot be controlled easily.

3.4.1 Coal

Coal is a primary solid fuel which is formed from the remains of decaying vegetable matter under the influence of heat, pressure and bacterial action underneath the earth. It is composed of C, H, O, N and S atoms besides some non-combustible inorganic matter.

Classification of Coal Various forms of coal are recognised on the basis of rank or degree of alteration from the wood.

Wood → Peat → Lignite → Bituminous → Anthracite
— Calorific value, hardness, carbon content → increases
— Volatile matter, moisture H, O, S and N content → decreases.

Peat is the least ranking coal while anthracite is the highest ranking coal.

(i) Peat It is a brown fibrous jelly like mass and recognised as the first stage in coalification of wood. The average composition of air dried peat is C = 57%, H = 6%, O = 35%, ash = 2.5 to 6.0%. Its calorific value is about 5400 K.Cal/kg.

(ii) Lignite It is a brown coloured coal between the peat and bituminous coal. The average composition of air dried lignite is C = 60–70%, H = 5.0%, O = 20%. Lignite is easily ignited and burns with a long brown flame. Its calorific value is about 6500–7100 K.Cal/kg.

(iii) *(a) Sub-bituminous coal* It is black in colour and more homogeneous. The carbon content varies from 75 to 80% and oxygen content from 10 to 20%. Its calorific value is about 7000 K.Cal/kg.

(b) Bituminous coal It is the common variety of coal and carbon content ranges from 78 to 90% and volatile matter 20 to 45%. Its calorific value is about 8000–8500 K.Cal/kg and used in manufacture of metallurgical coke, coal gas, etc.

(c) Semi-bituminous coal It has good carbon content (90–95%) and low volatile matter. Its calorific value is about 8500–8600 K.Cal/kg.

(iv) Anthracite coal It is the highest rank of coal and the carbon content of this coal is 92–98%. Its calorific value is about 8650–8700 K.Cal/kg. It has low volatile matter and moisture.

Analysis of Coal To assess the quality of coal, the following two types of analysis are carried out:

(i) Proximate analysis (ii) Ultimate analysis *(i) Proximate analysis* It is an imperial analysis, used for the determination of the moisture, volatile matter, ash and fixed carbon in coal (as percentage).

(a) *Moisture:* The coal sample (about 1 g) is finely powdered and air dried is weighed in a silica crucible. The crucible is heated in an oven at 105–110°C for one hour then taken out, cooled in a desiccator and weighed.

From the loss in weight the percentage of moisture can be calculated

$$\% \text{ Moisture} = \frac{\text{Loss in weight}}{\text{weight of coal taken}} \times 100$$

(b) *Volatile matter:* The coal powder left in crucible (a) is then covered with a lid and placed in a muffle furnace where the temperature is maintained at 950 ± 20°C for 7 minutes. The crucible is taken out, cooled and weighed. From the loss in weight after the moisture analysis, the percentage of volatile matter can be calculated

$$\% \text{ Volatile matter} = \frac{\begin{array}{c}\text{Loss in weight due to the}\\ \text{removal of volatile matter}\end{array}}{\text{Weight of coal taken}} \times 100$$

(c) *Ash:* The residual coal in the crucible (b) is then heated without lid in a muffle furnace at 700 ± 50°C for 30 minutes. The crucible is taken out, cooled and weighed.

$$\% \text{ Ash} = \frac{\text{Weight of residue}}{\text{Weight of coal taken}} \times 100$$

(d) *Fixed carbon:* This is reported as the difference between 100 and the sum of the percentage of moisture, volatile matter, ash.

$$\% \text{ Fixed carbon} = 100 - \% \text{ (miosture + volatile matter + ash)}$$

Significance of Proximate Analysis

(a) *Moisture:* The miosture lowers the colorific value of coal. Therefore, lesser the moisture content better the quality of coal.

(b) *Volatile matter:* The higher volatile matter content in coal is undesirable. Because it lowers the calorific value, burns with a long flame and high smoke. Hence lesser the volatile matter, better the rank of the coal.

(c) *Ash:* It is a non-combustible useless matter present in the coal. Presence of high ash content in coal is undesirable because it can reduce the calorific value, creates cleaning and disposal problems, etc. Hence lower the ash content, better the quality of coal.

(d) *Fixed carbon:* High percentage of fixed carbon is desirable because it can increase the calorific value and quality of coal. It also helps in designing the furnace and the shape of the fire box.

(ii) Ultimage analysis It is the elemental analysis of coal used for the determination of carbon, hydrogen, sulphur, nitrogen, ash and oxygen.

(a) *Carbon and hydrogen:* About 1 g of weighed coal is completely burnt in a stream of oxygen in a combustion tube. Carbon burns to CO_2 and hydrogen to H_2O. The CO_2 and H_2O are sbsorbed separately in anhydrous $CaCl_2$ tubes and KOH bulbs respetively. From the increase in weights of the tubes the percentage of carbon and hydrogen can be calculated.

$$\%\text{ of carbon} = \frac{\text{Increase in weight of KOH tube}}{\text{Weight of coal sample taken}} \times \frac{12}{44} \times 100$$

$$\%\text{ of hydrogen} = \frac{\text{Increase in weight of CaCl}_2\text{ tube}}{\text{Weight of coal sample taken}} \times \frac{2}{18} \times 100$$

(b) *Nitrogen* (*Kjeldahl method*): About 1 g of weighed coal is oxidised by heating with con. H_2SO_4 along with K_2SO_4 and $HgSO_4$. After the solution has become clear it is treated with excess of KOH and liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is determined by titration with standard NaOH. From the volume of acid used, the percentage of nitrogen in coal can be calculated

$$\%\text{ of nitrogen} = \frac{\begin{array}{l}\text{Volume of acid used}\\ \times\,\text{Normality of acid}\end{array}}{\text{Weight of coal taken}} \times \frac{14}{1000} \times 100$$

(c) *Sulphur:* It is determined from the washings obtained from the known mass of coal used in bomb calorimeter for determination of calorific value. During the experiment, sulphur is converted to sulphate. The washings are treated with $BaCl_2$ to precipitate $BaSO_4$. It is filtered, washed and heated to constant weight. From the weight of $BaSO_4$, percentage of sulphur can be calculated

$$\%\text{ of sulphur} = \frac{\text{Weight of BaSO}_4}{\text{Weight of coal taken}} \times \frac{32}{233} \times 100$$

(d) *Ash:* It is carried out in the same way as in proximate analysis.

(e) *Oxygen:* Percentage of oxygen is obtained by subtracting the sum of the percentage of C, H, N, S and ash from 100.

$$\%\text{ of oxygen} = 100 - \%\,(\text{C} + \text{H} + \text{N} + \text{S} + \text{ash})$$

Significance of Ultimate Analysis

(a) *Carbon and Hydrogen:* The quality of coal is based on the percentage of carbon in it. Higher the percentage of carbon and hydrogen, better is the quality of coal and higher is its calorific value.

(b) *Nitrogen:* It has no calorific value and hence its presence in coal is undesirable.

(c) *Sulphur:* Though, sulphur increases the calorific value, its presence is undesirable because the combustion products SO_2 and SO_3 can corrode the equipment and also causes air pollution.

(d) *Ash:* Same as in proximate analysis.

(e) *Oxygen:* High oxygen content can reduce the calorific value of coal. 1% increase of oxygen content, decreases the calorific value of coal by about 1.7%. Hence it is undesirable.

3.4.2 Metallurgical Coke

The process of preparing coke from coal is known as carbonisation of coal. When bituminous coal is heated strongly in the absence of air, the dense strong, porous mass obtained is called metallurgical coke.

Characteristics of Metallurgical Coke

(i) *Purity:* It should contain less percentage of moisture, ash, phosphorus and sulphur.

(ii) *Porosity:* It should be porous, so that combustion should be uniform and complete.

(iii) *Strength:* The mechanical strength of coke should be very high, to withstand the load of overlying solids like ore and flux.

(iv) *Size:* Coke should have medium size, i.e. neither too big nor too small in size.

(v) *Calorific value:* Coke should possess a very high calorific value.

(vi) *Cost:* Coke should be cheap and easily available.

(vii) *Combustibility:* Coke should burn easily.

(viii) *Reactivity:* The reactivity of coke should not be very high.

Manufacture of Metallurgical Coke by Otto–Hoffmann's By-product Oven Process In order to increase the thermal efficiency of carbonisation process and to recover the valuable by-products, Otto–Hoffmann developed a modern by-product coke oven (Fig. 3.1). It consists of number of narrow silica chambers. Each chamber is provided with a charging hole at the top, a gas off-take and a refractory lined cast iron door at each end for discharging coke.

Coal is introduced into the chambers and the chambers are closed (to prevent access of air). The ovens are heated to 1200°C by burning a gaseous fuel (producer gas) and usually employs a regenerative principle to active economical heating. The flue gases produced during combustion are passed to the regenerators chequer brickwork that takes up the heat and gets heated to about 1000°C. The flow of heating gases is then reversed so that the hot flue gases preheat the other chambers. The heating is continued till the evolution of volatile matter ceases completely which is about 11 to 18 hours. When coke is formed, a massive ram pushes the red hot coke outside. It is subsequently quenched by water spray (wet quenching). The coke can also be quenched by inert gases like nitrogen (dry quenching). The coke obtained by dry quenching is drier, clean and stronger than wet quenched coke.

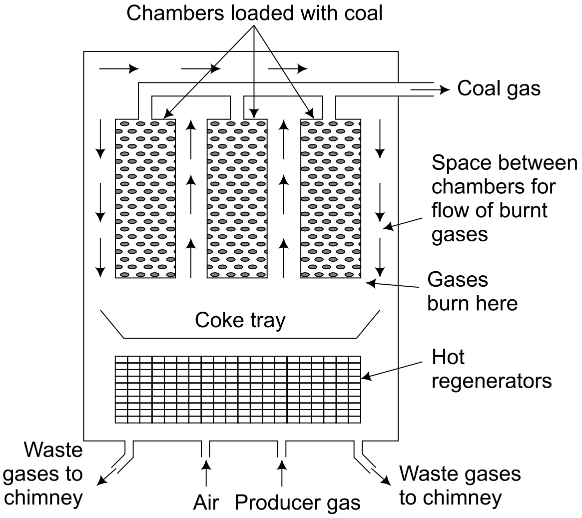


Fig. 3.1 *Otto-Haffmann's by-product method for code manufacture*

Recovery of By-products The gas coming out from the oven is called coke oven gas and is composed of NH_3, H_2S, naphthalene, tar, benzene, etc., which can be separated from each other.

Coal tar The coke oven gas is passed through a tower where liquor ammonia is sprayed from the top. Dust and tar gets collected in a tank which is heated by steam coils to recover ammonia back.

Ammonia The gas is then passed through a tower where water is sprayed. Ammonia goes into solution forming NH_4OH.

$$NH_3 + H_2O \rightarrow NH_4OH$$

Naphthalene The gas is then passed to a cooling tower where water is sprayed at a very low temperature. Condensation of some gases takes place and naphthalene is recovered.

Benzene The gas is then sprayed with petroleum. Here benzene and its homologues are recovered.

Removal of Hydrogen Sulphide The gas is passed through a purifier filled with ferric oxide.

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$$

After all the Fe_2O_3 is exhausted, the purifier is exposed to atmospheric air when Fe_2O_3 is regenerated and leaving SO_2 gas

$$Fe_2S_3 + 4O_2 \rightarrow 2FeO + 3SO_2\uparrow$$
$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

3.5

LIQUID FUELS

Advantages

(i) Liquid fuels are clean and require less amount of air for complete combustion.
(ii) They possess higher calorific value than solid fuels.
(iii) They are easy to transport through pipes.
(iv) Due to cleanliness, loss of heat to chimney is low.
(v) They require less amount of air for complete cumbustion.
(vi) Easily ignited and emission can be easily controlled.
(vii) They are used as internal combustion fuels.
(viii) They burn without forming dust, ash, etc.

Disadvantages

(i) Care must be taken during storage.
(ii) Cost is relatively higher than solid fuels.
(iii) They give bad odour.
(iv) Greater risk of fire hazards.

3.5.1 Petroleum or Crude Oil

The word 'petroleum' is derived from the Latin 'Petra' (rock) and 'Oleum' (oil). It is also known as crude oil or mineral oil. Petroleum is the main source of liquid fuels. Petroleum is a dark greenish-brown viscous liquid found in the earth's crust. The average composition of petroleum shows

$$\begin{aligned} C &= 79.5 \text{ to } 87.1\% \\ H &= 11.5 \text{ to } 14.8\% \\ S &= 0.1 \text{ to } 3.5\% \\ O + N &= 0.1 \text{ to } 0.5\% \end{aligned}$$

Classification of Petroleum According to chemical nature, there are three types of petroleum:

(a) Paraffin-base petroleum composed of saturated hydrocarbons up to $C_{35}H_{72}$ which are semi-solids, called waxes.
(b) Asphaltic-base petroleum composed mainly of naphthalenes and cycloparaffins with smaller amounts of paraffins and aromatics.
(c) Mixed-base petroleum contains both the above type of compounds but is rich in semi-solid waxes.

Mining of Petroleum Petroleum is brought to the surface by drilling holes up to oil bearing area and sinking pipes. Generally, oil is pushed out due to hydrostatic pressure of natural gas. When the pressure of natural gas is not sufficient, then air pressure is applied through lift pumps to force the oil out of the well. Two coaxial pipes are lowered to the oil reservoir, compressed air is forced through the outer pipe, whereby the oil comes out through the inner pipe (Fig. 3.2) which is sent to the refineries for further processing.

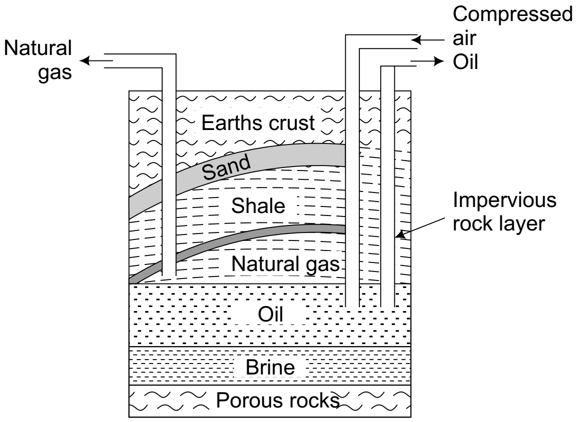


Fig. 3.2 *Mining of petroleum and use of air lift pumps*

3.5.2 Refining of Petroleum

Petroleum obtained from the ground is a mixture of oil and unwanted impurities (water, dirt, sulphur compounds, etc). The process of removal of impurities from crude oil and separation of various fractions with different boiling ranges is called refining of petroleum. The plants set up for this purpose are called oil refineries. The whole process of refining of petroleum involves the following steps.

Step 1 *Separation of water (Cottrell's Process)*

The crude oil is an emulsion of oil and salt water. It is allowed to flow through two highly charged electrodes. The colloidal water droplets coalesce to form large drops which separate out from the oil.

Step 2 *Removal of sulphur compounds*

Sulphur compounds have objectionable properties of pollution. When the crude oil is treated with copper oxide, a reaction occurs with sulphur compounds which results in the formation of copper sulphide precipitate which is then removed by filtration.

Step 3 *Fractional distillation*

The crude oil is then subjected to about 400°C temperature in an iron retort. All volatile constituents are evaporated. The constituents, tar and asphalt, do not vapourise and they settle at the bottom of the retort. The hot vapours are then passed through a fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless steel trays at a short distance. Each tray is provided with a small chimney, covered with a loose cap. As the vapours go up, they begin to cool and fractional condensation takes place at different levels of column (Fig. 3.3). Higher boiling fractions condense first while lower boiling fractions condense next. Thus the crude oil is fractioned into different fractions depending upon their boiling ranges.

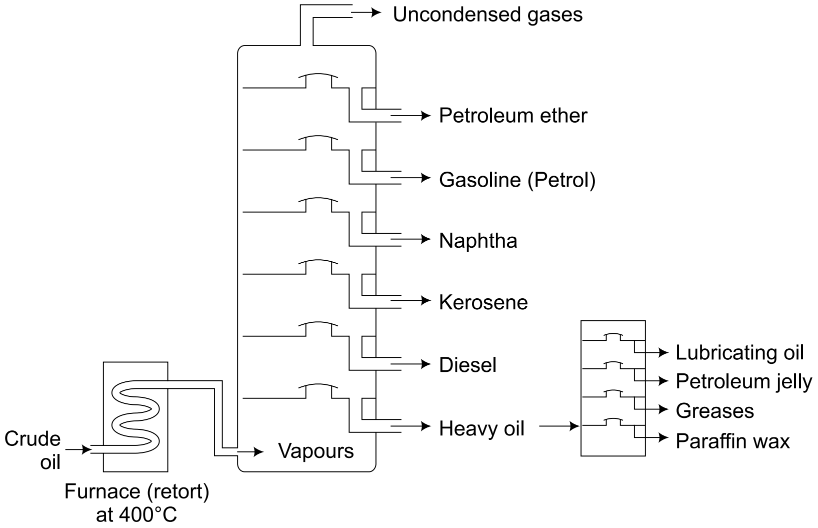


Fig. 3.3 *Fractional distillation of crude oil*

Table 3.1 *Common fractions from crude oil*

Fraction	*Boiling range*	*Composition*	*Uses*
Uncondensed gas	Below 30°C	$C_1 - C_4$	As domestic or industrial fuel (LPG)
Petroleum ether	30°C – 70°C	$C_3 - C_7$	As a solvent
Gasoline or petrol	40°C – 120°C	$C_5 - C_9$	As a motor fuel, solvent and in dry cleaning
Naphtha	120°C – 180°C	$C_9 - C_{10}$	As a solvent and in dry cleaning
Kerosene oil	180°C – 250°C	$C_{10} - C_{16}$	As an illuminant, fuel for stoves
Diesel oil	250°C – 320°C	$C_{15} - C_{18}$	As a fuel for diesel engines
Heavy oil	320°C – 400°C	$C_{17} - C_{30}$	For setting gasoline by cracking process
This on refractionation gives			
(a) Lubricating oil			As lubricant
(b) Petroleum jelly			Used in cosmetics and medicines
(c) Grease			As lubricant
(d) Paraffin wax			In candles, boot polishes, wax paper

Important petroleum products and their uses

(i) *Gasoline or Petrol* It is obtained between 40°C–120°C and is a mixture of hydrocarbons such as C_5H_{12} to C_9H_{20}. Approximate composition is C = 84%, H = 15%, N + S + O = 1%. Its calorific value is 11250 K.cal/kg and is used as a fuel for internal combustion engines of automobiles and aircrafts.

(ii) *Kerosene Oil* It is obtained between 180°C–250°C and is a mixture of hydrocarbons such as $C_{10}H_{12}$ to $C_{16}H_{34}$. Approximate composition is C = 84%, H = 16%, S = less than 0.1%. Its calorific value is 11,100 K.cal/kg and used as fuel in stores, jet engine fuel and for making oil gas.

(iii) *Diesel Oil* It is a fraction obtained between 250–320°C and is a mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbons. Its calorific value is 11000 K.cal/kg and is used as a diesel engine fuel.

3.6

GASOLINE

Knocking: In an internal combustion engine a mixture of fuel (petrol vapours) and air is highly compressed before it is ignited in order to have maximum efficiency. During the process there is a sharp metallic sound known as knocking. Thus there is a huge loss of energy and increased engine wear. Knocking tendency of various hydrocarbons is as follows

Straight chain Paraffins > branched chain paraffins > olefines > cycloparaffins > arromatics.

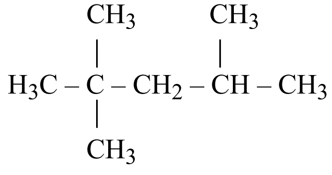
Knocking can be decreased by the addition of certain compounds to the fuel and these compounds are called antiknock compounds. Eg: tetra ethyl lead (TEL) is a very important alkylated product and the principle antiknock compound for gasoline.

3.6.1 Octane Number

The gasoline vary in their resistance to knocking. In order to evaluate their quality, an arbitrary octane scale was developed by measuring their knocking characteristics. Octane number of gasolines are simply defined with reference to η-heptane and iso-octane. η-heptane produces maximum knocking and has been assigned an octane number of zero where as iso-octane (2,2,4–tri methyl pentane) produces minimum knocking and has been assigned octane number 100. Thus The octane number of a gasoline is defined as "The percentage of iso-octane present in a mixture of iso-octane and η-heptane which has the same knocking characteristics as the gasoline sample under test." Higher the octane number of gasoline, least is its tendency for knocking, but higher is its combustion characteristics. If we say that the octane number of fuel is 80, it means that this has the same combustion characteristics of as a mixture of 80% iso-octane and 20% η-heptane.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

n-heplane
(octane number = 0)



$$H_3C-\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}-CH_2-\overset{\substack{CH_3\\ |}}{CH}-CH_3$$

2, 2, 4-trimethyl pentane
(Iso-octane)
(octane number = 100)

3.7
POWER ALCOHOL

When ethyl alcohol is used as an additive to motor fuels to act as a fuel for internal combustion engines, it is called power alcohol. Blends containing up to 25% of alcohol with petrol are used.

Manufacture of power alcohol

The important raw materials for manufacture of power alcohol or ethyl alcohol are saccharine material such as molasses, sugar beets etc. Starch material such as starch, potatoes, cereal grains etc.

Ethyl alcohol from molasses

Fermentation processes is used for manufacture of ethyl alcohol from molasses. It is a dark colored viscous liquid left after crystallization of cane sugar from cane juice. It contains 20-30% of sugar or sucrose. Molasses is converted in to ethyl alcohol by means of yeast, which gives enzymes invertse and zymase responsible for fermentation. Before mixing with yeast, the molasses is diluted with water, P^H is maintained between 4 and 5, at 30°C by adding sulphuric acid. Fermentation is completed between 2 to 3 days. Repeated distillation and condonation can raise the alcohol content to 97.6%

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2\uparrow$$

Advantages of alcohol blended petrol

(i) Addition of power alcohol to petrol increases the octane number. Hence alcohol blend petrol possesses better antiknock properties.
(ii) There are no starting difficulties with alcohol petrol blend.
(iii) Air required for complete combustion is less.
(iv) Alcohol blended petrol can be used in engines with higher compression ratio.

Disadvantages of alcohol blended petrol

(i) Alcohol is easily oxidized to acids. Hence alcohol may cause corrosion
(ii) Alcohol Lowers the calorific value of petrol
(iii) Because of its considerable surface tension, it is difficult to atomize alcohol at low temperature. Hence specific arrangements for starting alcohol-petrol blend in carburettor are to be provided.

3.8

SYNTHETIC PETROL

Petrol is generally synthesised by the following two methods:

(i) Fischer–Tropsch Process
(ii) Bergius Process

(i) Fischer–Tropsch Process Water gas is a mixture of carbon monoxide and hydrogen (CO + H_2), produced by passing steam over red hot coke. It is mixed with hydrogen. The gaseous mixture (water gas + hydrogen) is purified by passing over Fe_2O_3, to remove H_2S, then passing over Fe_2O_3, Na_2CO_3 mixture to remove organic sulphur compounds. The purified gas is compressed to 5 to 25 atm at 200°C–300°C passed through a converter containing catalyst which is a mixture of 100 parts cobalt, 5 parts thorium, 8 parts magnesium and 200 parts Kieselguhr. A mixture of saturated and unsaturated hydrocarbons is formed.

$$nCO + 2nH_2 \rightarrow \underset{\text{Unsaturated hydrocarbon}}{C_nH_{2n}} + nH_2O$$

$$nCO + (2n + 1)\, H_2 \rightarrow \underset{\text{Saturated hydrocarbon}}{C_nH_{2n+2}} + nH_2O$$

The outcoming hot gaseous mixture is cooled in a cooler where a liquid resembling crude oil is obtained which is then subjected to fractionation to yield gasoline and heavy oil (Fig. 3.4). The heavy oil is reused for cracking to get more gasoline.

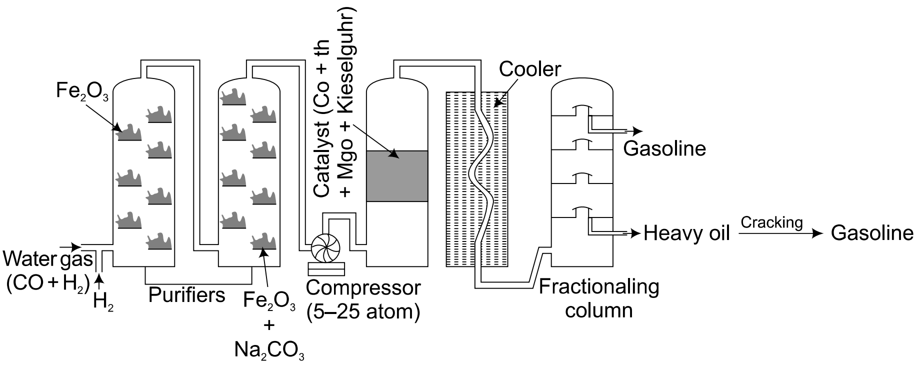


Fig. 3.4 *Fischer–Tropsch method*

(ii) Bergius Process Coal is powdered and made into a paste with heavy oil and a catalyst (nickel oleate (or) tin oleate) is mixed with it. This mixture is sent to a converter maintained at 400°C–500°C and a pressure of 200–250 atm, where it meets the hydrogen. Hydrogenation takes place to form higher hydrocarbons. These are further decomposed to produce lower hydrocarbons. When these lower hydrocarbons are passed through a cooler, a liquid resembling crude oil is obtained. This oil on fractional distillation gives gasoline, middle oil and heavy oil. The middle oil is subjected to hydrogenation in presence of a catalyst to produce more gasoline. The heavy oil is recycled to make a paste with fresh coal powder (Fig. 3.5).

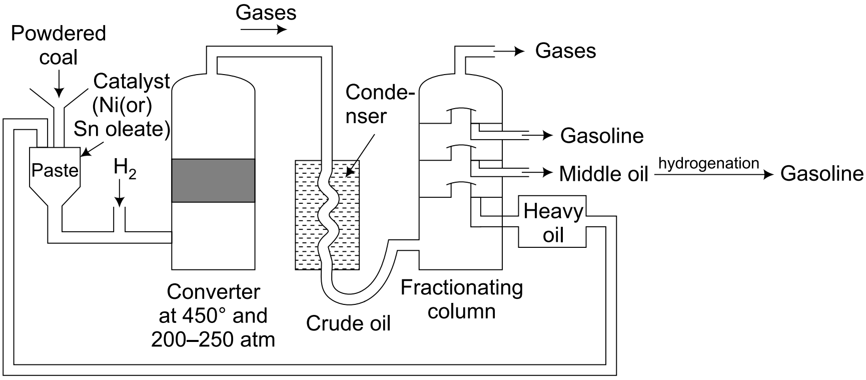


Fig. 3.5 *Bergius Process*

3.9 GASEOUS FUELS

Advantages

(i) Their combustion can easily be controlled.
(ii) They possess high calorific value.
(iii) They easily transport through pipe lines.
(iv) They require less amount of air for complete combustion.
(v) They are free from solid and liquid impurities.
(vi) They are easy to ignite.
(vii) They burn without smoke and produce no ash.

Disadvantages

(i) They are highly inflammable.
(ii) They require very large storage tanks.
(iii) They are costlier than solid and liquid fuels.

3.9.1 Important Gaseous Fuels

The most important gaseous fuels are

(i) Natural gas
(ii) Producer gas
(iii) Water gas
(iv) Coal gas
(v) Bio gas

(i) Natural gas Natural gas is generally associated with petroleum deposits. When natural gas occurs along with petroleum in oil wells, it is called wet gas, and when it is associated with crude oil, it is called dry gas. Natural gas is a mixture of methane, ethane, propane, butane, pentane, carbon dioxide, nitrogen, etc. The approximate composition of natural gas is

$$CH_4 = 70\text{–}90\%$$
$$C_2H_6 = 5\text{–}10\%$$
$$H_2 = 3\%, \text{ the rest is CO and } CO_2$$

The calorific value of natural gas is 12000–14000 K.cal/m^3.

Uses Natural gas is used

(a) As a domestic fuel
(b) As a raw material for manufacture of various chemicals
(c) For manufacture of hydrogen.

(ii) Producer gas It is a mixture of carbon monoxide and nitrogen. H_2, CO_2, etc. are other gases associated with producer gas. It is prepared by passing a mixture of air and steam over a bed of red hot coke maintained at about 1100°C in a spcial reactor called gas producer (Fig. 3.6), lined with refractory bricks.

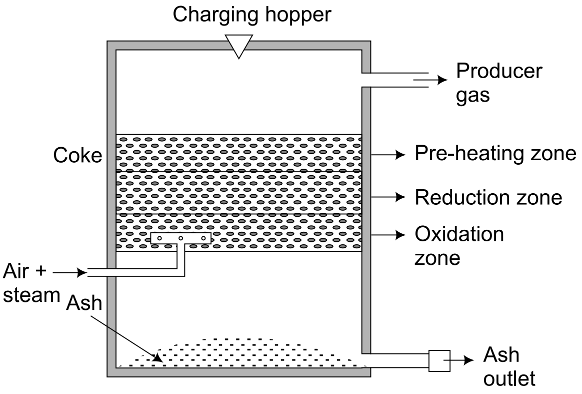


Fig. 3.6 *Gas producer*

Reactions involved

Oxidation zone

$$C + O_2 \rightarrow CO_2 + 97 \text{ K.cal}$$
$$C + \frac{1}{2} O_2 \rightarrow CO + 29.5 \text{ K.cal}$$

Reduction zone

$$CO_2 + C \rightarrow 2CO - 36 \text{ K.cal}$$
$$C + H_2O \rightarrow CO + H_2 - 29 \text{ K.cal}$$
$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 19\text{K.cal}$$

The average composition of producer gas is CO = 22–30%, H_2 = 8–12 %, N_2 = 52–55% CO_2 = 3%.

The calorific value is about 1300 $K.cal/m^3$

Uses It is used

(a) as a reducing agent in metallurgical operations
(b) as a fuel for heating open hearth furnaces, muffle furnaces, etc.

(iii) Water gas It is a mixture of carbon monoxide and hydrogen. CO_2, N_2, etc. are other gases associated with water gas. It is also known as blue gas. Water gas is prepared by passing alternatively steam and air through a bed of red hot coke at about 900°C–1000°C in a reactor. It is lined inside with refractory bricks (Fig. 3.7)

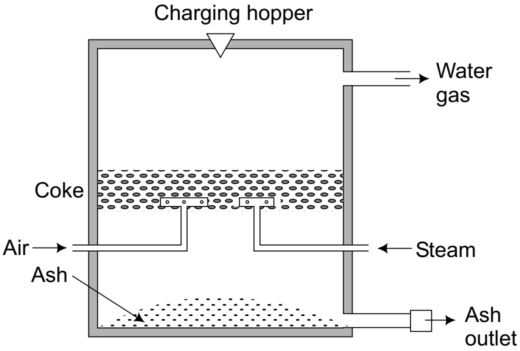


Fig. 3.7 *Water gas production*

Reactions involved

$$C + O_2 \rightarrow CO_2 + 97 \text{ K.cal (Exothermic)}$$
$$C + H_2O \rightarrow CO + H_2 - 29 \text{ K.cal (Endothermic)}$$

The average composition of water gas is

$$CO = 41\%, H_2 = 51\%, N_2 = 4\%, CO_2 = 4\%$$

Its calorific value is about 2800 $K.cal/m^3$

Uses It is used

(a) as a source of hydrogen and in the synthesis of NH_3
(b) for the preparation of carbonated water gas
(c) as an illuminant
(d) as a fuel in industries

(iv) Coal gas It is produced by the high temperature carbonisation of coal. The approximate composition of coal gas is

$$H_2 = 40\%, CH_4 = 32\%, CO = 7\%, C_2H_2 = 2\%, C_2H_4 = 3\%, N_2 = 4\%, CO_2 = 1\%, \text{others} = 4\%$$

Its calorific value is 4900 $K.cal/m^3$.

Uses It is used

(a) as a fuel
(b) as an illuminant
(c) for providing reducing atmosphere in metallurgical operations

(v) Biogas It is produced by the degradation of biological matter in the presence of anaerobic bacteria. The cheapest biogas is *gobar* gas which is obtained by the anaerobic degradation of cattle dung. This can also be prepared from the sewage waste and other organic wastes.

Composition of biogas is

$CH_4 = 55\%$, $CO_2 = 35\%$, $H_2 = 7.4\%$, $N_2 = 2.6\%$ and traces of H_2S.

Its calorific value is 1200 K.cal/m^3

Uses It is used

(a) as a domestic fuel
(b) as an illuminant.

3.10
CALORIFIC VALUE

The efficiency of fuel is expressed in terms of calorific value. Calorific value of a fuel is defined as the total quantity of heat liberated by burning a unit mass or volume of fuel completely.

3.10.1 Units of Heat

(i) Calorie or Gram Calorie The amount of heat required to raise the temperature of 1 g of water through 1°C is called calorie

$$1 \text{ Cal} = 4.185, \text{ Joules} = 4.185 \times 10^7 \text{ ergs.}$$

(ii) Kilo Calorie or Kilogram Calorie (K.cal) The amount of heat required to raise the temperature of 1 kg of water through 1°C is called kilo calorie

$$1 \text{ K.cal} = 1000 \text{ cal.}$$

(iii) British Thermal Unit (B.Th.U) The amount of heat required to raise the temperature of one pound (lb) of water through 1°F is called British Thermal Unit.

$$1 \text{ B.Th.U} = 252 \text{ Cal} = 1054.6 \text{ Joules} = 1054.6 \times 10^7 \text{ ergs.}$$

(iv) Centigrade Heat Unit (CHU) The amount of heat required to raise the temperature of one pound of water through 1°C is called Centigrade Heat Unit.

$$1 \text{ K.Cal} = 1000 \text{ Cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

3.10.2 Units of Calorific Value

The calorific value is expressed in cal./g or K.cal/kg (or) B.Th.U/lb in case of solid or liquid fuels. While in the case of gaseous fuels, the units are K.cal/m^3 or B.Th.U/ft^3.

Gross Calorific Value (GCV) (or) Higher Calorific Value (HCV) The total amount of heat produced when a unit quantity of fuel is completely burnt and the products of combustion are cooled down to room temperature is called gross calorific value. Hydrogen is found to be present in almost all fuels. During combustion, the hydrogen present undergoes combustion and is converted to steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved, which is included in the gross calorific value.

Net Calorific Value (NCV) or Lower Calorific Value (LCV) The amount of heat liberated when a unit of fuel is completely burnt and the combustion products are allowed to escape is called net calorific value. Generally, during the combustion of a fuel, the water vapours escape as such along with combustion products and are not condensed.

$$\text{NCV} = \text{GCV} — \text{latent heat of water vapour formed}$$

$$\begin{array}{lll} H_2 + & \frac{1}{2}O_2 \rightarrow & H_2O \\ 2\text{ g} & 16\text{ g} & 18\text{ g} \\ 1\text{ g} & 8\text{ g} & 9\text{ g} \end{array}$$

1 part by weight of hydrogen gives 9 parts by weight of water.

The latent heat of steam is 587 cal/g or 1060 B.Th.U/lb of water vapour produced.

$$\therefore \quad \text{NCV} = \text{GCV} - 9 \times \frac{H}{100} \times 587$$

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

where H = % of hydrogen in the fuel

3.11

DETERMINATION OF CALORIFIC VALUE BY BOMB CALORIMETER

Calorific value of solid and non-volatile liquid fuels is determined by using bomb calorimeter. The apparatus consists of a cylindrical stainless steel bomb in which the combustion of fuel takes place. The bomb has a gas tight screw cap to which a couple of stainless steel electrodes, an oxygen inlet valve and a pressure release valve are fitted. A crucible is supported by a ring attached to one of the electrodes. The bomb is placed in a copper calorimeter which is surrounded by an air jacket and outer water jacket to prevent heat loss due to radiation. The calorimeter is provided with an electrically operated stirrer and a Beckmann thermometer to measure the rise in temperature (Fig. 3.8).

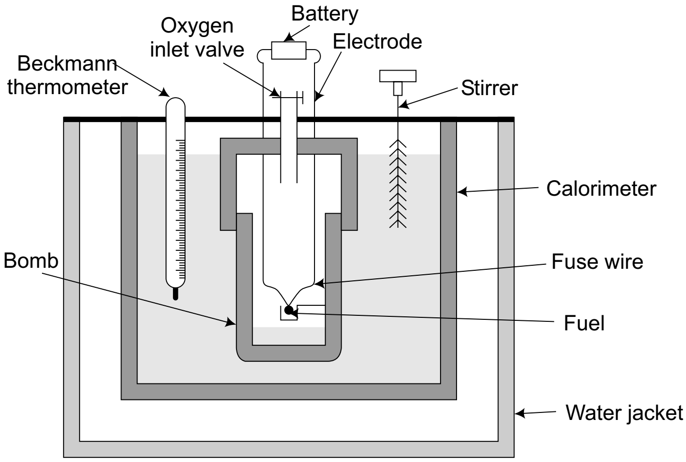


Fig. 3.8 *Bomb calorimeter*

Procedure About 0.5 to 1.0 g of air dried fuel is taken in the clean crucible which is supported over the ring. A fine magnesium fuse wire is placed on the fuel sample and stretched across the electrodes. About 10 ml of water is filled in the bomb to absorb any vapours. The bomb lid is tightly screwed and the bomb is filled with oxygen gas up to 25 atmosphere pressure. The bomb is then lowered into the calorimeter containing a known mass of water. The stirrer is worked and initial temperature of the water is noted. The electrodes of the bomb are connected to a 6 volts battery and circuit is completed. The fuel burns and heat is liberated. The temperature of water gradually increases with uniform stirring and attained maximum temperature (final) is noted.

Calculations

Let:

Weight of the fuel = mg
Weight of the water taken in the calorimeter = W.g
Water equivalent of the calorimeter, bomb, stirrer etc. = Wg
Initial temperature of water = t_1°C
Final temperature of water = t_2°C
Higher calorific value of the fuel = L cal./g
Heat liberated by fuel = Heat absorbed by water and calorimeter

$$\text{mL} = (W + w)\,(t_2 - t_1)$$

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

Hence, $\text{LCV} = \text{L} - 0.09 \times \text{H} \times 587\ \text{cal/g}$

Note: To get more accurate results fuse wire correction, acid correction and cooling correction has to be taken into consideration

$$\mathrm{L} = \frac{(W+w)(t_2 - t_1 + \text{cooling correction}) - (\text{acid correction} + \text{fuse wire correction})}{m}$$

Solved Problem

1. **Calculate the gross and net calorific value of a coal sample from the following data obtained from bomb calorimeter. Weight of coal 0.73 g, weight of water in the calorimeter 1500 g, water equivalent of calorimeter 470 g, initial temp 25°C and final temp. 28°C, percentage of hydrogen in coal 2.5% and Latent heat of steam 587 cal/g.**

Solution

Weight of Coal (m) = 0.73 g
Weight of water in the calorimeter (W) = 1500 g
Water equivalent of calorimeter = 470 g
Initial temperature t_1 = 25°C
Final temperature t_2 = 28°C
% of hydrogen = 2.5%
Latent heat of steam = 587 cal/g

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

$$= \frac{(1500+470)\,(28-25)}{0.73}$$

$$= 8095.89 \text{ cal/g}$$

$$\text{Net calorific value (NCV)} = \text{GCV} - 0.09 \times \text{H} \times 587$$

$$= 8095.89 - 0.09 \times 2.5 \times 587$$

$$= 7963.82 \text{ cal/g}$$

Exercise Problems

1. Calculate the gross calorific value of a fuel sample from the following data obtained from bomb calorimeter. Weight of fuel sample 0.935 g, increase in temperature 2.40°C, weight of water in the calorimeter 1365 g, water equivalent of calorimeter etc. 135g. (*Ans:* HCV = 3850.26 cal/g)
2. 0.834 g of a fuel on complete combustion in excess of oxygen in bomb calorimeter, the temperature increased from 14.36°C to 18.10°C. The weight water 1350 g, water equivalent of calorimeter, etc. 135 g. Calculate higher calorific value of a fuel. (*Ans:* HCV = 6659.35 cal/g)
3. Calculate the gross and net calorific value of a coal sample from the following data. Weight of coal 0.75 g, weight of water in the calorimeter 1450 g, increase in temperature 3.0°C, percentage of hydrogen in coal 2.3%, latent heat of steam 587 cal/g and water equivalent of calorimeter, etc. 450 g.
(*Ans:* GCV = 6000 cal/g; NCV = 5878.49 cal/g)

3.12

DETERMINATION OF CALORIFIC VALUE BY JUNKERS GAS CALORIMETER

The calorific value of gaseous and volatile liquid fuels is measured by using an apparatus known as Junkers gas calorimeter. The equipment consists of pressure governor, gas flow meter, bunsen burner, calorimeter, etc. The calorimeter is fixed on a tripod stand (Fig. 3.9) having leveling screws to keep the calorimeter in perfectly vertical position. The calorimeter mainly consists of a gas combustion chamber, heat exchanger and water flow system. The entire system is covered by an outer jet in order to reduce the heat loss by radiation and convection (acts as an insulator). Two thermometers are used to record the temperatures of inlet water (initial temp.) and outlet water (final temp.) respectively.

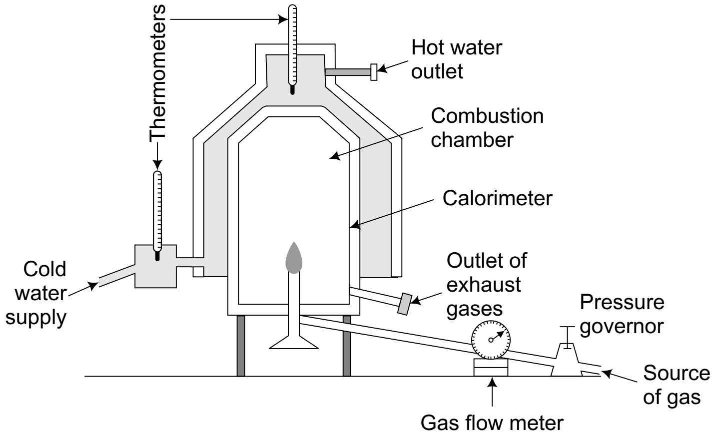


Fig. 3.9 *Junkers gas calorimeter*

Water enters into the calorimeter through a constant heat and its temperature is noted. The sample of gas whose calorific value is to be determined passes through a pressure governor (can control the pressure of the gas), and then through gas flow meter (can record the volume of the gas used) and finally burns in Bunsen burner. The hot products of combustion move upward in the chamber, then downward and finally escape through the exit where its temperature is measured. The heat generated by combustion of gas is absorbed by the circulated cold water. When the steady conditions are established, then the volume of gaseous fuel burnt, the weight of the water circulated, the steady rise in temperature are recorded.

Calculations

Let volume of burns at STP = V

Mass of cooling water used = w

Temperature of inlet water = t_1

Temperature of outlet water = t_2

Higher calorific value of fuel (HCV) = L

Heat produced by combustion fuel = VL

Heat absorbed by circulated water = $W(t_2 - t_1)$

$$\therefore \quad VL = W(t_2 - t_1)$$

$$\text{HCV } (L) = \frac{W(t_2 - t_1)}{V}$$

3.13
COMBUSTION

Combustion process is an exothermic chemical reaction which is accompanied by heat and light. In other words, it is the union of an element or substance with oxygen. During combustion, the combustible substance or element when brought to their ignition temperature, burn in presence of air (oxygen) instantly with the development of heat and thus there is a considerable increase in temperature.

Calculation of air required for combustion

Combustion of carbon

$$\underset{12}{C} + \underset{32}{O_2} \rightarrow \underset{44}{CO_2}$$

According to it 12 kg of carbon required 32 kg of oxygen and produce 44 kg of CO_2.

Carbon required 32 kg of oxygen and produce 44 kg of CO_2.

Oxygen required for carbon = $\frac{32}{12}$ C kg

CO_2 formed from carbon = $\frac{44}{12}$ C kg

where ‘C’ is the amount of ‘C’ in kg in 1 kg of fuel.

Combustion of Hydrogen

$$\underset{4}{2H_2} + \underset{32}{O_2} \rightarrow \underset{36}{2H_2O}$$

Oxygen required for hydrogen = $\frac{32}{4}$ H kg

H_2O formed from hydrogen = $\frac{36}{4}$ H kg

1 part of hydrogen reacts with 8 parts of oxygen. Available hydrogen for combustion = $H - \frac{(O)}{8}$

∴ Oxygen required for hydrogen $= \frac{32}{4}\left(\mathrm{H} - \frac{(\mathrm{O})}{8}\right)$

Combustion of Sulphur

$$\underset{32}{\mathrm{S}} + \underset{32}{\mathrm{O_2}} \rightarrow \underset{64}{\mathrm{SO_2}}$$

Oxygen required for sulphur $= \frac{32}{32}\mathrm{S}$ kg

SO_2 formed from sulphur $= \frac{64}{32}\mathrm{S}$ kg

(a) Total theoretical oxygen required for combustion of C, H and S $= \frac{32}{12}\mathrm{C} + 8\left(\mathrm{H} - \frac{(\mathrm{O})}{8}\right) + \mathrm{S}$

(b) Minimum oxygen required for combustion = Theoretical oxygen required – Oxygen present in fuel

(c) Air contains 23% by weight of oxygen and 21% by volume of oxygen.

∴ Minimum weight of air required for combustion $= \frac{100}{23} \times$ minimum oxygen required

$$= \frac{100}{23}\left[\frac{32}{12}\mathrm{C} + 8\left(\mathrm{H} - \frac{(\mathrm{O})}{8}\right) + \mathrm{S}\right]$$

∴ Minimum volume of air required for combustion

$$= \frac{100}{21} \times \text{minimum oxygen required}$$

$$= \frac{100}{21}\left[\frac{32}{12}\mathrm{C} + 8\left(\mathrm{H} - \frac{(\mathrm{O})}{8}\right) + \mathrm{S}\right]$$

Solved Problems

1. **A sample of coal has the following composition: C = 76.0%, H_2 = 5.2%, O_2 = 12.0%, S = 1.2%, N_2 = 2.7% and ash = 2.2%. Calculate the quantity of air required for complete combustion of 1 kg of this coal.**

Solution

C = 76.0% = 0.76 kg

H_2 = 5.2% = 0.052 kg

O_2 = 12.0% = 0.12 kg

S = 1.2% = 0.012 kg

N_2 = 2.7% = 0.027 kg

Ash = 2.2% = 0.022 kg

Minimum amount of air required for complete combustion of 1 kg of coal

$$= \frac{100}{23}\left[\frac{32}{12}\text{C} + 8\left(\text{H} - \frac{(\text{O})}{8}\right) + \text{S}\right]$$

$$= \frac{100}{23}\left[\frac{32}{12} \times 0.76 + 8\left(0.052 - \frac{0.12}{8}\right) + 0.012\right]$$

$$= 10.17 \text{ kg}$$

2. A sample of coal contains the following composition: C = 72%, H_2 = 6.2%, O_2 = 14.8%, S = 1.6%, N_2 = 2.8% and ash = 2.6%. Calculate the minimum amount of air required for complete combustion of 1 kg of coal and give the percentage composition of dry products of combustion.

Solution

C = 72%	= 0.72 kg
H_2 = 6.2%	= 0.062 kg
O_2 = 14.8%	= 0.148 kg
S = 1.6%	= 0.016 kg
N_2 = 2.8%	= 0.028 kg
Ash = 2.6%	= 0.026 kg

Minimum amount of air required for complete combustion of 1 kg of coal

$$= \frac{100}{23}\left[\frac{32}{12}\text{C} + 8\left(\text{H} - \frac{(\text{O})}{8}\right) + \text{S}\right]$$

$$= \frac{100}{23}\left[\frac{32}{12} \times 0.72 + 8\left(0.062 - \frac{0.148}{8}\right) + 0.016\right]$$

$$= \frac{100}{23} \times 2.276 = 9.89 \text{ kg}$$

Dry products of Combustion

Reaction	Products
$C + O_2 \rightarrow CO_2$	$0.72 \times \frac{44}{12} = 2.64$ kg
$S + O_2 \rightarrow SO_2$	$0.016 \rightarrow \frac{64}{32} = 0.032$ kg

$$N_2 = \text{From fuel + air (77\%)} = 0.028 + 9.89 \times \frac{77}{100}$$

$$= 7.62 \text{ kg}$$

$$\text{Total weight of products} = 2.64 + 0.032 + 7.62$$

$$= 10.29$$

$$\% \text{ of } CO_2 = \frac{2.64}{10.29} \times 100 = 25.66\%$$

$$\% \text{ of } SO_2 = \frac{0.032}{10.29} \times 100 = 0.31\%$$

$$\% \text{ of } N_2 = \frac{7.62}{10.29} \times 100 = 74.05\%$$

Exercise Problems

1. A sample of coal was found to contain the following composition: C = 81%, H_2 = 4.0%, O_2 = 2%, N_2 = 10% the remaining being ash. Estimate the quantity of minimum air required for complete combustion of 1 kg of the coal. (*Ans.* 10.69 kg)
2. A sample of coal has been found to contain the following composition: C = 75%, H_2 = 5.2%, O_2 = 12.8%, S = 1.2%, N_2 = 3.7% and ash = 2%. Calculate the minimum amount of air necessary for complete combustion of 1 kg of coal. (*Ans.* 9.96 kg)
3. Calculate the quantity of air required for the complete combustion of 1 kg of the fuel of the following composition: C = 74%, H_2 = 5%, S = 1%, O_2 = 5%, moisture = 7% and ash = 6.0% (*Ans.* 10.13 kg)

3.14

FLUE GAS ANALYSIS BY ORSAT'S APPARATUS

The efficiency of the combustion can be determined experimentally by the analysis of flue gas coming out from the combustion chamber. Flue gas is mainly the mixture of CO_2, CO and O_2. Flue gas analysis is carried out by using Orsat's apparatus. It consists of a horizontal tube provided with a three way stop cock at one end and 100 ml graduated burette at the other end which is surrounded by a water jacket to keep the temperature of gas constant during the experiment. The lower end of the burette is connected to a water reservoir by means of a rubber tube. The level of water in the burette can be raised or lowered with the help of water reservoir. The horizontal tube is also connected with three different absorption bulbs (A, B and C) 'A' bulb contains potassium hydroxide which can absorb CO_2, 'B' bulb contains alkaline pyrogallol which can absorb CO_2 and O_2, 'C' bulb contains ammoniacal cuprous chloride which can absorb CO_2, O_2 and CO (Fig. 3.10). Hence it is necessary that flue gas is passed first through 'A' bulb where CO_2 is absorbed, then through 'B' bulb where only O_2 is absorbed (CO_2 has already been removed) and finally through 'C' bulb where only CO is absorbed (CO_2 and O_2 are already removed).

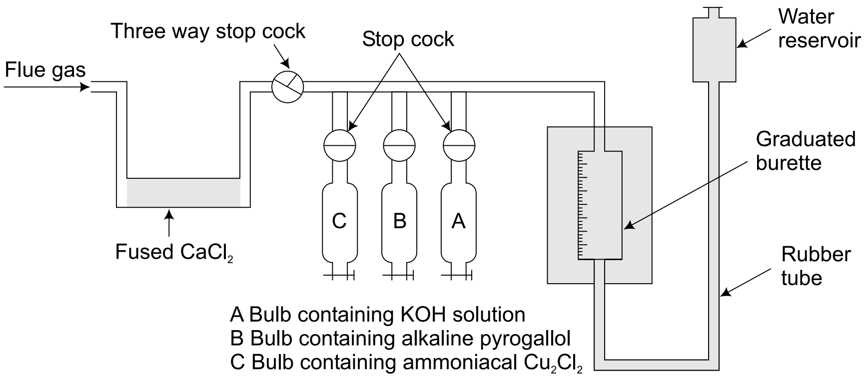


Fig. 3.10 *Orsat's apparatus*

Procedure The apparatus is cleaned and the absorption bulbs are filled with respective solutions and their stop cocks are closed. The three way stop cock is opened to the atmosphere, then the reservoir is raised till the burette is completely filled with water and air is completely removed from the tube and burette. The flue gas is sucked into the burette and the volume is adjusted to 100 ml (i) The stop cock of the bulb ‘A’ is opened and the water reservoir is raised to force the gas inside the bulb. The KOH solution absorbs CO_2. The gas is again passed to the burette. The process is continued until the complete absorption of CO_2 and stop cock of ‘A’ is closed. The decrease in volume of flue gas gives the volume of CO_2 in 100 ml of flue gas. (ii) The stop cock bulb ‘B’ is opened where O_2 of flue gas is absorbed. The decrease in volume of flue gas gives the volume of O_2 and stop cock of bulb ‘B’ closed. (iii) Finally the stop cock of bulb ‘C’ is opened where CO is absorbed. The decrease in volume of flue gas gives the volume of CO.

The volumes of O_2 and CO are measured using the same process of CO_2. The remaining gas in burette after absorption of CO_2, O_2 and CO is taken as nitrogen.

Significance From the flue gas analysis, it is possible to know whether the fuel is burnt completely or not.

(i) If the flue gas contains high percentage of CO, it indicates incomplete combustion and oxygen supply is less than required amount.

(ii) If there is high percentage of O_2 in flue gas, it indicates complete combustion and oxygen supply is more than required amount.

Short Answer Question

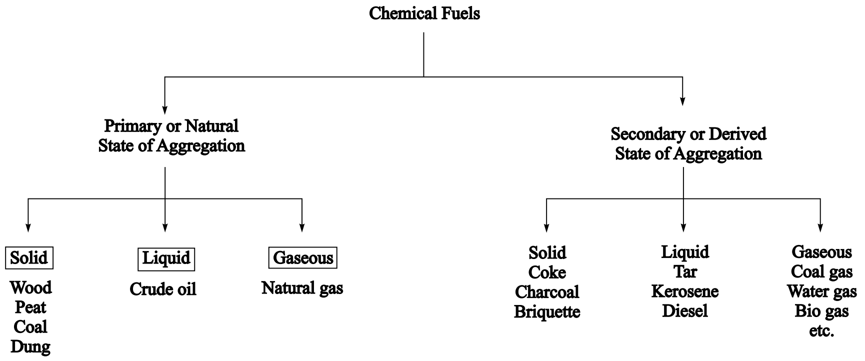
1. Define a chemical fuel

   Ans. A fuel is a combustible substance which on proper burning in presence of oxygen or air gives large amount of heat energy that can be used economically for domestic and industrial purposes.

2. What are different types of fuels?

   Ans. The fossile fuels have been classified according to their

   (1) occurrence and (2) the state of aggregation.



3. Give four characteristics of a good fuel.

Ans. (i) It should have less moisture and ash

(ii) It should possess high calorific value

(iii) The velocity of the combustion should be moderate

(iv) It should be cheap and readily available

(v) It must be easy to handle, store and trans port at minimum cost.

4. What is meant by calorific value of fuel?

Ans. It is the total quantity of heat liberated when a unit mass (or volume) of the fuel is burnt completely in presence of sufficent quantity of air/oxygen.

5. Calculate the grass calorific value of a coal sample from the following data obtained form bomb calorimeter. Weight of coal 0.73g, weight of water in the calorimeter 1500g, water equivalent of calorimeter 470g, intial temp 25°C and final temp. 28°C

Ans. Weight of coal (m) = 0.73g

Weight of water in the calorimeter (w) = 1500g

Water equivalent of calorimeter (c) = 470g.

Intial temperatures $t_1 = 25°C$

Final temperature $t_2 = 28°C$

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

$$= \frac{(1500 + 470)(28 - 25)}{0.73}$$

$$= 8095.89 \text{ cal/g}$$

6. Write short-note on degree of alteration from wood.

Ans. Wood, Peat, Lignate, Bituminous, Anthracite. Calorific value, hardness, carbon content increase from wood.

7. Why is coke preferred in metallurgical processes?

Ans. Coke posseses

(a) Higher strength

(b) Medium size

(c) Higher calorific value

(d) lesser sulphur content

(c) low ash and porosity

8. What is synthetic petrol?

Ans. Petrol synthesised either by polymerizations of low molecular mass olefins and alkanes or from finely powdered coal and heavy oil is called synthetic petrol.

9. What do you mean by refining of petroleum

Ans. The process of removel of impurities Form crude oil and separation of various fractions with different boiling ranges is called refining of petroleum

10. What are the products obtained by Fractional distilation.

Ans. Heavy oil, Diesel, Kerosene, Naphtha, Gasoline (Petrol), Petroleum ether and un condensed gases. Heavy oil repeat fractional distilation we get paraffin wax, Greases, petroleum jelly and Lubricating oil.

11. What is meant by octane number of gasoline?

Ans. The percentage of isooctane in a mixture of isooctane and η-heptane, which matches the gasoline under test in knocking characteristics.

12. What is power alcohol?

Ans. Ethyl alcohol is an important fuel and when it is used in a internal combustion engine it is called power-Alcohol.

13. What are the advantages of power alcohol.

Ans. (i) Alcohol has an octane value of about 90:

(ii) it has better anti-knock properties

(iii) Alcohol- petrol blends have lesser starting difficulties

(iv) The great-advantages of adding alcohol to petrol is that alcohol is capable of absorbing any traces of moisture present.

14. Arrange the Gaseous fuels in increasing order of their calorific values

Ans. Producer gas < water.gas < biogas < LPG

15. What is wet gas

Ans. When natural gas occurs along-with petroleum in oil wells, its is called wet gas.

16. Why a good fuel must have low ash content.

Ans. Ash is useless, non-combustible matter present a fuel it reduces the calorific value, causes hindrance in the flow of air and heat, thereby reducing the temperature attained.

17. What energy conversion takes place when fuel is burnt?

Ans. Chemical energy is converted into heat and light through combustion reaction.

18. Which components present in produce gas

Ans. it is a mixture of CO and Nitrogen. H_2, CO_2 etc are other gases associated with producer gas.

19. What are petrochemicals?

Ans. Those derived form the crude oil or Natural gas they include light hydrocarbons obtained by fractional distillisation.

20. How can you analyse the masses of CO_2 and CO_2 produced during combustion of a fuel sample?

Ans. The flue gas analysis by or sat's apparatus CO_2 can be absorbed in a pre weighted sample of alkali (like KOH). CO can be absorbed by a pre-weighed sample of anhydrous $Cucl_2$

Review Questions

Short Type Questions

1. What are Fuels? Give their classification with suitable examples
2. Write a brief account of Solid fuels?
3. What is meant by refining of petroleum?
4. Define Calorific value of Fuel? Write its units.

5. Define Octane Number? Explain its significance.
6. Write short note on power alcohol?
7. What are the advantages of Gaseous Fuels?
8. What are the characteristics for good fuel?
9. What is Bio gas? Explain briefly
10. Explain the significance of the flue gas analysis by Orsat's Apparatus
11. What is meant by Net calorific value? Write related formula for combustion of Fuel?
12. Write formula for calculation of minimum amount of air required for combustion of Fuel?
13. Write formula for minimum volume of Air is required for complete combustion of Fuel?
14. What are the advantages of using alcohol gasoline blends in combustion reaction?
15. Why is calorific value of Coal gas higher than producer gas and Bio gas? Justify.

Essay Type Questions

1. What are chemical fuels? Give their classification with examples.
2. Discuss the characteristics of good fuel. Give the classification of coal and explain each class with examples.
3. Define calorific value of a fuel. Distinguish gross and net calorific value.
4. Describe the method of determination of calorific value of solid fuel by bomb calorimeter.
5. Describe the fractional distillation of petroleum.
6. How do you synthesise petrol by Fisher–Tropsch process?
7. Describe the analysis of Flue gas by Orsat's apparatus.
8. What are the characteristics of metallurgical coke? Describe the manufacture of metallurgical coke by Otto-Hoffmann's method.
9. Discuss in detail about Bergius process for the manufacture of synthetic petrol.
10. What do you mean by refining of petroleum? List out the various fractions obtained during refining of crude oil with their approximate composition, temperature range and uses.
11. Explain Junker's gas calorimeter for the determination of calorific value of a gaseous fuel.
12. Give the approximate compositions and uses of producer gas and water gas.
13. Write short notes on
    (a) Coal gas
    (b) Bio gas
    (c) Water gas
    (d) Producer gas
    (e) Natural gas
14. Explain the significance of the following constituents present in coal
    (a) Moisture
    (b) Volatile matter
    (c) Ash
    (d) Fixed carbon
15. Give the classification of coal. Discuss the qualities of good coal.
16. Explain the proximate analysis of coal to ascertain its quality.
17. Discuss the ultimate analysis of coal with its significance.

Multiple Choice Questions

1. The highest ranking coal is

(a) anthracite (b) peat

(c) lignite (d) bituminous.

2. Which of the following is a natural fuel?

(a) coal (b) coke

(c) petrol (d) oil gas.

3. Bomb calorimeter is used for determining the calorific value of

(a) solid

(b) gaseous

(c) liquid

(d) both (a) and (c).

4. Main constituent of LPG is

(a) methane (b) propane

(c) benzene (d) butane.

5. A good fuel should possess

(a) high calorific value

(b) low calorific value

(c) high ignition temperature

(d) moisture.

6. The calorific value of a fuel is expressed as

(a) K.cal/cm^3 (b) K.cal/cm

(c) cal/cm^3 (d) K.cal/m^3.

7. Laboratory gas is produced by cracking

(a) diesel oil (b) kerosene oil

(c) petrol (d) peat.

8. Gobar gas mainly contains

(a) CO (b) CH_4

(c) N_2 (d) SO_2.

9. Composition of water gas is

(a) $CO + N_2$ (b) $CO + CH_4$

(c) $CH_4 + N_2$ (d) $CO + H_2$.

10. Producer gas is a mixture of

(a) $CO + CH_4$ (b) $CO + N_2$

(c) $CO + H_2$ (d) $CO + O_2$.

11. Which of the following is motor engine fuel?

(a) diesel (b) petrol

(c) kerosene (d) heavy oil.

12. Calorific value of diesel is

(a) 11250 K.cal/kg

(b) 11200 K.cal /kg

(c) 11000 K.cal/kg

(d) 11100 K.cal/kg.

13. Flue gas analysis is done by using

(a) Beehive oven

(b) Junkers gas calorimeter

(c) Bomb calorimeter

(d) Orsat's apparatus.

14. By alternatively passing air and steam on to the red hot coke, we get

(a) producer gas (b) water gas

(c) bio gas (d) oil gas.

15. In Orsat's apparatus, KOH is used for absorption of

(a) CO_2 (b) CO

(c) O_2 (d) N_2.

16. The only liquid fuel in nature is

(a) petrol (b) diesel

(c) petroleum (d) kerosene.

17. ______ is a biogas produced from cattle dung.

(a) Gobar gas (b) Oil gas

(c) Natural gas (d) SO_2.

18. The latent heat of steam is

(a) 250 K.cal/kg (b) 587 K.cal/kg

(c) 300 K.cal/kg (d) 450 K.cal/kg.

19. An example of secondary fuel is

(a) petroleum (b) natural gas

(c) coke (d) coal.

20. The calorific value of producer gas is

(a) 1300 K.cal/m^3

(b) 1500 K.cal/m^3

(c) 1800 K.cal/m^3

(d) 2500 K.cal/m^3.

21. The catalyst used in Bergius process is
   (a) Nickel Oxalate
   (b) Nickel Oleate
   (c) Iron
   (d) Platinum.

22. The boiling range of petrol fraction is found to be
   (a) 120°C–180°C
   (b) 250°C–320°C
   (c) 40°C–120°C
   (d) 180°C–250°C.

23. The raw materials used in Bergius process for production of synthetic petrol are
   (a) coal and hydrogen
   (b) coke and oil
   (c) water gas and hydrogen
   (d) producer gas and oil.

24. The calorific value of water gas is
   (a) 2800 K.cal/m^3
   (b) 1800 K.cal/m^3
   (c) 1300 K.cal/m^3
   (d) 2000 K.cal/m^3.

25. The total heat liberated by the complete combustion of one unit of fuel with oxygen is called
   (a) calorie
   (b) kilocalorie
   (c) calorific value
   (d) centigrade heat unit.

Answers

1. (a)	**2.** (a)	**3.** (d)	**4.** (d)	**5.** (a)
6. (a)	**7.** (b)	**8.** (b)	**9.** (d)	**10.** (b)
11. (b)	**12.** (c)	**13.** (d)	**14.** (b)	**15.** (a)
16. (c)	**17.** (a)	**18.** (b)	**19.** (c)	**20.** (a)
21. (b)	**22.** (c)	**23.** (a)	**24.** (a)	**25.** (c)

Fill Up the Blanks Questions

1. Fuel + $O_2 \rightarrow$ Products + ________.
2. The only gaseous fuel in nature is ________.
3. Gross calorific value________ latent heat of condensation of steam is called _____.
4. The one of the catalysts used in Bergius process is ________.
5. Least ranking coal is ________.
6. $n\text{CO} + 2nH_2 \rightarrow$ ________ + nH_2O.
7. The process of preparing coke from coal is called ________.
8. The calorific value of anthracite coal is ________.
9. The calorific value of water gas is ________ than that of producer gas.
10. The amount of heat required to raise the temperature of 1 kg of water through 1°C is called ________.
11. In Orsat's apparatus ________ is used for absorption of CO_2 and O_2.
12. The calorific value of natural gas is ________.
13. In proximate analysis, the percentage of fixed carbon = ________.
14. A good quality coal should have ________ nitrogen content.
15. Boiling range of kerosene oil is ________.

Answers

1. Heat
2. Natural gas
3. Net calorific value
4. Nickel oleate (or) tin oleate
5. Peat
6. $C\mathit{n}\ H_2\mathit{n}$
7. Carbonisation
8. 8650–8700 K.cal/kg
9. Higher
10. Kilocalorie
11. alkaline pyrogallol
12. 12000–14000 K.cal/m^3
13. 100–% of (moisture + volatile matter + ash)
14. Very little
15. 180–250°C

4

Chemistry of Engineering Materials

Classification of Materials

According to ability of the material's to conduct electricity, the materials are classified into four categories. They are insulator, conductor, semiconductor and superconductors.

Insulators: A material with a very high resistivity (> 1012Ωcm)), which is rather independent of temperature, is classified as an insulator

Conductor: A material having very low resistivity ie. <10-4 Ω–cm, which increases the resistivity as the temperature increases, is considered as a metal conductor

Semiconductor: A material with an intermediate ranged resistivity between 10-3Ωcm to 1011Ωcm and which decreases the resistivity with increasing temperature is considered as a semiconductor.

Super conductor: A superconductor is a material whose resistance is identical to that of a metal at high temperature, but whose resistance drops to zero below a particular temperature.

Basic Principle of Conductors

The Energy band containing the valence electrons is known as the valence band. The energy band of unoccupied orbital's is known as the conduction band. Conduction happens when electrons are promoted from the valence band to the conduction band and this phenomenon occurs for the movement of electrons throughout the solid. The energy gap between the valence and conduction bands is known as the band gap energy (Eg). For metal conductors, band gap energy is essentially zero and electrons are prompted to the conduction band quite easily and hence make the metals good conductors. The schematic representation in respect of band energy gap of insulators, semiconductors and conductors are shown in Figure. 4.1.

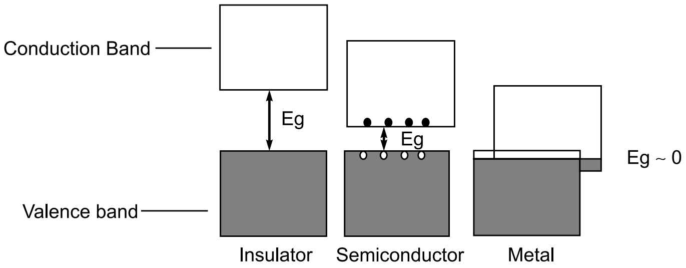
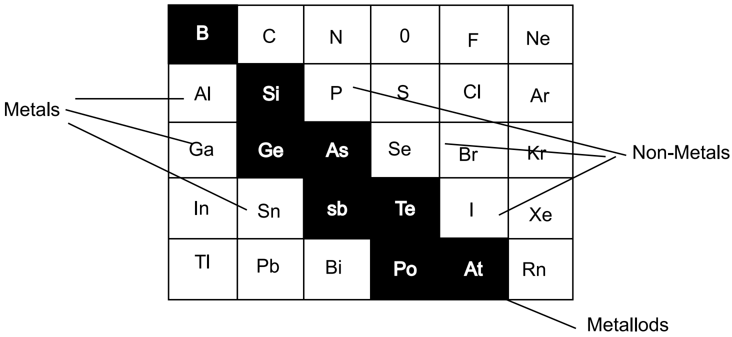


Fig. 4.1 *Band Energy diagrams of an insulator, a semiconductor, and a metal. Double-headed arrow indicates Band Gap Energy (Eg) between valence and conduction band. The length of the band gap decreases from an insulator to a metal, where it is found effectively zero. In semiconductor , Electron hole pairs shown as filled circles in conduction band and as open circles or holes valence band.*

4.1

SEMICONDUCTOR MATERIALS

A semiconductor may be defined as a material which has electrical conductivity between that of a conductor such as copper and an insulator such as glass. Further, Semiconductors are substances with a little electrical conductivity which may be increases with temperature. Diamond is a non-conductor. The high electronegativity of Carbon attracts the electrons in the C-C bonds. Silicon also considered as semiconducting material and found less electronegativity than Carbon. Si-Si bonds are weaker than C-C bonds. Electrons can be migrated from the bonds in Silicon through heating. When a voltage is applied across the materials, these free electrons can migrate through the lattice resulting in electrical conductivity. The higher the temperatures the more number of bonds break and higher the conductivity. Silicon is therefore a 'semiconductor'. Semiconductors or metalloids lie at the division between the metals and the non-metals found in the periodic table which is shown in Figure. 4.2. Most of electronic devices use semiconductor components to perform electron control



B	C	N	0	F	Ne
Al	**Si**	P	S	Cl	Ar
Ga	**Ge**	**As**	Se	Br	Kr
In	Sn	**sb**	**Te**	I	Xe
Tl	Pb	Bi	**Po**	**At**	Rn

Fig. 4.2 *Metalloids or Semiconductors shows in the division between the metals and non-metals*

Electrons can also be displaceable from the bonds in semiconductors with the help of light energy is called the photovoltaic effect. This is used in solar cells to convert sunlight into electricity.

4.1.1 Basic Principle of Semiconductors

The Chemical bond in semiconductors is primarily covalent, which is quite different from metallic bond. When the atoms are brought near to each in the solid, the splitting of the energy levels produces two bands and they do not overlap . The conduction band lies higher in energy and is not occupied with electrons at 0 K. The valence band lies lower in energy and is filled electrons at 0 K. The energy splitting between the top of the valence band and the bottom of the conduction band is called the energy gap (E_g). The valence band of semiconductor is full and the conduction band is empty at 0 K .The energy separating the valence and conduction bands is the intrinsic energy gap, $E_g = (E_c - E_v)$. Figure 4.3 shows the Energy level difference at different energies.

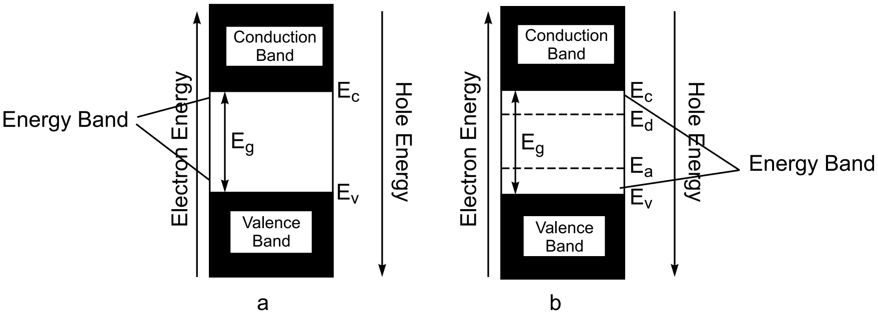


Fig. 4.3 *Energy level diagram of semiconductor for the electronic bands.*

(a) An Intrinsic semiconductor with an energy gap of E_g, a valance band of E_v and a conduction band of E_c.

(b) Extrinsic semiconductor (Doped) with donor level E_d and acceptor level E_a

If the semiconductor having impurity (dopant) atoms, energy states can exist in between the conduction band (E_c) and the valence band (E_v). If an atom contains one more valence electron than the semiconductor atom will occupy in the lattice only but not used in bonding. Instead of using in bond formation, this electron would be localized on the impurity atom and have an energy (E_d) just below that of the conduction band (E_c). For example, phosphorus atom doped in silicon type. This type of impurity is known as donor and the semiconductor is referred to as an n-type. In contrast to n-type semiconductor, an impurity atom with one less valence electron than the semiconductor atom will act as a hole (this may be filled with an electron) with an energy level(E_a) just above the valence band. Suitable example under this category is aluminum atom in silicon. This kind of impurity or dopant is called an acceptor or a p-type semiconductor. These dopant atoms dramatically change and improve the semiconductor's conductivity. In the case of InSb crystal, Sb atom act as donor and In atom act as acceptor. Hence, p or n-type semiconductor can be produced.

Doping

Addition of trace amounts of other elements to a semiconductor lead to increase the conductivity of the material is called doping. There are two kinds of doing techniques to get in n-type or p-type semiconductors. By considering silicon is an example, to illustrate n-type and p-type semiconductors.

n-type Semiconductors: In this type of semiconductors, add trace amounts of Phosphorus to Silicon. As per electronic configuration, phosphorus has five outermost electrons so there is one left over once the bonds formed with Silicon. This extra or nonbonding electron can move freely through the lattice to increase the conductivity of Silicon. The extra electron between the P and Si creates a small negative charge in that area hence the name **n-type** (n-stands for negative). The pictorial diagram is shown in Figure 4.4

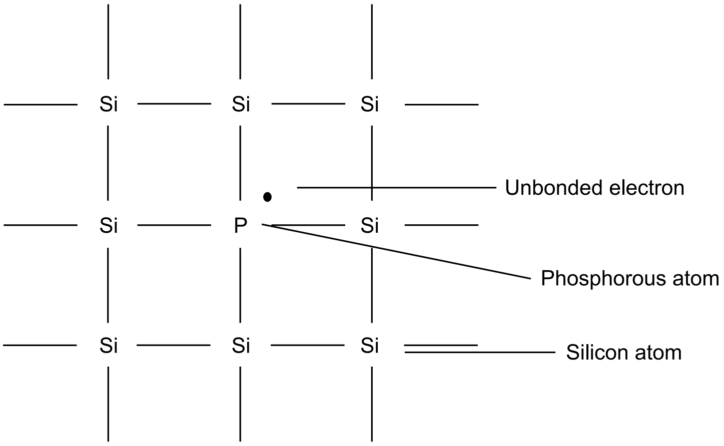


Fig. 4.4 *Pictorial diagrammatic representation of n-type semiconductor*

p-type Semiconductors: This type of semiconductors produced with the addition of small amounts of Boron to Silicon. Boron electronic configuration shows, it has three outer electrons which are insufficient to make four bonds with Silicon. One electron on Silicon is left over and found nonbonding electron. This extra electron can move freely through the crystal lattice to increase the conductivity of Silicon. The lack of an electron between the boron and silicon atoms creates a small positive charge in that area and is often called as positive hole, hence the name of p-type semiconductor. The diagrammatic representation is shown in Figure. 4.5.

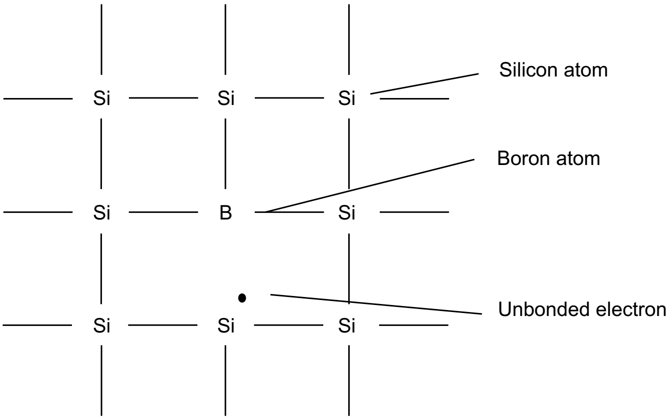


Fig. 4.5 *Pictorial diagrammatic representation of p-type semiconductor*

One of the main applications of n-type and p-type semiconductor was making of rectifier. It is noting that if an n-type and p-type semiconductor joins together, the extra electrons in the n-type move into the positive holes in the p-type of semiconductor. However, electrons cannot flow from p-type semiconductor to n-type semiconductor since there is no vacant orbital to accommodate extra electron. Therefore, the p-n junction will allow current to flow through it in one direction only. This kind of device is known as a rectifier, which is the main basis for the modern electronics industry.

4.1.2 Applications of Semiconductors

Semiconductors are of enormous wide technological importance because of their special properties, which can be modified by doping. Some applications include:

1. Semiconductors are the foundation for modern electronics which includes radio, computers, and telephones.
2. Semiconductor-based electronic components employed in various applications including transistors, solar cells, light-emitting diodes (LEDs), and digital and analog integrated circuits
3. The resistivity of semiconductors changes with temperature. On the basis of this, semiconductors enable to be used as thermometers
4. Semiconductor are used in making of Hall Probes. These are measure magnetic field strengths with the a small piece of semiconductor with known properties.
5. IR Sensors/Optoelectronic devices are made using semiconductors. Optoelectronic devices are capable of recognizing or responding to light of different wavelengths. This is called as a phenomenon of photo-conductivity whereby a semiconductor can greatly increase its electrical conductivity if the radiation energy has resonance with band gap energy can able to promote electrons across the band gap. Various semiconductors are available with different band gaps to suit particular applications.

4.2

SUPERCONDUCTORS

Most of the conductors lose all of their electrical resistance when cooled to very low temperatures which is near to absolute zero or -273°Celsius. Superconductors are materials that show almost zero electrical resistance at temperatures near 0 K. The threshold temperature for a superconductor to switchover from normal conduction to superconductivity is called the **transition temperature**. Transition temperatures for classic superconductors are in the cryogenic range ie. near to absolute zero. Hundreds of materials are known to become superconductors at low temperatures. At low temperatures and low pressure, nearly 27 chemical elements, in which all of them metals are considered as superconductors with their normal crystallographic forms. Among these the common known metals are: aluminum, tin, lead, and mercury and less common ones such as rhenium, lanthanum and protactinium. Further, 11 elements which are metals, semimetals and semiconductors are superconductors at low temperatures and high pressures. Examples of such elements are uranium, cerium, silicon, and selenium. Bismuth and five other elements are not superconducting with their normal crystallographic form, can be made superconducting in a highly disordered form, which is stable at extremely low temperatures. Most of the known superconductors are alloys or compounds. **Superconductivity is not exhibited by any of the magnetic material chromium, manganese, iron, cobalt and nickel.**

Recently enough progress have been observed in the development of superconductors which have zero resistance just above the boiling point of liquid Nitrogen (77 K) which are less costly to achieve. For example $YBa_2Cu_3O_7$ becomes superconducting below 92 K. C_{60} (Fullerenes) doped with Potassium and Rubidium is exhibits superconducting at these more manageable temperatures. Ideally, a superconductor should be able to operate within the range of ambient temperatures. The critical temperatures for a few common substances are shown here in this table.

Table. 4.1 *Typical critical temperature of some of the materials*

Material	*Element/compound/alloy*	*Critical Temperature K*
Aluminum	Element	1.02
Cadmium	Element	0.56
Lead	Element	7.2
Mercury	Element	4.16
Niobium	Element	8.70
Thorium	Element	1.37
Tin	Element	3.72

Contd.

Titanium	Element	0.39
Uranium	Element	1.0
Zinc	Element	0.91
Niobium/Tin	Alloy	18.1
Cupric SulPhide	Compound	1.60

Limitations: Superconducting materials should interact with magnetic fields and found variations in conductivities. In the superconducting state, a superconducting material will tend to absent all magnetic fields and such a phenomenon known as the Meissner effect. When, the magnetic field increases beyond a critical level, the superconducting material will converted into non-superconductive. Hence, superconducting materials will lose their superconductivity, if it exposed to very strong magnetic field. In fact, the presence of any magnetic field leads to decrease the critical temperature of any superconducting material. Therefore, strong magnetic fields present, the colder you have to make the material before it will super conduct. This is another practical limitation to superconductors in circuit design, since electric current through any conductor develops a magnetic field.

Advantage: Discovery of Superconductors promises extensive capabilities in the case of electric circuits. If one can eliminate entire resistance of a conductor, there will be no power losses in electrical power systems due to stray resistances. Under such conditions, electric motors could be made almost perfectly or100% efficient. Electrical components such as capacitors and inductors, whose ideal characteristics are generally affected by inherent wire resistances, could be made ideal in a practical sense. Some practical superconducting conductors, motors and capacitors were developed. But their use in the present time is limited due to the practical difficulties intrinsic to maintain super-cold temperatures.

4.2.1 Applications of Superconductors

The following are important applications of superconducting materials:

1. A superconducting material widely used in the construction of electromagnetic materials is an alloy of niobium and titanium. Hence these materials may employ in a wide variety of applications, ranging from electric power transmission to high-speed computing.
2. High-temperature superconductors are many applications in metrology, electromagnetic sensing, and analog and digital circuits.
3. Superconductors are also able to maintain a current with no applied voltage. This property used in superconducting electromagnetic materials found in MRI machines. Experiments have illustrated that currents in superconducting coils can persist for many years without any noticeable

degradation. Experimental evidence reveals that current lifetime of superconductors at least 100,000 years.

4. Niobium-titanium (NbTi) alloy used in industrially as superconductor wire for superconducting magnets, normally as Nb-Ti fibres in an aluminium or copper matrix.
5. Niobium superconducting alloys, also containing titanium and tin are widely used in the superconducting magnets of MR/NMRI scanners.
6. Niobium-titanium superconducting magnet coils under liquid helium cooled were built to be used in the Alpha Magnetic Spectrometer mission to be flown on the international space station.

4.3

MAGNETIC MATERIALS

The materials that shows response towards the magnetic field is called Magnetic material which is independent of the direction of response whether it be positive (attractive nature) or negative (repulsive nature). All materials are influenced to some extent by a magnetic field.). Substances that are negligibly affected by magnetic fields are known as non-magnetic substances. They include copper, aluminium, gases, and plastic. Pure oxygen exhibits magnetic properties when cooled to a liquid state.The magnetic state (or phase) of a material depends on temperature (and other variables such as pressure and the applied magnetic field) so that a material may exhibit more than one form of magnetism depending on its temperature, etc. Most common examples of magnetic materials used in daily life is Iron, nickel and cobalt.Formation of magnetic lines under the bar magnetic field shown in Figure 4.6.

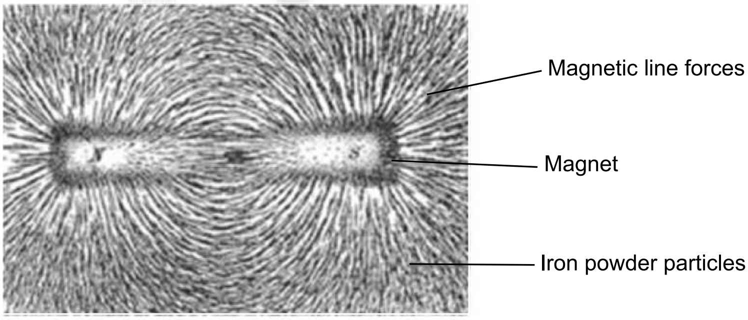


Fig. 4.6 *Magnetic lines of force of a bar magnet shown by iron filings on paper*

4.3.1 Classification of Magnetic Materials

The magnetic materials are classified based on two important criteria. They are (i) Behavior in magnetic field and (ii) on the basis of hysteresis loop.

Behavior in magnetic field: On the basis of response of the materials in the magnetic field, they are can be classified into the following five major groups:

1. Diamagnetic
2. Paramagnetic
3. Ferromagnetic
4. Ferrimagnetic
5. Antiferromagnetic

1. Diamagnetic Materials: In a diamagnetic material, the atoms have not shown net magnetic moment when there is no applied field. Under the influence of an applied field (H) the spinning electrons precess and this motion, which is a type of electric current, exhibits a magnetisation (M) in the opposite direction to that of the applied field. Diamagnetic materials show a weak, negative susceptibility to magnetic fields. They are slightly repelled by a magnetic field and the material does not retain the magnetic properties when the external field is absent or removed. In diamagnetic materials all the electron are paired so there is no permanent net magnetic moment per atom. Diamagnetic properties arise from the realignment of the electron paths under the influence of an external magnetic field. Note that when the field is zero the magnetization is zero. The other characteristic and significant property of diamagnetic materials is that the susceptibility to temperature which is independent.

Some of the examples of diamagnetic materials including copper, silver, quartz, calcite, water and gold are diamagnetic. Gases and liquids are also included to the classes of diamagnetic materials which includes: Alcohol, Hydrogen, Nitrogen and water are diamagnetic in their nature

2. Paramagnetic Materials: When the material is slightly attracted by magnetic field, the material is known as paramagnetic material**.** In a paramagnetic material there are unpaired electrons in atomic or molecular orbital's with exactly one electron in them. An unpaired electron is free to align its magnetic moment in any direction under applied magnetic field. These magnetic moments will tend to align themselves in the same direction against an external magnetic field is applied and hence reinforcing it. These materials have relative permeability slightly greater than 1 and are slightly magnetized in the direction same as that of applied magnetic field.

At room temperatures and in moderate magnetic fields, the paramagnetic susceptibility is small but larger than the diamagnetic contribution. Under very low temperature (<<100 K) or the magnetic field is very high, paramagnetic susceptibility is independent of the applied field. In such conditions, paramagnetic susceptibility is proportional to the total iron content. Many iron bearing minerals are paramagnetic at room temperature.

Some of the common example of such behavior are Aluminium, Chromium, Copper sulphate, Manganese, Palladium, Platinum, Potassium and Tungsten Tin, Platinum, magnesium, molybdenum, lithium, and tantalum etc.

3. Ferromagnetic Materials: The atomic moment in ferromagnetic materials is exhibits strong interactions when compared to paramagnetic materials. These materials have a large, positive susceptibility to an external magnetic field. They exhibit a strong attraction to magnetic fields and are able to retain their magnetic properties even after the external field has been removed. Ferromagnetic materials have some unpaired electrons and hence their atoms have a net magnetic moment These interactions are shown due to electronic exchange forces and ultimately align in a parallel or antiparallel atomic moments. Spin alignment of ferromagnetic material under magnetic field is shown in Figure 4.7. Exchange forces are very high, which is equivalent to a field on the order of 1000 Tesla, or around a 100 million times the strength of the earth's field.

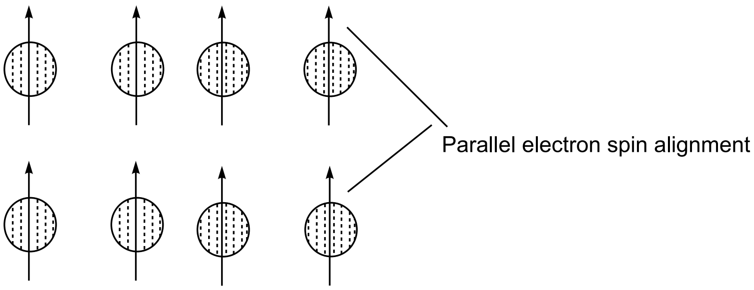


Fig. 4.7 *Electronic spin alignment of ferromagnetic materials under magnetic moment.*

In the periodic table of elements iron, cobalt and nickel are ferromagnetic at and above room temperature. As ferromagnetic materials are heated then the thermal agitation of the atoms causes decreases the degree of alignment of the atomic magnetic moments and hence the saturation magnetisation also decreases.

When a ferromagnetic material is in the absence of magnetized state, the magnetic domains are nearly randomly oriented and the net magnetic field for the part as a whole is zero. When a magnetic field is applied, the domains become aligned to produce a strong magnetic field within the part.

Most common examples are Iron, nickel, and cobalt and many of their alloys are typical ferromagnetic materials.

4. Ferrimagnetic Materials: Ferimagnetic materials are one which have complex crystal structures than pure elements. These materials retain their magnetization in the absence of applied field like ferromagnetic materials. Similar to antiferromagnetic materials, within the crystal structure of these materials, electron pairs of neighboring element spins like to point in opposite direction. Within these materials the exchange interactions leads to parallel alignment of atoms in some of the crystal lattice sites and anti-parallel alignment of others (Figure 4.8).

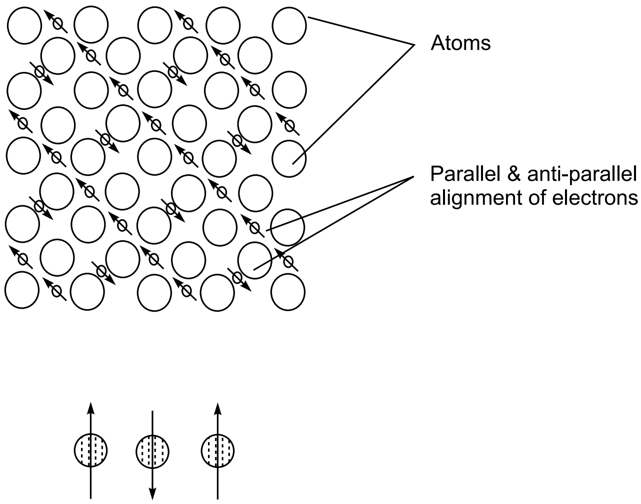


Fig. 4.8 *Magnetic moment direction of Ferrimagnetic materials*

For example, barium ferrite ($BaO.6Fe_2O_3$) the unit cell contains 64 ions of which the barium and oxygen ions have no magnetic moment, 16 Fe^{3+} ions have magnetic moments aligned parallel and 8 Fe^{3+} aligned anti-parallel gives a net magnetisation parallel to the applied field, but with a relatively low magnitude as only ⅛ of the ions contribute to the magnetisation of the material. Ferrites are best example for Feerimagnetic materials.

5. Antiferromagnetic materials: Unlike a ferromagnetic materials, an antiferromagnetic materials having a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in *opposite* directions (Figure 4.9). When all atoms are arranged in a substance in the same manner so that each neighbor is anti-aligned, the substance becomes an antiferromagnetic property. Antiferromagnetic materials show a zero resultant magnetic moment, meaning that there is no magnetic field is produced by them. In the periodic table, Chromium is only element exhibiting antiferromagnetism at room temperature.

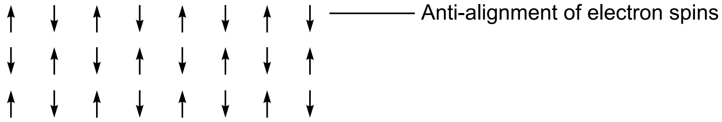


Fig. 4.9 *Electronic Spin alignment of antiferromagnetic materials*

Antiferromagnetic materials are less common compared to the other types of behaviors, and are mostly observed at low temperatures. In varying temperatures, antiferromagnetic materials can be seen to exhibit diamagnetic and ferrimagnetic properties.

4.3.2 Applications of Magnetic Materials

1. Magnetic materials are used in electric motors, in electric generators.
2. For making of CD ROMS, cassette tapes, DVD ROMs, all use magnetic material in order to store data.
3. Electromagnetic materials are also used in starter circuits of automobiles. Magnets are used to generate electricity..
4. They can be used to magnetize other ferrous material. These materials are used in the strips of cheques, credit cards and any uses.
5. Applied to lifting and transporting magnet-conductive materials such as steels and irons in metallurgy industry ,mine industry, machinery industry and transportation industry and etc in the form of scrap.
6. Alnico is an alloy made from aluminum, nickel and cobalt with iron. This is one of the first magnet materials used during World War II in military, electronic applications
7. Ceramic or Hard Ferrite is used in arc shaped magnets for motors, magnetic chucks and magnetic tools. This is the least expensive class of permanent magnet materials. The raw material, iron oxide is mixed with either strontium or barium and milled down to a fine powdered form. The powder is then mixed with a ceramic binder and magnetic materials are produced through a compression moulding technique.
8. ***Samarium Cobalt*** is the first commercially viable rare earth permanent magnetic material, is considered to still be the premium material for many high performance motor applications. Sm-Co can typically be used up to 300°C.
9. Neodymium Iron Boron material is an excellent corrosion resistance and has also offered a high degree of comfort to those looking to use magnetic materials in medical applications. With its excellent magnetic characteristics Nd-Fe-B offers flexibility for new designs or as a substitute for traditional magnet materials such as ceramic, Alnico and Sm-Co for achieving higher efficiency and more compact devices.

Table 4.2 *Typical some more Application of Magnetic Material*

Field of Specialisation	***Product***	***Material***
Power conversion Electrical- Mechanical	Motors Generators Electromagnets	Fe based materials, e.g. Fe + ≈ (0,7 - 5)% Si Fe + ≈ (35 - 50)% Co
Power Adaption	(Power) Transformers	
Signal Transfer	Transformer	
	LF (“low” frequency; up to □ 100 kHz)	Fe + ≈ 36 % Fe/Ni/ Co ≈ 20/40/40

Contd.

	HF ("high" frequency up to □ 100 kHz)	Ni - Zn ferrites
Permanent magnets	Loudspeaker Small generators Small motors Sensors	Fe/Co/Ni/Al/Cu ≈ 50/24/14/9/3 SmCo5, Sm2Co17 "NdFeB" (= Nd2Fe14B)
Data storage analog	Video tape Audio tape	NiCo, CuNiFe, CrO2
Data storage digital	Ferrite core memory Drum	Fe2O3
	Hard disc, Floppy disc	
	Bubble memory	Magnetic garnets (AB2O4, or A3B5O12), example: with A = Yttrium (or mixtures of rare earth), and B = mixtures of Sc, Ga, Al Most common: Gd3Ga5O12

4.4

CEMENT

A finely powdered mixture of calcium silicate and calcium aluminate is called cement. It has the property of setting to a hard solid structure in several hours with varying degrees of strength, and is capable of bonding with stones, bricks, etc.

4.4.1 Classification of Cement

(a) ***Natural cement*** This is obtained by calcining naturally occurring limestone containing 20–40% of clay at a high temperature and subsequently pulverising the calcined mass. During heating, silica and alumina present in the clay reacts with lime to produce calcium silicate and calcium aluminate. Natural cement is quick setting and possesses low strength.

(b) ***Slag cement*** This is produced by mixing blast furnace slag and hydrated lime and grinding with small quantity of gypsum. Slag cement sets very slowly and has low strength.

(c) ***Pozzolana cement*** This is obtained by mixing pozzolana (deposits of volcanic ash) and slaked lime Pozzolana cements harden very slowly.

(d) ***High alumina cement*** This is mainly a calcium aluminate cement and is prepared by mixing lime stone and bauxite at 1550–1600°C. High alumina cement has a rapid rate of development of strength and has superior resistance to sea and sulphate waters.

(e) ***Portland cement*** This is produced by mixing of calcarious matter (lime containing) and orgillaceous matter (clay containing) and powdered with the addition of 2–3% gypsum. Portland cement was discovered by Joseph

Aspidin of England in the year 1824. This has quick setting and hardening property when made into a paste with sand and water.

4.4.2 Chemical Composition of Portland Cement

Portland cement is defined as a finely powdered mixture of calcium silicates and calcium aluminates of varying compositions. According to I.S. 269–1975, composition of Portland cement should satisfy:

(a) Ratio of the percentage of lime (CaO) to that of silica (SiO_2), alumina (Al_2O_3) and iron oxide when calculated by the formula:

$$\frac{CaO}{2.8\,SiO_2 + 1.2\,Al_2O_3 + 0.65\,Fe_2O_3}$$

should be greater than 1.02 and not less than 0.66.

(b) Weight of insoluble residue should not exceed 2%.

(c) Ratio percentage of alumina (Al_2O_3) to that of iron oxide (Fe_2O_3) should not be less than 0.66.

(d) Weight of magnesia should not be more than 6%.

(e) Total sulphur contents, calculated as SO_3 should not be more than 2.75%.

(f) Total loss on ignition should not exceed 4%.

Table 4.3 *Chemical composition range of Portland cement*

Ingredient	*% Limit*
Lime (CaO)	60 – 69
Silica (SiO_2)	17 – 25
Alumina (Al_2O_3)	3 – 8
Iron oxide (Fe_2O_3)	0.5 – 6.0
Magnesia (MgO)	0.1 – 5.5
Sulphur tri oxide (SO_3)	1 – 3
Alkali ($Na_2O + K_2O$)	0.3 – 1.5

Average compound composition of portland cement is given in Table 8.2.

Table 4.4 *Chemical constituents of Portland cement*

Name of the Constituent	*Chemical Formula*	*Average Percentage*
Tricalcium silicate	$3CaO{\cdot}SiO_2$ (or) C_3S	45
Dicalcium silicate	$2CaO{\cdot}SiO_2$ (or) C_2S	25
Tricalcium aluminate	$3CaO{\cdot}Al_2O_3$ (or) C_3A	1
Tetracalcium alumino ferrite	$4CaO{\cdot}Al_2O_3 \cdot Fe_2O_3$ (or) C_4AF	9
Calcium oxide	CaO	2
Calcium sulphate	$CaSO_4$	5
Magnesium oxide	MgO	4

4.4.3 Manufacture of Portland Cement

There are two methods for manufacturing portland cement. They are wet and dry processes. The two processes differ only in the treatment of raw material. In dry processes, water is not added to the material during grinding.

Raw Materials

(a) Calcareous materials rich in lime such as lime stone, chalk and marble.
(b) Argillaceous materials rich in silica and alumina such as clay, shale, slate, etc.
(c) Powdered coal or fuel oil.
(d) Gypsum ($CaSO_4 \cdot 2H_2O$)

The following steps are involved in manufacture of Portland cement:

(i) Mixing of raw materials (ii) Burning
(iii) Grinding (iv) Packing

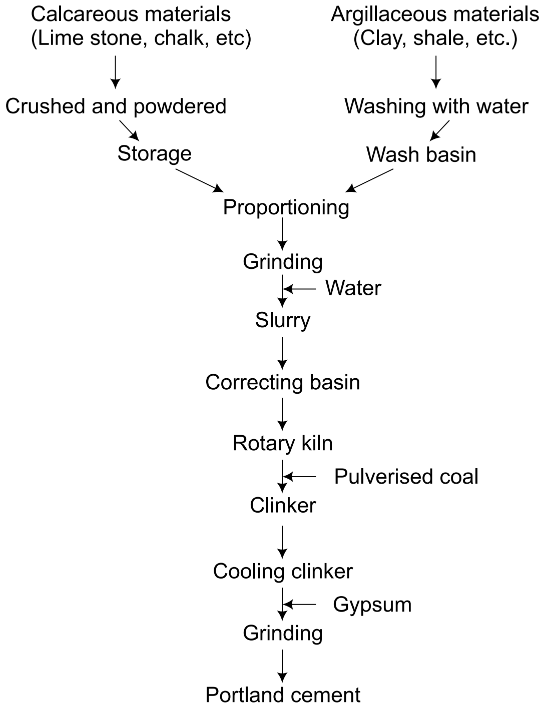
(i) Mixing of raw materials This can be done either by dry process or wet procsss.

In dry process, the raw materials are crushed in gyratory crushers and ball mills, and then burnt in dry condition in a rotary kiln.

In the wet process, the calcarious materials (Lime) are crushed and powdered. The argillaceous material (clay) is mixed with water and made into slurry. The powdered lime and clay slurry are mixed in requisite proportions and then fed to a rotary kiln.

(ii) Burning It is done in rotary kiln which is a steel cylinder, about 2.5 to 3.0 m diameter and 90 to 120 m length and lined inside with refractory bricks. The kiln is laid in slightly inclined position towards the lower end. The upper part of kiln temperature is 400°C but the temperature gradually increases up to 1750°C at the bottom.

Flow chart of manufacture of cement



The raw slurry from the wet process, or the dry powder from the dry process is passed into the rotary kiln through the upper end while hot flames are introduced into the kiln through the lower end. The following reactions takes place in the rotary kiln (Fig. 4.10).

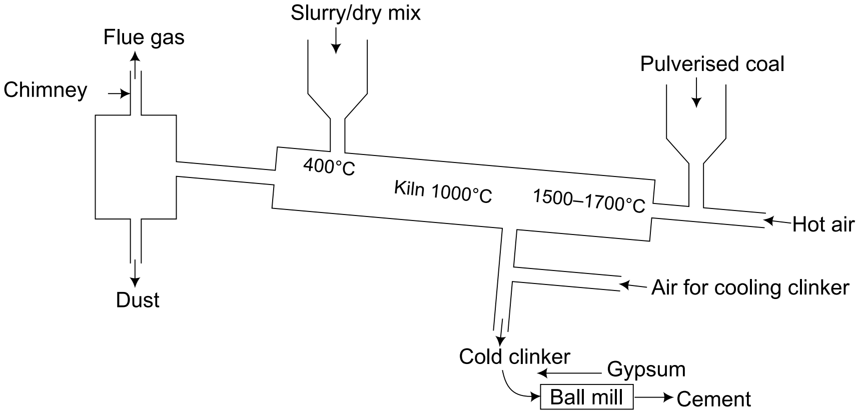


Fig. 4.10 *Rotary kiln for cement manufacture*

(a) *Drying zone* The upper part of the kiln where the temperature is only 400°C and the slurry gets dried (most of the water is evaporated).

(b) *Calcination zone* It is the central part of kiln where the temperature is around 1000°C. Limestone of dry mix or slurry undergoes decomposition to form quick lime and carbon dioxide.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

(c) *Clinkering zone* In the lower part of the rotary kiln, the temperature is between 1500°C to 1700°C. Here lime and clay combine to form calcium aluminates and calcium silicates.

$$2CaO + SiO_2 \rightarrow \underset{\text{dicalcium silicate } (C_2S)}{2CaO \cdot SiO_2}$$

$$3CaO + SiO_2 \rightarrow \underset{\text{tricalcium silicate } (C_3S)}{3CaO \cdot SiO_2}$$

$$3CaO + Al_2O_3 \rightarrow \underset{\text{Tricalcium aluminate } (C_3A)}{3CaO \cdot Al_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow \underset{\text{tetracalcium alumino ferrite } (C_4AF)}{4CaO \cdot Al_2O_3 \cdot Fe_2O_3}$$

The aluminates and silicates of calcium fuse together to form hard greyish stones called clinkers. The cooled clinkers are collected in trolleys.

(iii) *Grinding* The cooled clinkers are ground to fine powder in ball mills together with 2–3% of gypsum. The mixture of clinkers and gypsum powder is called cement. Here, gypsum acts as a retarding agent for early setting of cement.

(iv) *Packing* The ground cement is stored in silos, from which it is fed into automatic packing machine.

4.4.4 Setting and Hardening of Cement

Portland cement on mixing with water is converted into a plastic mass called cement paste which sets to a hard mass (rock like mass). The process of solidification consists setting and hardening.

Stiffening of the original plastic mass due to internal gel formation is called *setting*.

Development of strength due to crystallisation is called *hardening*.

(a) The initial setting reaction is

$$3CaO \cdot Al_2O_3 + 6H_2O \rightarrow \underset{\text{Hydrated tricalcium aluminate}}{3CaO \cdot Al_2O_3 \cdot 6H_2O} + 880\text{ kJ/kg}$$

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 7H_2O \rightarrow \underset{\text{(Crystalline)}}{3CaO \cdot Al_2O_3 \cdot 6H_2O}$$

$$+ \underset{\text{(gel)}}{CaO \cdot Fe_2O_3 \cdot H_2O} + 420\text{ kJ/kg}$$

(b) The initial setting and hardening of cement paste is also due to the formation tobermonite gel.

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow \underset{\text{Tobermonite gel}}{3CaO \cdot 2SiO_2 \cdot 6H_2O} + Ca(OH)_2 + 250\text{ kJ/kg}$$

(c) The final setting and hardening of cement paste is due to the formation of tobermonite gel, crystallisation of calcium hydroxide.

$$2(2CaO \cdot SiO_2) + 6H_2O \rightarrow \underset{\text{Tobermonite}}{3CaO \cdot 2SiO_2 \cdot 3H_2O} + \underset{\text{(Crystalline)}}{3Ca(OH)_2} + 500\text{ kJ/kg}$$

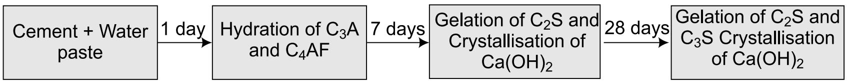


Fig. 4.11 *Setting and hardening of cement*

4.4.5 Analysis of Cement

Analysis of cement is an essential factor with its production. Various types of cements have varying compositions. But the most common cement, i.e. Portland cement has the composition as mentioned in Table 8.1 and physical factors are given below:

(a) *Setting time* It should not be less than 30 minutes and greater than 600 minutes.

(b) *Compressive strength* 1:3 cement mortar cubes

3 days—not less than 1.6 kgf/mm^2
7 days—not less than 2.2 kgf/mm^2
($\because$ kgf is kilogram force = 9.807 Newtons)

As mentioned earlier the oxides present in the raw materials when subjected to high temperature combine with each other to form complex compounds like C_3S, C_2S, C_3A and C_4AF.

The equations suggested by R.H. Bogue's for calculating the percentages of major compounds are given as follows:

$$C_3S = 4.07\,(CaO) - 7.60\,(SiO_2) - 6.72\,Al_2O_3 - 1.43(Fe_2O_3) - 2.85\,(SO_3)$$
$$C_2S = 2.87\,(SiO_2) - 0.754\,(3CaO \cdot SiO_2)$$
$$C_3A = 2.65\,(Al_2O_3) - 1.69\,(Fe_2O_3)$$
$$C_4AF = 3.04\,(Fe_2O_3)$$

Here, the oxide shown within the brackets represents the percentage of that oxide in the raw material.

Table 4.5 *The oxide composition of Portland cement and the corresponding calculated compound composition*

Oxide composition percent		*Calculated compound composition by using Bogue's equation percent*	
CaO	63	C_3S	54.1
SiO_2	20	C_2S	16.6
Al_2O_3	6	C_3A	10.8
Fe_2O_3	3	C_4AF	9.1
MgO	1.5		
SiO_2	2		
$Na_2O + K_2O$	1.0		

4.5
REFRACTORIES

Refractories are inorganic materials and are used as construction materials. It is resistant to melting or fusion. 'An inorganic material that can withstand very high temperatures without softening or deformation in shape is called refractory'. These are chemically inert, resistant towards corrosion, abrasion, etc. by hot gases, molten metals, slages, etc. (which usually surrounded the refractories). Refractories are used for the construction of lining in furnaces, retorts, kilns, crucibles, etc. which are employed in metallurgical and industrial purposes.

4.5.1 Characteristics of a Good Refractory Material

A good refractory material should

(i) be infusible at the temperature to which it is to be exposed.
(ii) be chemically inert by actions of corrosive gases, molten metals, slages, etc. produced in furnaces.
(iii) be resistant to the abrasing action of flue gases, flames, slages, etc.

(iv) not crack and suffer loss in size at operating temperatures.
(v) be able to withstand the overlying load at operating conditions.
(vi) expand and contract uniformly at high and low temperatures.

4.5.2 Classification of Refractories

Based on the chemical properties, refractories are classified into three categories.

(i) Acidic refractories, (ii) Basic refractories, (iii) Neutral refractories

(i) Acidic refractories These refractories are made of acidic materials like alumina (Al_2O_3), Silica (SiO_2), etc. They can withstand acidic materials but are easily attacked by basic materials.

e.g., Silica, alumina and fire clay refractories.

(ii) Basic refractories These refractories consist of basic materials like lime (CaO), magnesia (MgO), etc. They are resistant to basic materials but easily attacked by acidic materials.

e.g. Magnesite, dolamite and chrome-magnesite refractories.

(iii) Neutral refractories These refractories are made of weakly acidic/basic materials like carbon, chromite and zirconia. They are not attacked by either acidic or basic materials.

e.g., carborundum, graphite and chromite.

4.5.3 Criteria of Refractories or Properties of Refractories

(i) Refractoriness It is the ability of the refractory to withstand high temperature without appreciable deformation or softening under service conditions. It is generally measured by the softening temperature of the refractory material. The softening temperature of the refractory material are usually determined by the pyrometric cones test or Seger cones test.

Measurement of Refractoriness Generally, the refractoriness is measured in terms of pyrometric cone equivalent (PCE) by comparing the softening behaviour of the test cone with that of the standard cone. These cones are small pyramid shaped, 38 mm high and 19 mm long sides with a triangular base (Fig. 4.12). Test cone along with standard cones are heated under standard conditions of 10°C per minute. The PCE value of given refractory (test cone) is taken as the number of the standard cone, which fuses along with the test cone. The temperature at which the fusion of the test cone occurs is indicated by its apex touching the base. If the test cone softens earlier than one standard cone but later than the next cone, the PCE value of test cone is taken as the average value of the two standard cones. Thus a good refractory should have high refractoriness.

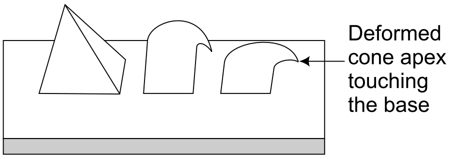


Fig. 4.12 *Seger cone test*

Examples: (1) Silica bricks – PCE number 32 and softening temp. 1710°C

(2) Magnesite bricks – PCE number 38 and softening temp. 1850°C

(ii) Refractoriness under load (RUL) or strength Refractories should have high mechanical strength to withstand the load applied under operating temperatures. Thus a good refractory should have high load bearing capacity which can be measured by RUL test.

(iii) Chemical inertness The refractory selected for a specific purpose should be chemically inert and not react with the slages, furnace gases, etc. It is always advisable not to employ an acidic refractory in contact with an alkaline product and vice-versa.

(iv) Dimensional stability The resistance of material to any volume changes, which may occur on its exposure to high temperature over a prolonged period is called dimensional stability. A good refractory should have high dimensional stability.

(v) Thermal spalling It is the property of breaking, cracking or fracturing of a refractory under high temperature. So, a good refractory should show a high resistance to thermal spalling.

Control of thermal spalling: Thermal spalling can be controlled by the following factors:

(a) Low porosity and low coefficient of expansion

(b) By avoiding sudden changes in temperatures

(c) By modification of furnace design.

(vi) Porosity Refractories generally contain pores either due to manufacturing defects or incorporation of saw dust, etc. during manufacture. Porosity is defined as the ratio of its porous volume to the bulk volume

$$P = \frac{W - D}{W - A} \times 100$$

where P = Porosity

W = Weight of saturated specimen (with water) in air

D = Weight of dry specimen.

A = Weight of saturated specimen (with water) in water.

Porosity is an important property of refractory because it affects many other properties like strength, themal conductivity and abrasion resistance.

Advantages

(a) Highly porous refractory reduces thermal spalling.

(b) Highly porous refractory can be used for lining in furnaces, ovens, retorts, etc.

Disadvantages

Highly porous refractory reduces

(a) strength
(b) the resistance to corrosion
(c) resistance to abrasion.

(vii) ***Thermal expansion*** The refractory tends to expand when temperature increases and contract when temperature decreases. Thermal expansion affects all dimensions of body. So a good refractory should have less thermal expansion.

(viii) ***Thermal conductivity*** It depends upon the chemical composition and degree of porosity of refractory. Most of the furnaces are lined inside with refractory materials of low thermal conductivity in order to reduce heat losses to outside by radiation. However, in muffle furnaces, retorts, etc. high thermal conductivity refractories are employed.

(ix) ***Abrasion resistance*** A good refractory should resist the abrasion action of flue gases, flames, slages, etc.

(x) ***Electrical conductivity*** Generally, refractories are poor conductors of electricity (except graphite). So, refractories should have low electrical conductivity.

4.5.4 Causes for the Failure of Refractories

The efficiency of the refractory product mainly depends on its constituents, processing and final curing.

(i) The most common cause for failure of refractory is chemical reaction with the environment in which it is operating. For example, an acidic refractory should not be used in furnaces using basic fluxes, slag, etc. and vice-versa.

(ii) The porosity of refractory plays an important role in the chemical reaction. The more porous it is, the greater will be the depth to which the slag will penetrate and destroy the refractory.

(iii) The deposition of carbon from carbon monoxide in fire clay refractories in a blast furnace is an important cause of its failure.

(iv) As the temperature increases the rate of chemical reaction gradually increases. Sometimes, rise in temperature beyond the safe limit quickly brings about the destruction of the refractory.

(v) The other important cause is spalling. It may be thermal, mechanical or structural. Thermal spalling may be due to unequal expansion or contraction caused by the difference in temperature at different parts. Mechanical spalling is mostly due to carelessness in loading the furnace or in the removal of materials from the furnace, thereby damaging the refractory. Structural spalling takes place due to change in composition of the refractory because of reaction with slages, flux, etc. as a result its coefficient of expansion changes. Thus, different parts expand and contract to a different extent.

4.6

LUBRICANTS

In all machines, the surface of moving, rolling or sliding parts rub against each other. All materials, how smooth they are show many irregularities in the form of peaks and valleys on the surfaces. When two solid surfaces, are placed over each other, the real contact between these surfaces happens only at limited number of asperities/peaks. Thus, the real or true area of contact is only a small fraction of the apparent contact area between the two solid surfaces. All types of machines when they are operational, the moving parts rub against each other. The mutual rubbing of one part against another generates frictional forces which cause resistance to the relative motion of these surfaces. Wear results when applied forces overcome this resistance. So friction causes lot of wear and tear of surfaces of moving/sliding/rolling parts which consequently requires repeated replacement. Friction also generates heat which gets dissipated thereby causing the loss of efficiency of the machine.

The study of wear and tear, mechanism of friction between two surfaces and lubrication is called 'Tribology'. The main aim of tribology is to minimise the friction thereby reducing the loss of material due to wear.

During a motion of the sliding surface, a considerable amount of frictional heat is evolved at the rubbing surfaces due to frictional resistance. As a result, high local temperature even under relatively light loads, speeds and asperities are crushed, and undergo plastic deformation. Further, the temperature of surfaces raise near the melting point of the material thereby causing the formation of welding junctions. Strong weld may form between hard surfaces causing considerable physical damage on both the surfaces.

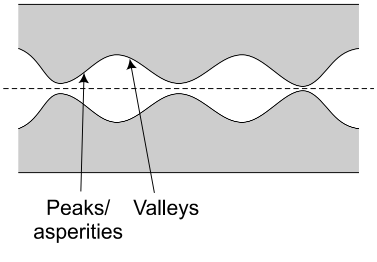


Fig. 4.13 *Contact between two surfaces and roughness*

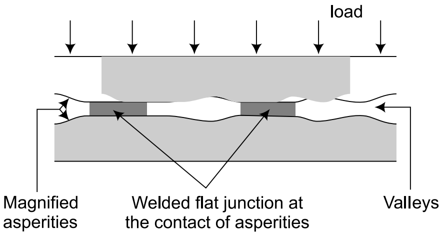


Fig. 4.14 *Contact of asperities between two surfaces at high load*

The drawbacks of frictional resistance can be minimised by applying some material in the form of a thin layer known as lubricant. Any substance used between two moving/sliding surfaces to reduce frictional resistance between them is known as lubricant. The process by which frictional resistance between two or more moving bodies or sliding surfaces is minimised is known as 'lubrication'.

4.6.1 Functions of Lubricants

The following are the important functions of lubricants which enhance the efficiency of a machine and life of materials:

1. The first and foremost important function of lubricant is to reduce frictional resistance.
2. It reduces wear, tear and surface deformation because direct contact between moving/sliding surfaces is avoided.
3. It acts as a coolant by reducing the loss of energy in the form of heat.
4. The use of lubricant reduces the liberation of frictional heat and hence it avoids the expansion of metal and seizure of moving surfaces. Ultimately, it improves the efficiency of the machine.
5. Lubricant prevents rust and corrosion. Hence, it reduces maintenance and running cost of the machine.
6. Since lubricants always cover the moving parts of the machines, they act as seal in many cases. For example, the lubricant used between piston and cylinder of internal combustion engine acts as a seal thereby avoiding the leakage of gases under high pressure from the cylinder.
7. Lubricants may also absorb shock between bearing and other engine parts, thereby reducing noise also.

4.6.2 Classification of Lubricants

Lubricants are classified into the following categories based on their natural state of existence:

(a) Liquid lubricants or lubricating oils
(b) Semi-solid lubricants or greases
(c) Solid lubricants.

(a) Liquid Lubricants A liquid lubricant is used (i) to reduce friction and wear, (ii) as cooling medium, and (iii) as sealing agent and corrosion inhibitor. An ideal liquid lubricant should possess the following properties:

(i) Ideal viscosity
(ii) Non-corrosive and should not decompose at operational temperature
(iii) high boiling point and heat stability
(iv) low freezing temperature and high oxidation resistance.

The lubricating oils are further classified into the following:

(i) Animal and vegetable oils
(ii) Mineral or petroleum oils
(iii) Blended oils
(iv) Synthetic oils.

(i) Animal and Vegetable Oils Animal and vegetable oils were being used as lubricants before the advent of petroleum products. They have the property of sticking with metal surface even under high pressure and heavy load.

For example, oils of different categories used as lubricant are as follows:

Oil category	***Source***	***Use***
Vegetable oils		
1. Castor oil	Castor seed	For processes of high speed and low pressure
2. Olive oil	Olive tree	For low pressure and high speed machines
3. Palm oil	Kernels of palm fruit	In watches and scientific instruments
Animals oils		
1. Whale oil	Whale fish	Light machines lubricants
2. Lard oil	Pig	Ordinary machines

(ii) Minerals or Petroleum Oils They are derived from fractional distillation of petroleum at a temperature of about 300°C. The length of hydrocarbon chain in petroleum oil varies between 12–15 carbons. Longer chain hydrocarbons have higher viscosity than lower chain hydrocarbons. Petroleum oils are mostly used in lubricants due to availability, abundance, cheap cost and stability under working conditions.

Mineral oils and their uses in industrial lubricants are given below:

Category	***Use as lubricants***
(a) Light oil	Spindles, transformers and refrigerations
(b) Medium oil	Compressor, light machinery and cup grease
(c) Heavy oil	Internal combustion engines, gear oil, heavy machinery, and pressure gun greases
(d) Residue	Gear oil, steam cylinder oil and extreme pressure lubrication

(iii) Blended Oils For many modern engines working at high operational conditions, no single oil serves as the most satisfactory lubricant. The best properties of lubricating oils can be achieved by addition of certain chemicals called additives. These oils with additives are called ‘blended oils’. The main uses of additives are to improve oiliness, inhibit sludge formation or break down by oxidation, reduce rust formation and impart detergent action of blended oil.

Examples of additives: Vegetable oils, fatty acids, polystyrene, sulphonates, polyester and aromatic phenolic compounds.

Additives for lubricating oil are given below.

Additive	*Improved property of lubricant*	*Examples*
1. Oiliness carriers	Lubricant oiliness improved	Vegetable oils, fatty acids
2. Viscosity index improves	Thinning at high temp. and freezing at low temp. of lubricant prevented	Hexanol, polyisobutylene, polystyrene
3. Thickness	Priovide higher viscosity to lubricant	Polystyrene, polyesters
4. Detergents	They carry away the dirty particles from metal surface	Sulphonates
5. Corrosion inhibitors	Reduce the corrosion of bearings and other metal surfaces	Organic compounds of P and Sb.
6. Antioxidants	Resists the oxidation of lubricant	Aromatic phenolic amino compounds.
7. Abrasion inhibitors	Decrease abrasion	Tricresyl phosphate
8. Emulsifiers	They promote formation of emulsion between oil and water	Sodium salt of sulphuric acid, mono ester of polyhdric alcohols.
9. Boundary lubrication improves	They create long wearing lubricants film	Compounds containing O, S or P castor oil, etc.

(iv) Synthetic Lubricating Oil Synthetic lubricating oils are used under very severe conditions where petroleum lubricants fail to work effectively. They are used in military jet engines, submarines, rocket motors, and atomic energy plants. They possess high thermal stability, high flash points, high viscosity index, etc. Some of the important synthetic lubricating oils are as follows:

Lubricant	*Important property*	*Used in*
1. Dibase acid ester	Withstand high temperature	Jet engine, submarine engines and lubrications.
2. Silicones	Viscosity is affected at low and high temperature, water repellent and corrosive resistances	Furnace doors, electroplating equipment under highly corrosive environment.

(b) Semi-solid Lubricants or Greases Greases are generally intimate mixtures of soap and mineral oil. Additives are added for special requirements of greases. They are prepared by saponification of fat with alkali, followed by addition of hot lubricating oil under constant stirring yield greases.

The structure of lubricating greases are that of gel. At high temperature, the soap dissolves in the oil where upon the interconnected structure ceases to exist and grease is liquefied.

Several types of greases are available on the basis of soaps used in their manufacture. They are given below:

(i) *Calcium based greases:* They are emulsions of petroleum oils with calcium soap. They are cheap, water resistant and used in low temperature.

(ii) *Soda based greases:* They are petroleum oil thickened by mixing sodium soap. They are not water resistant and used in high temperature (175°C).

(iii) *Lithium based greases:* Lithium soap is added to petroleum oil. They are water resistant and suitable even at low temperature (15°C).

(iv) *Axle Grease:* There are resin greases and prepared by addition of lime to resin and fatty oils. They are water resistant and suitable for less delicate working under high load and low speed.

(c) Solid Lubricants Some of the solid substances possess strong adherence property, little shearing strength and good plastic properties. Hence, they may be useful in reducing frictional resistance by separating two moving surfaces under boundary conditions. Such substances are called solid lubricants. These lubricants are very important under high temperature and heavy load. The most common solid lubricants are the minerals such as graphite, talc, soap stone, mica, molybdenum sulphide and zinc oxide.

Solid lubricants find applications in (i) commutator bushes of motor and electric generators where contamination of lubricating oils or greases is susceptible which is unacceptable (ii) internal combustion engines desires a tight film between piston ring and cylinder for increasing compression. In this case combustible lubricants and lubricants (oils and greases) film is not so stable at operating temperature and must be avoided.

The two most commonly used solid lubricants are

(i) Graphite (ii) Molybdenum disulphide.

(i) Graphite It consists of multitude of flat plates made up of a network of hexagons in which each carbon is in sp^2 hybridisation state. Since the separation between the plates/layers is about 3.4 Å, the little van der Waals forces enough to slide the layers parallel to each other. Hence, it has low coefficient of friction. It is very soapy to touch, non-flammable and not oxidised in air below 375°C. Graphite can be employed in the form of powder or suspension in oil or water using tannin emulsing agent. The suspension of graphite in oil is termed 'oil dag' and used in internal combustion engines. Graphite dispersed in water is termed 'aquadag' and finds application in food industries.

Graphite is used as lubricant in air compressors, food stuff industries, railway track joints, open gears, machine shop works, etc.

(ii) Molybdenum Disulphide It has a sandwich like structure in which molybdenum atoms lie between two layers of sulphur atoms. MoS_2 has higher specific gravity than graphite but is slightly softer. MoS_2 is commercially availables as 'molykotes'.

The inter laminar attraction is very weak (3.13°Å), which is responsible for low shear strength in a direction parallel to the layers. That is why MoS_2 has very low frictional coefficient. It is stable at high temperature (400°C). A solid film lubricating surface useful for space vehicles is made from (70% MoS_2 + 7% graphite) bonded with 23% silicates, which can withstand extreme temperature and low pressure and nuclear radiations.

A good solid lubricant should possess the following properties:

1. It should have a very low coefficient of friction
2. It should be stable in air at 400°C
3. It should have adhesion to the metal part of the surface
4. The cohesive forces between lubricant particle should be high
5. The fine powder should be sprinkled on surfaces sliding at high velocities
6. It should be employed even along with solvents and greases.

The structure of graphite and molybdenum sulphide is as shown in Fig. 4.14.

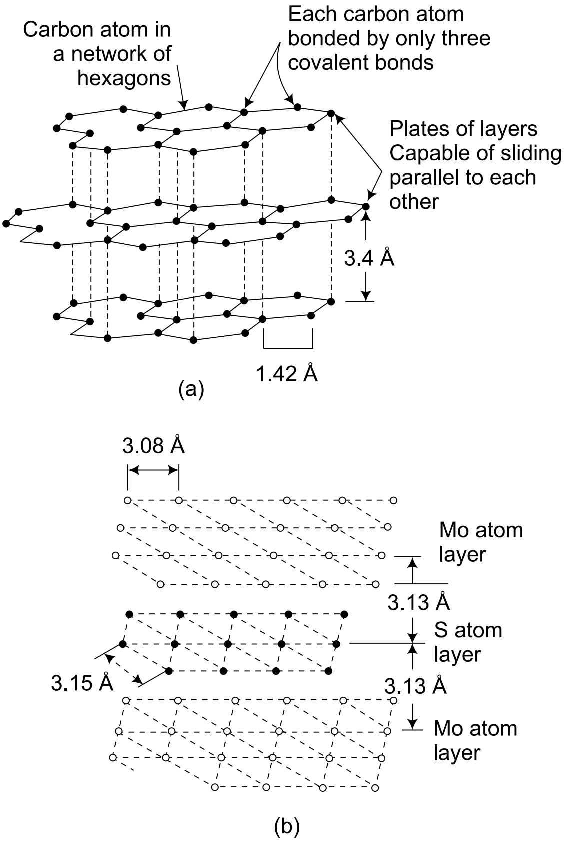
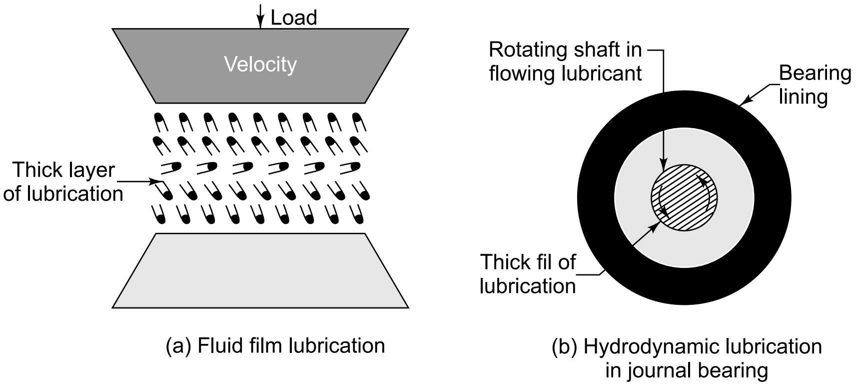


Fig. 4.14 *(a) Layered structure of graphite (b) Sandwich-like structure of molybdenum disulphide*

4.6.3 Mechanism of Lubrication

Lubrication mechanism is classified into 3 types. They are: (a) Fluid film (or) Hydrodynamic lubrication, (b) Thin-film (or) Boundary lubrication, and (c) Extreme pressure lubrication.

(a) Fluid-film (or) Hydrodynamic Lubrication This is also called thick film lubrication. In this type of lubrication, two surfaces of moving/sliding surfaces are physically separated from each other by bulk of lubricant film with a thickness at least 1000°A between them. This bulk lubricant film can prevent metal-to-metal contact so that small peaks and valleys do not interlock. Consequently it will reduce friction and prevents wear. This condition is known as fluid film lubrication as shown in Fig. 4.15(a) and (b).



(a) Fluid film lubrication

(b) Hydrodynamic lubrication in journal bearing

Fig. 4.15 *Mechanism of fluid film lubrication*

The small friction (if any) mainly due to the internal resistance between the particles of the lubricant moving over each other. It is also known as hydrodynamic lubrication based on the theory of hydrodynamics, a pressure is sufficient to keep the moving surfaces apart is created under such conditions. In this type, the lubricant used should have minimum viscosity under working condition and at the same time it should remain to place (better oiliness) and separate the surface. In addition to viscosity thickness of lubricant, the relative viscosity and area of surfaces are also points of consideration of friction in this case of hydrodynamic lubrication.

The coefficient of friction in the case of hydrodynamic lubrication is as low as 0.001 to 0.03 in comparison to 0.5 to 1.5 for unlubricated surfaces.

Hydrodynamic friction occurs mainly in the case of shaft running at fair speed and in well lubricated bearings with application of small load. In journal bearing a film of lubricating oil covers the irregularities of shaft as well as bearing surfaces and the metal surfaces do not come in contact. At start up, the coefficient of friction is high is the presence of boundary lubrication. After, start up, however, coefficient fall repidly. This is due to fact that metal surfaces do not come in direct contact with each other.

This type of lubrication is generally found in delicate, instruments, light machines like guns, sewing machines, watches, clocks, scientific instruments, etc.

Hydrocarbon oils are generally suitable for hydrodynamic lubrication blended with some antioxidants to prevent gummy formation as well as oxidation of unsaturated hydrocarbons. Sometimes at operational conditions decomposition of hydrocarbon oils may be happened which leads to formation of solid carbon particles. For keeping carbon particles in suspension with lubricating oils, organo metallic detergents need to be added.

(b) Thin Film (or) Boundary Film Lubrication Boundary lubrication occurs whenever, a continuous fluid film of lubricant cannot be maintained. When the lubricant is not enough viscous to generate a sufficient thickness of film to separate the surfaces at heavy loads, friction may yet to be reduced with the application of proper lubricant. Boundary lubrication involves the shearing of lubricant as well as metallic weld. Such condition arises at the starting and stopping of the machine at very heavy loads (or) at very low speed of movements. Solid lubricants, greases and oils with proper additives function in this manner.

In this case, lubricant is adsorbed on the metallic surface in this form of thin layer which avoid the metal-to-metal direct contact. The load is carried by the thin layer adsorbed on both the metal surfaces. The distance between the sliding/moving surface is very small in the case of boundary film lubrication in the order of heights asperities. The contact between metal surfaces is possible by squeezing out the oil lubricating film. When this occurs, the load would be taken on the high spot of the journal and the bearing and the two surfaces tend to become welded with appreciable heat generation causes prevents motion. This is known as seizure. If motion proceeds with removal of some metal from one of the surfaces the result is known as "scuffing".

Seizure and scuffing generally are delayed by the fact that the formation of film on the metal surfaces prevents the metal to metal contact temporarily. The useful materials for boundary lubrication should have:

(i) Long hydrocarbon chain such as fatty acids i.e. stearicacid, oleic acid palmitic acid, etc. (ii) Active functional groups which can form chemical bonds with the metals or other surfaces (iii) lateral attraction between the chains (iv) polar groups to promote spreading or wetting over the surface (v) good oiliness (vi) high viscosity Index (vii) low pour and oxidation, and (viii) resistance to heat and oxidation.

Lubricants used for boundary lubrication are graphite and molybdenum disulphide either alone or stable suspension is also suitable for boundary lubrication. Then meterials reduce friction between metallic surfaces by forming films on the surfaces and they can bear compression and also high temperature. Other materials such as mineral oils, vegetable oils and animal oils with thin soaps are also suitable for boundary lubrication mainly due to their better oiliness. They are thermally stable and physically adsorbed to metal surfaces (or) react chemically at the metal surfaces, forming a thin film of metallic soap which acts as lubricant.

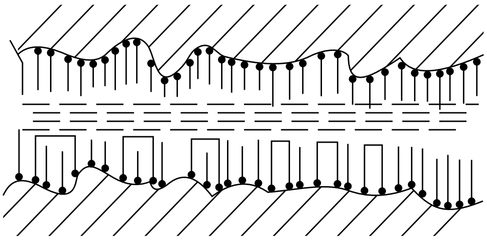


Fig. 4.16 *Mechanism of a boundary lubrication*

(c) Extreme Pressure Lubrication The moving/sliding surfaces are subjected to high pressure, and speed, excessive frictional heat will be generated under these conditions of high load, temperature, ordinary thick film or boundary film lubricants are not so effective due to decomposition (or) evaporation. To provide effective lubricants under these extreme conditions, special additives called "Extreme pressure additives" are used along with the lubricants. Chlorinated esters, sulphurised oils and tricresy phosphate are examples for extreme pressure additives. The chemical reactions with these additives at prevailing temperature to form solid surface film of metallic chlorides, sulphides or phosphides. These films can withstand very high loads and temperature due to higher melting point, i.e. iron chloride 1200°F, iron sulphide: 2150°F.

They serve as good lubricant under extreme pressure and extreme temperature conditions. The additional advantage in these lubricants that if the low shear strength film formed on the moving parts are broken by the rubbing action, they are replenished immediately.

Applications of extreme pressure additives are:

(i) Wire drawing of titanium only into wire in the presence of a chlorine containing additive which reacts with the stable oxide film of the metal surface.

(ii) In machining of tough metals, cutting fluids are used as lubricants. The typical lubricant consists of hydrocarbon oil, a small amount of fatty acid as boundary lubricant and an organic chloride (or) sulphide additive is fed into the cutting surface.

(iii) In the 'hypoid' gears used in the rear axle drive of cars which as both longitudinal sliding motion and normal rolling moment.

4.6.4 Properties of Lubricants

A large number of substances are available to be utilised as lubricants in various type of machines. The selection of a lubricant for a specific application is based on the properties of the lubricant. Some of the important properties of lubricants which are generally tested are given below:

(i) viscosity
(ii) flash and fire points
(iii) cloud and pour point
(iv) aniline point
(v) neutralisation number
(vi) mechanical strength.

(i) Viscosity Viscosity is one of the important properties of a lubricating oil. It is the property of the fluid that determines its resistance to flow. Viscosity is measured in terms of viscosity coefficient. The coefficient of viscosity is defined as 'force per unit area required to maintain a unit velocity gradient between two parallel layers'. The unit of viscosity is poise. Less viscous lubricants having low viscosity are generally employed for bearings subjected to high speed and low pressure. On the other hand, low speed and high pressure bearing requires lubricants which have high viscosity.

For sewing machines, light lubricating oils having low viscosity are useful while for heavy trucks, thick viscous liquids having high viscosity.

Measurement of Viscosity It can be measured with the help of viscometer. Redwood viscometer is used to measure the viscosity of lubricating oils. For determining viscosity of thin lubricating oils, Redwood Viscometer No. 1 is used. It has an orifice of diameter 1.62 mm and length of 10 mm. For measuring viscosity of heavy viscous oils, Redwood Viscometer No. 2 is used. It has an orifice of diameter 3.8 mm and length of 15 mm.

Redwood Viscometer No.1 consists of the following parts:

(i) *Oil cup:* A cylindrical brass oil cup (90 mm height and 46.5 mm in diameter). The bottom of the cylinder is fitted with an agate jet (of diameter 1.62 mm and length 10 mm). The jet is opened or closed with the help of valve rod. It has small silver plated brass ball at the end. Oil is to be filled in the cylinder up to the level of pointer. A thermometer is fitted to the lid which gives the oil temperature.

(ii) *Heating bath:* Oil cup is surrounded by a water bath fitted with a thermometer and stirrer. Thermometer indicates the temperature of waters.

(iii) *Stirrer:* Stirrer has four blades for stirring to maintain uniform desired temperature. It also has shield at the top to prevent water splashing into the oil in the cylinder.

(iv) *Kohlrausch flasks:* A calibrated receiving flasks called Kohlrausch flask is provided for receiving the oil from polished agate discharge tube.

(v) *Spirit level and levelling screws:* For levelling of instrument, the lid of the cup is provided with a spirit level. The entire apparatus rests on a tripod stand with levelling screws.

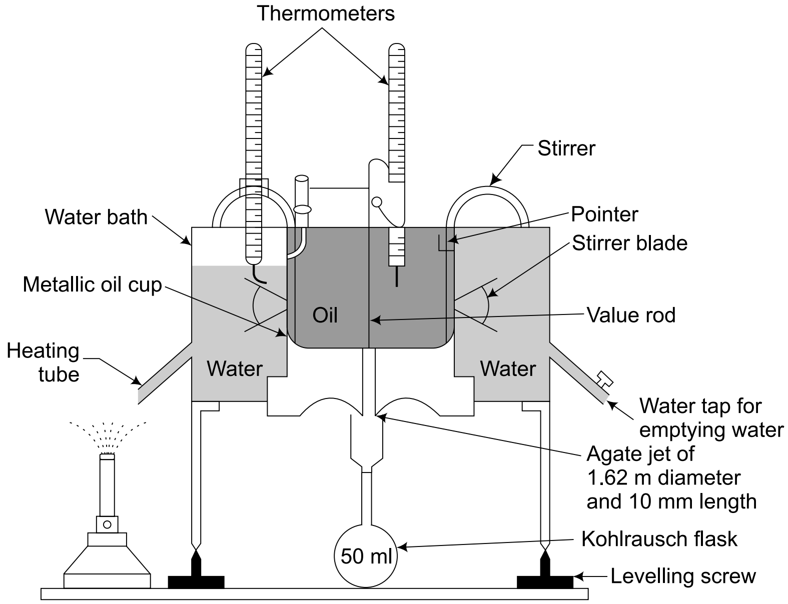


Fig. 4.17 *Redwood viscometer no. I*

Working Procedure The oil to be tested is filled in the oil cup to the pointer level after the ball of valve rod is placed on the agate jet to close. The Kohlrausch's flask is kept below the jet outlet to collect the oil. Water is filled in the water bath and heating is initiated. When the oil reaches desired temperature, stop the heating and remove valve from jet hole. Time taken to collect 50 ml of oil in the flask is noted. The result is expressed in Redwood No. 1 seconds at the definite temperature. It is observed that higher the flow of time, lesser is the viscosity of the oil.

Viscosity Index A good lubricating oil should not change with operating temperature. It is found that viscosity of liquids decreases with increasing temperature. As a result, the lubricant will become thinner. Hence, viscosity of a good lubricating oil should not change much as it will change the temperature also.

The rate at which the viscosity of an oil changes with temperature is measured by an arbitrary scale "viscosity index".

The rate of variation of viscosity with temperature is different for different base oils or fluids. A relatively small change in viscosity with temperature is indicated by high viscosity index, whereas low viscosity index shows relatively large change in viscosity with temperature. The Pennsylvanian oil consisting mainly of paraffins is arbitrarily assigned a viscosity index (VI) value of 100 which shows little variation of viscosity with a rise in temperature. Oils of Gulf-coast origin consists mainly. They are of alicyclics (naphthenes), are arbitrarily assigned a viscosity index value of zero as they possess a higher change in viscosity with a rise in temperature.

The viscosity index of test oil is measured with the help of two types of standard oils namely Pennsylvanian oil and Gulf oils having VI's 100 and 0 respectively.

$$VI = \frac{L - U}{L - H} \times 100$$

where VI = viscosity index of the oil under test

L = viscosity of Gulf oil at 100°F and also having same viscosity as the oil under test at 210°F

U = viscosity of oil under test at 100°F

H = viscosity of Pennsylvanian oil at 100°F having VI, 100 and also having the same viscosity as the oil under test 210°F.

The viscosity index of lubricating oils can be increased with addition of certain polymers which are partially soluble in the oils. By adding correct composition of polymer, it is possible to produce oil-polymer blends possess slight temperature coefficient of viscosity or is negligible.

(ii) Flash and Fire Points A good lubricating oil should not be volatile in working temperature. Under working conditions of lubrication, if some volatilisation takes place, the formed vapour should not form inflammable mixture with air. Under these circumstances, flash and fire points are so significant for lubricants.

The flash point of a lubricating oil is defined as 'the minimum or lowest temperature at which the oils give off enough vapour to ignite for a moment when a tiny flame is brought near it'. Lubricants with higher flash points are preferred to avoid any kind of explosions.

The fire point of lubricating oil is defined as 'the lowest temperature at which vapour of the oil burns continuously for at least 5 seconds when a tiny flame is brought near it.'

A good lubricant should have flash point above the temperature than the operating temperature. In majority of the cases, the fire points of an oil are about 5° to 40°F higher than its flash points.

Determination of flash and fire points The flash and fire points are usually measured by Pensky Martens apparatus.

It consists of an oil cup of about 5 cm in diameter and 5.5 cm depth with a led providing four open. A thermometer and stirrer are introduced in two openings respectively and for air passage as well as introducing of flame, the rest of openings are used. It also provides shutter operating by lever mechanism and air-bath.

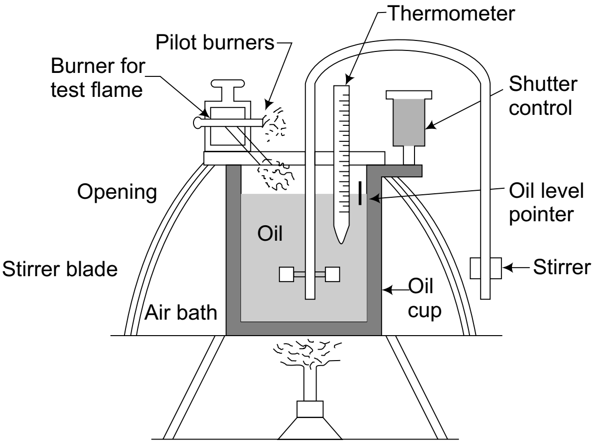


Fig. 4.18 *Pensky-Marten's flash point apparatus*

Working Oil under examination is filled in the oil cup up to the mark and heated by heating air bath using a burner. The stirrer helps to keep the oil heat uniform. Heat is applied so as to raise the temperature at about 5°C per minute. Test flame is introduced through opening in shutter for every 1°C rise in temperature. The temperature at which there is ignition for a moment is recorded as 'flash point'. The heating is continued at the rate of 4–5°C per minute. The temperature at which the oil ignites and continues to burn for a period of at least 5 seconds is noted and recorded as fire point of the oil.

(iii) Cloud and Pour Point Petroleum oils are complex mixtures of chemical compounds and do not show a fixed freezing point. The cloud point is the temperature at which solidifiable compounds such as paraffin, wax in the form of a cloud or haze is noticed, when the oil is cooled in a standard apparatus at a standard rate.

The pour points of petroleum oil is defined as "the temperature at which oil ceases to flow or pour".

The cloud and pour points reveal the suitability of lubricating oils in low temperature. The lubricant should have low cloud and pour point at the working conditions, i.e. lower than the operating temperature of the machine.

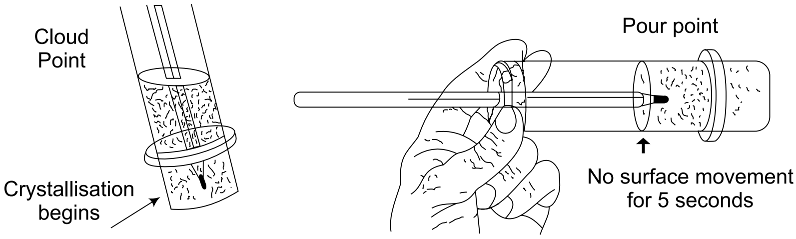


Fig. 4.19 *Cloud and pour points*

Cloud and pour points are determined with the help of pour point apparatus. It has a flat bottom tube of 3 cm diameter and 12 cm height. This is kept in an air jacket which is cooled surrounded with freezing mixture (ice + $CaCl_2$). Thermometers are fixed in the mixture and in the oil. The tube is half filled with oil. With the help of a thermometer, temperature is noted for every 1°C fall tube is withdrawn for a moment to find out the cloudiness. The point at which cloudiness is noticed is recorded. The cooling is continued and the same procedure is repeated. The temperature at which the oil does not flow for 5 seconds even when kept in horizontal, that temperature is recorded as pour point.

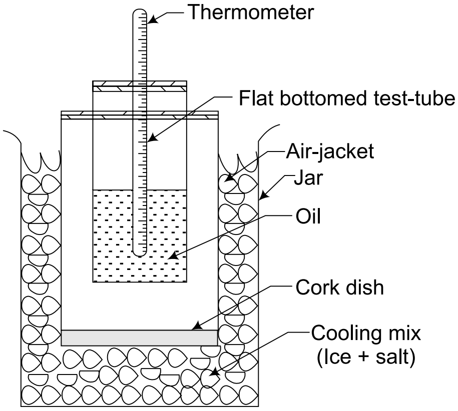


Fig. 4.20 *Cloud and pour point apparatus*

(iv) Aniline Point It is defined as 'the lowest equilibrium solution temperature at which equal volume of lubricating oil dissolves in equal volume of aniline.

It is determined by taking equal volume of aniline and lubricating oil into a test-tube and heating the mixture until a homogeneous solution is obtained. Then, it is allowed to cool at a controlled rate. The temperature at which oil and aniline separate is recorded as Aniline Point.

Aniline point gives an indication of the possible deterioration of an oil in contact with rubber sealings, packing, etc. Aromatic hydrocarbons have a greater tendency to dissolve rubber, hence low aromatic content in lubricating oil is desirable. Hence, lubricants with higher aniline points are preferred.

(v) Neutralisation Number It is also called 'acid number or value'. It is defined as 'the number of milligrams of KOH required to neutralise free acids in 1g of oil'. A lubricating oil should possess an acid value less than 0.1. The acid values higher than 0.1 show that the oil has been oxidised, which will lead to corrosion in addition to gum and sludge formation.

A good lubricant is that which should not possess acidity and is not liable to be oxidised to an acid.

(vi) Mechanical Strength The suitability of a lubricant under the condition of very high pressure in different mechanical tests are conducted. One of such test is four balls extreme pressure lubricant test, where the lubricant under test is placed in a machine containing four balls. The lower three balls are stationary and the upper ball is rotated. The balls are withdrawn to examine the scale formation, at specific intervals, after imposing heavy load gradually. For a good or satisfactory lubricant under the given load, all the balls bearings tests come out clear. When the load is progressively increased, and if the liberated heat causes the weld the balls, then the lubricant is said to have failed. This test is carried out to examine the maximum load that can be conducted safely with a lubricant.

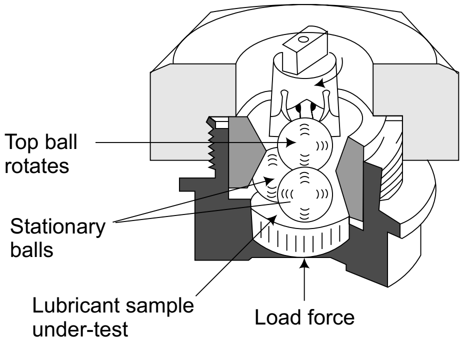


Fig. 4.21 *Four Ball extreme pressure lubricant tester*

4.6.5 Selection of Lubricants

The selection of lubricant for the specific purpose is made on the basis of service conditions required and properties of lubricant. The properties of selected lubricant should not vary under working conditions. The principal consideration of working requirements for selection of lubricant includes:

(i) Speed of moving parts
(ii) pressure between moving parts
(iii) Presence of moisture
(iv) Temperature of operation and type of lubricant system.

Thus a good lubricant will provide an oil film between moving/rolling parts, withstand at high pressure, without leakage, with resist corrosion, action of water, oxidation and carbonisation, will retain the enough fluidity at low temperature and without attack on the metal surfaces. Selection of lubricant for a few typical job purposes are described below:

1. *Lubricants for Internal Combustion Engines:* In I.C engines, the lubricant is to be exposed to high temperature reaching during the combustion cycle. Therefore, the lubricant should have high viscosity index (VI) and high thermal stability. Hence petroleum oils with additives impart high viscosity index and oxidation stability are used as lubricants for I.C. engines.

2. *Lubricants for Cutting Tools:* Cutting fluids are the lubricants used in cutting metal tools for performing machine operations like cutting, sewing, turning, drilling, etc. The main function of cutting fluids are:
   (i) To cool the cutting tool and the working environment.
   (ii) To provide lubrication action between the tool and the job work.
   (iii) To carry away any matter produced in machine operations
   (iv) To protect the final finished product from corrosion and rust.
   (v) To give a fine finish with the cutting tool during operation, when grinding (or) machining operations is carried out with cutting tool, lot of heat is produced due to friction between the tool and work. Consequently, temperature of tool and work increases considerably if the generated heat is not reduced, the edges of the tool may be broken. Under these conditions, cutting fluid help in reducing friction between the tool and work as well as removal of generated heat which enable the cutting tool withstand for longer time with cutting action.

   For the cutting tool purpose, heavy oils, soluble in water are used as cutting fluids. The soluble oils are formed by heating an oil with NaOH (or) alkali. They emulsify and miscible with water in all proportions. Lard oil is considered as good cutting tool fluid but has high cost. But generally used by mixing with vegetable and mineral oils.

   - The mineral-lard oil used in machining of copper alloy (or) for turning steel.
   - Lard oil mixed with kerosene is used for aluminium and many other metal cutting.
   - Ordinary mineral oils used for light cutting operations.
   - An emulsion of oil in soap is used for cutting of brass.
   - Sulphurised oils are used for the tougher and harder bronzes and brasses.

3. *Lubricants for gears:* The lubricants in gear system subjected to extreme pressure. Hence it should possess (i) good oiliness (ii) not to be squeezed from the centrifugal forces from the place of application area (iii) resistant to oxidation and (iv) heavy load bearing capacity.

   Keeping in view of the above conditions, thick lubricating mineral oils with extreme pressure additives like metallic soaps and chlorides, sulphur (or) phosphorous compounds are used for lubrication of gears.

4. *lubricants for refrigeration system:* The lubricants which are employed for refrigeration system should have (i) low viscosity (ii) low cloud point, and (iii) low pour point Naphthalene-base oils are generally used which are fulfilling these properties. The viscosity range is 85 to 325 SUS (Say bold Universal Seconds) at 100°F. The pour point requirement for lightest grade and heaviest grade oils are – 40°F and – 13°F respectively.

4.7

ROCKET PROPELLANTS

Rocket propellants are the mixture of fuel and oxidant whose combustion takes place in a definite time and controlled manner with production of huge volume of gas.

A propellant reacts quickly and produces a large volume of hot gases at a temperature of 3000°C and a pressure of 300 kg/cm^2. The evolved hot gases exit through a nozzle at highest velocities, i.e., 2–3 km/sec facilitating upward movement of the rocket, according to Newton's third law of motion.

4.7.1 Characteristics of a Good Propellant

The important characteristics of rocket propellants include:

(i) They should produce low molecular weight products (H_2, CO, CO_2, N_2, etc.) during combustion.

(ii) They should burn at slow and steady rate producing high temperature.

(iii) They should possess high density.

(iv) They should be non-hygroscopic and non-corrosive.

(v) The time taken by the propellant to catch fire in the presence of oxidizing agent is called 'ignition delay'. A good propellant should possess a low ignition delay.

(vi) They should not leave any solid residue after combustion.

(vii) They should not evolve toxic products during burning.

4.7.2 Classification of Rocket Propellants

These are generally classified into (a) solid, and (b) liquid propellants.

(a) *Solid Propellants* It may be homogeneous or composite.

The homogeneous solid propellant is a solid propellant or mixture of propellants thoroughly mixed in a colloidal state. They are of two types:

(i) *Single base propellant* Nitrocellulose

(ii) *Double base propellants* Containing a binary mixture of propellants in colloidal state. For example, Ballisite which is a mixture of nitrocellulose and nitroglycerine. Cordite (65% nitrocellulose + 30% nitroglycerine + 5% petroleum jelly)

Composite solid propellants are heterogeneous solids containing oxidising agents dispersed in the fuel mass. For example, Gun powder.

Common oxidising agents are KNO_3, $KClO_4$ and NH_4ClO_4 incorporated in a PVC or Thiokol rubber.

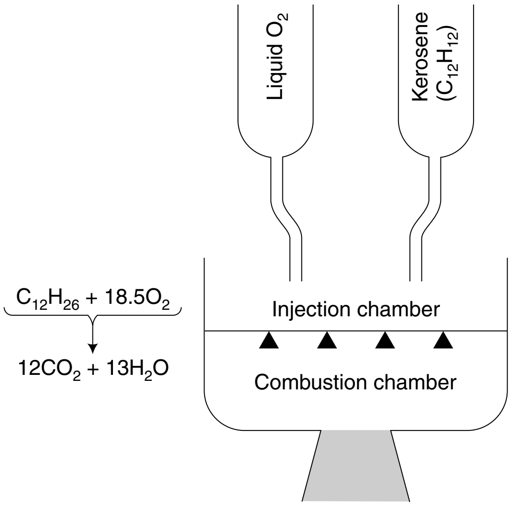


Fig. 4.22 *Bipropellant in rocket*

(b) *Liquid Propellants* They have greater advantage, versatility and high specific impulse but are difficult to handle and store safely. The liquid propellants may be monopropellants or bipropellants.

Monopropellant They have the fuel and oxidiser available in the same molecule or as a solution of both.

For example, Nitro methane, hydrogen peroxide, hydrazine, ethylene oxide and a mixture of 21.4% methanol and 78.6% hydrogen peroxide.

Bipropellant contains the liquid fuel and oxidiser is kept separately and injected into the combustion chamber.

For example, Liquid hydrogen, hydrozine, kerosene, aniline, ethyl alcohol and ammonia, etc.

The common oxidisers are liquid oxygen, ozone and hydrogen peroxide.

Comparison of Solid and Liquid Propellants

S.No.	*Solid propellant*	*Liquid propellant*
1.	They can be easily handled, safely stored and transported.	1. They have handling, storage and transport problems.
2.	Manipulation with solid propellants is difficult.	2. They are more versatile.
3.	They have low specific impulse.	3. They have higher specific impulsion.
4.	They are economical in use.	4. They are less economical in use.
5.	It is difficult to calibrate and check the engine using solid propellants.	5. It is easy to calibrate and check the engine using liquid propellants.
6.	The engine used has a simple design.	6. The engine used are more delicate and can't withstand any rough handling.

4.8

NANOMATERIALS

Nano chemistry is a new discipline concerned with unique properties and associated with arrangement of atoms/molecules on a nanoscale range (between 1–10 nanometres) between that of individual building blocks. It also plays an important role in the synthesis of nano-building blocks of desired shape, composition, size and surface structure with optical target and controls self-assembly of these building blocks at different scale lengths.

The term ‘nano’ stands for 1 billionth of a metre in a physical scale length. Nano chemistry is defined as ‘the study of synthesis and analysis of materials in nanoscale range (1–10 nanometres) including large organic molecules, inorganic cluster compounds and metallic or semiconductor particles’.

Synthesis of nanoscale inorganic and organic materials is important because small size endows these particles with unusual structural and optical properties which find numerous applications in catalysis and electro-optical devices. For example, the electronic structures of metal and semiconductor crystals differ from the isolated atoms and bulk materials. Even metals show non-metallic band gaps in 1–2 nm sized nano crystals in the case of ‘Ag’ clusters (band gap decreases with an increase in cluster size). In a similar way, nano sized (1–2 nm) gold metal particles exhibit unusual catalytic activity.

The synthetic way for preparation of nanomaterials that are inspired by biological processes results in the deposition of inorganic materials such as bones, teeth and shells. The deposition and growth of inorganic materials through biological processes such as bones and teeth is called ‘Biomineralisation’.

The use of nanomaterials had been recognised even in the fourth century A.D. Roman glass makers fabricated coloured articles of glass, embedded with nano particles of silver and gold. Some of the important developments in the area of nanotechnology in the chronological order are as follows:

- Fabrication of nanosized quantum wells in 1970 by thin fibres expitaxial technique
- Synthesis of fullerenes (C_{60})
- Invention of Scanning Tunnelling Microscope (STM) and atomic force microscope (AFM) for viewing
- Characterisation and manipulation of nano structures
- Fabrication of single electron transistor
- Synthesis of carbon nanotubes, development of photonic crystals, molecular switches and fixed effect transistors during 1990s.

Some of the examples of nanomaterials are:

(a) nano particles of ceramic oxides, semiconductors and magnetic materials
(b) nano crystals and clusters of metals, quantum dots
(c) nano wires and rods of metals and semiconductor oxides, nitrides and sulphides

(d) carbon nano tubes, layered metal chalcogenides
(e) nano porous solids of zeolites and phosphate
(f) super lattices of three-dimensional structures of metals, magnetic materials and semi-conductors.

These materials have potential applications in materials technology, nanoelectronics, information technology, medicines and semiconductors.

4.8.1 Classification of Nanomaterials

Nanomaterials are classified into 3 types based on atoms/molecules array:

(a) Materials with one dimension in the nano scale.

For example, Thin films, surface coatings

(b) Materials that have two dimensions in nano scale.

For example, Nanowires, nano-tubes, Biopolymers, inorganic nano tubes

(c) Materials in 3 dimension in nano scale are quantum dots

For example, Tiny particles of semiconductors materials such as nanometre sized grains, fullerenes, nano particles, dendrimers.

4.8.2 Properties of Nanomaterials

The properties of nanomaterials depend on size, crystal structure and surface characteristics. The two principal factors for the properties of nanomaterials to differ significantly from other materials are: (i) to increase relative surface area, and (ii) quantum effect. These two factors can change or enhance properties such as reactivity, strength, electrical properties and optical characteristics.

(a) *Size:* Nano crystals have a large surface area. Colloidal particles have a large surface area and remain single crystalline and hence are named as nanocrystals. For example, Nano crystals of 10 nm size (containing about 1000 atoms) have approximately 15% of its atoms on the surface and smaller nano crystal of 1 nm size will be about 30% of its atoms on the surface. Hence, size of crystal is important for available active surface area.

(b) *Catalytic activity:* Catalytic activity of nano particles in the form of colloids and nano clusters have been investigated in a wide variety of reactions in homogeneous and heterogeneous phases. For example,

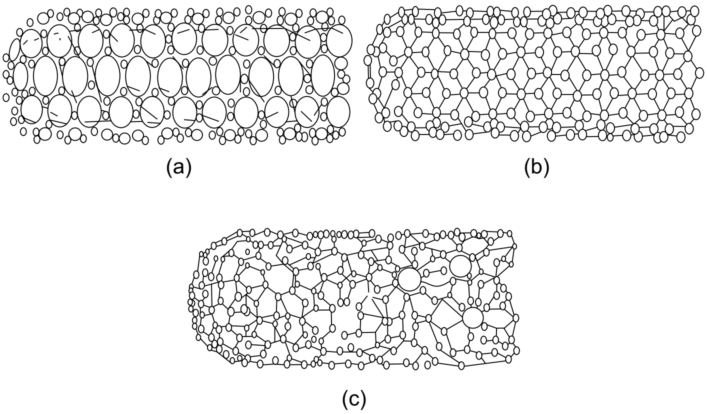
  (i) Rhodium hydrosols have been shown to be effective catalyst for hydrogenation of Olefins dissolved in organic phase.

  (ii) Palladium colloids have been shown to catalyse reactions in reduction of carbon–carbon multiple bonds in presence of formic acid. It is also used in reduction of nitriles and nitroarenes.

  (iii) Cortex catalyst, i.e., palladium metal nano particle (10 nm) on alumina support shows high catalytic activity for olefins hydrogenations.

  (iv) MoS_2 has shown catalytic activity for methanation of $CO + H_2$ at low temp.

(c) *Electrical properties:* Nanomaterials shows electrical properties vary between semiconducting to metallic depending upon the diameter and chirality of the molecules. For example, carbon nano tubes reveal electrical properties and act as semiconducting and metallic nature on the basis of chirality and diameter of a tube. Carbon nano tubes have been identified and show three structures, namely, arm chair, zigzag and chiral structure (see Fig. 4.23)



(a) (b)

(c)

Fig. 4.23 *Structures of carbon nanotubes: (a) arm chair, (b) zigzag, and (c) chiral*

If ($n - m$) is a multiple of 3, the tube is metallic, otherwise, the tube is semiconductor metallic. Nano tubes have high electrical conductivity, to be about billion amperes/cm^2 (much higher than copper wires).

The high electrical conductivity of nano tubes is mainly due to negligible amount of defects and hence, they possess low resistance. Nano tubes of MoS_2 and WS_2 have shown semiconductors at low temperature due to electrical conductivity.

(d) *Mechanical properties:* Nanomaterials exhibit unusual mechanical properties. For example, the tensile strength of carbon nano tube is about 604 pa (i.e. > 20 times that of steel). They are among the stiffest and strongest fibres known.

(e) *Optical properties:* Nanomaterials that are provided large surface area exhibit better optical properties. For example, silicon nanowires show strong photoluminescence characteristics. Indium phosphide nano wire shows isotropic photoluminescence with lot of applications in constructing polarisation sensitive photodetectors. Zinc oxide nano wire exhibits room temperature ultraviolet laser action.

(f) *Semiconductors:* Most of the nanomaterials exhibit semiconductivity properties. For example, carbon nanotubes, nanowires, some metal oxides (MoS_2 and WS_2) and inorganic nanotubes show, semiconductor properties. Semiconductor nano wires can be used as components in making field effect transistors, $P - n$ diodes, bipolar junction transistors and complementary invertors.

(g) *Superconductors:* There are some nanomaterials which show superconductivity properties. Nanotubes of NbS_2 and $NbSe_2$ are metallic in nature with $NbSe_2$ becomes a superconductor at low temperature.

Some of the important nanomaterial structures and their applications are shown in Figs 4.24 to 4.27.

Certain statistical information on producing of nano materials and universities involved in the research as on 2003 is shown in Figs 4.28 and 4.29.

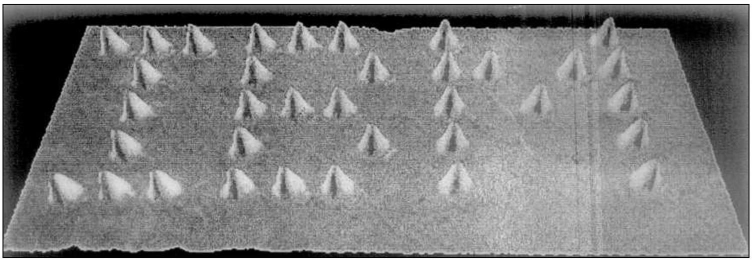


Fig. 4.24 *IBM researchers manipulating xenon atoms scanning tunnelling microscope to move 35 xenon atoms to spell out the letters "IBM"*

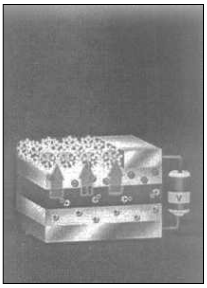


Fig. 4.25 *Graphical representation of a rotaxane useful as a molecular switch*

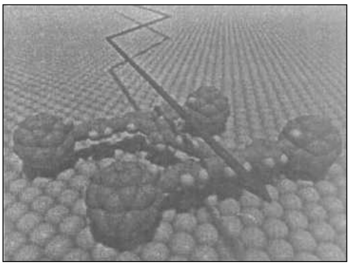


Fig. 4.26 *Space-filing model of the nanocar on a surface, using fullerenes as wheels*

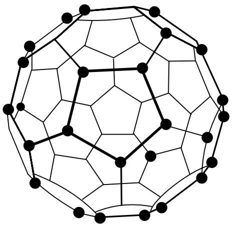
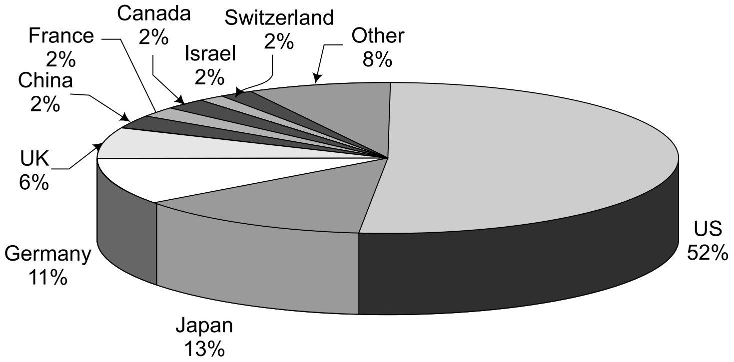
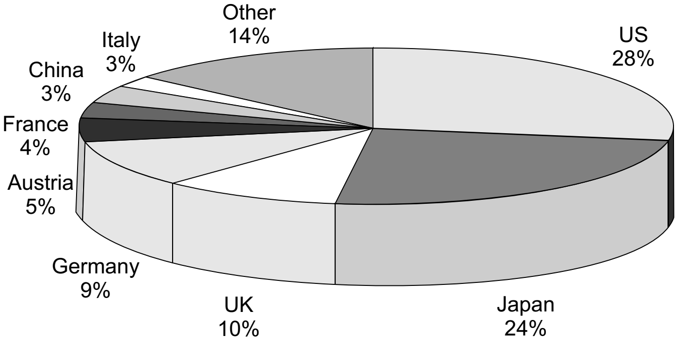


Fig. 4.27 *Structure of fullerene*



Note: Other includes Australia, Netherlands, Taiwan, Austria, Sweden, Finland, Korea, Russia, Italy, and Spain.
Source: Cientifica 2003.

Fig. 4.28 *Percentage of companies producing nanomaterials by country (as of June 2003)*



Note: Other includes Australia, Spain, Sweden, Switzerland, Belgium, Netherlands, Israel, Poland, Russia and Taiwan.
Source: Cientifica 2003.

Fig. 4.29 *Percentage of universities and institutions involved in nano-research by country (as of June 2003)*

4.8.3 Applications of Nanomaterials

Nanomaterials show potential applications because of their unusual and unique properties. Nano particles, nano tubes, nano rods and nano wires show the following applications:

(i) Nano particle

(a) These are used as important catalyst in hydrogenation and catalysis.
(b) As zero-dimensional quantum dots, one-dimensional quantum wires and in plannar arrays of ordered structures, they have been used in the design of new super computers.
(c) Magnetic nano particles have potential applications in magneto optical storage and magnetic drug transport.

(d) Nano particles are potential components in the generation of biometallic nanostructures and nanomechanical devices based on DNA.

(ii) Carbon Nano Tubes (CNT)

(a) Nano tube field emission transistors for use as switching components in computers.
(b) Protective shield against electromagnetic radiation due to high electrical conductivity and poor transmitters of electromagnetic radiation.
(c) They act as sensors of gases such as NO_2 and NH_3 on the basis of increase in electrical conductivity when NO_2 was allowed to flow over CNTs.
(d) They act as storage device in lithium batteries. This is due to every lithium atom stored for every six carbon atoms of CNT and hence, it can be used to store the charge carrier, lithium in lithium batteries.
(e) Field emission light devices for fluorescent displays.
(f) Quantum wires made up of metallic carbon nano tubes exhibit high electrical conductivity.
(g) Reinforced elements in composites. For example, Al powder mixed with CNT (5%) had greater tensile strength than rod of 'Al'.
(h) The nano tubes of MoS_2 and WS_2 used as solid lubricants. Boron nitride nano tubes show insulators with a wide range of band gap.

(iii) Nano rods of nano wires

(a) Silicon nano wires shows photoluminescence.
(b) Zinc oxide nanowires exhibit ultravoilet laser at room temperature.
(c) Semiconductor nanowires used in making of field effect transistor.

(iv) Other applications of nanomaterials and their uses

(a) Sunscreens, cosmetics, coating on surfaces, hard cutting tools.
(b) Fuel cells, displays, batteries, catalysts.
(c) Magnetic materials, lubricants, machinable ceramics, military bottle suits.

4.8.4

NEW FORMS OF CARBON

Carbon is one of commonest substances on earth and it is widely distributed in nature. Carbon has two type of allotropes, namely graphite and diamond. The third allotrope form of carbon was accidently discovered by Robert F. Furl, Harold W. Kroto and Richard E. Smalley. The discovery of this new form of pure carbon and the insight that lot of properties observed in terms of hollow carbon molecules.

(i) Fullerenes The discovery of C_{60} has a long and very interesting history. It is a new form of carbon called fullerene. The structure of fullerene was Cage and Richard Smalley succeded in building it. They named C_{60} as Buckminister fullerene because of similarity of the structure to be geodesic structures widely credited to R. Buckminister fuller. Because of this work, Harold W. Kroto, Richard E. Smalley and Robert P. Furl were awarded the Nobel prize in chemistry is 1996. The fullerenes are even number of Sp^2 hybrid carbon atoms over the surface of a closed hollow cage. The structure of C_{60} as shown in Fig. 4.30.

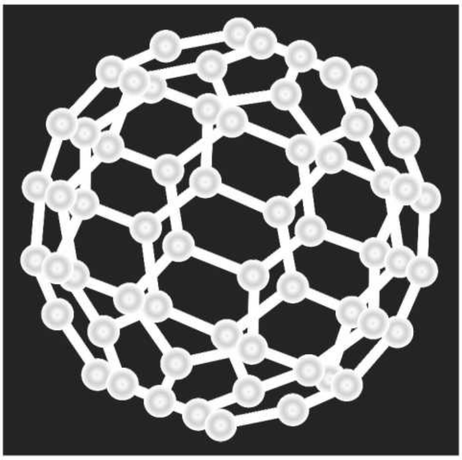


Fig. 4.30 *C_{60} fullerene*

Properties of fullerenes Unlike graphite and diamond fullerenes are closed-cage carbon molecules consisting of a number of five membered rings and six membered rings. The structure of C_{60} is truncated icosahedron which looks like a soccer ball with 12 pentagons and 20 hexagons. The bonds in C_{60} have two kinds. The bond length in a pentagon is 1.45 Å and that a bond between pentagons is 1.40Å. At room temperature the solubility of C_{60} is 2.8 mg/ml in toluene. As the size increases, the heat of sublimation of fullerene increases. Fullerenes are ready to reduce and hence it acts as good oxidising agent. It is unstable at higher temperature. C_{60} is a very poor conductor of electricity but when react with reducing agent (alkali) the resulting compound has high electrical conductivity and even become super conducting.

Preparation of fullerenes Fullerenes can be prepared in simple processes. Graphite rods are vapourised in an inert atmosphere (Helium), by passing a high electric current through them. This produces a light condensate called fullerene soot which contain variety of different fullerenes. The fullerenes can be extracted through toluene. Separation and purification can be achieved by column chromatography.

Applications Because of wide range of magnetic and conducting properties, fullerene has the following applications.

1. Microelectric devices, 2. Non-linear optical devices, 3. Micro-electronic devices, 4. Soft ferromagnetic materials, and 5. Superconductors.

(ii) Carbon Nano Tubes Carbon nano tubes also called Bucky tubes which is allotrope of carbon with a cylindrical nano structure. It was discovered by S. Limija in 1991. Nano tubes are the members of the fullerene structural family which includes the sperical buky balls. Their name is derived from their size since the diameter of a nano tube is in the order of a few nano metres (~1/50,000th of the width of a human air). Nano tubes characterised as single-walled nano tubes (SWNTs) and Multi-walled Nano-tubes (MWNTs).

The chemical bonding of a nano tubes is based on Sp^2 hybridisation similar to those of graphite. This bonding structure which is stronger than Sp^3 bonds found in diamonds provide the molecules with their unique strength. Nano tubes naturally align themselves into "ropes" held together by van der Waals forces.

Properties

(i) *Strength*: CNTs are the strongest and stiffest materials in terms of tensile strength and elastic module. A multi-walled carbon nano tube was tested and found tensile strength 63 giga pascals (GPa).

(ii) *Hardness*: The diamond is considered as hardest meterial. But synthesis of a super-hand material by compressing SWNTs to above 24 GPa at room temperature. The hardness of this material was measured with a nano indenter as 62–152 GPa. The hardness of reference diamond and Boron nitride samples was 150 and 62 GPa respectively. The bulk modules of compressed SWNTs was 462–546 GPa surprising the value of 420 GPa for diamond.

(iii) *Thermal conductivity*: All are expected to be very good thermal conductors along the tube, exhibiting a property known as "Ballistic conduction". Experimental results show that SWNT has at room temperature thermal conductivity along its axis of about 3500 $W.m^{-1} K^{-1}$. Compare this to copper metal well known for its good thermal conductivity which transmits 385 $W.m^{-1} K^{-1}$. But SWNT has a room temperature thermal conductivity across its axis of about 1052 $W.m^{-1} K^{-1}$ which is comparable thermal conductivity of soil.

(iv) *Temperature stability*: CNTs is estimated to be up to 2800°C in vacuum and about 750°C in air of temperature stability.

(v) *Defects*: CNTs defect is the "Stone wales defect" which creates a pentagon and heptagon pair by rearrangement of the bonds. Crystallographic defects also affect the tube's eletrical properties.

(vi) *Toxicity*: Determining the toxicity of CNTs has been one of the most pressing question in nano technology. Based on the available data show that under some conditions nano tubes can cross membrane barriers, which causes inflammatory fibrotic reactions.

A study led by Alexandra Porter from University of Cambridge shows that CNTs can enter into human cells and accumulate in the cytoplasm causing cell death.

4.9
INSULATORS

Insulators are the materials employed to minimise the loss of electricity through certain parts in an electrical system. If insulation is the main function, then materials are called ‘insulators’ and if charge storage is the main function, they are called ‘dielectrics’. Insulators offer high resistance to the flow of electric current mainly due to tightly bounded valency electrons resulted zero electrons flow through them at normal voltages. In addition to insulation property, it also provides mechanical support to the conductors and is useful in the transfer of heat which minimising excessive heat accumulation in the apparatus.

4.9.1 Characteristics of Insulators or Dielectrics

A good insulating material should possess the following characteristics properties:

1. ***Resistivity*** It is defined as the resistance offered by a unit cube of the material or it is reciprocal of conductivity. A good insulator should have low conductivity or high resistivity. Insulators have resistivity ranging between 10^9 to 10^{20} ohm-cm at room temperatures.

   For example, Glass: 10^{15} ohm cm, Mica: 9×10^6 ohm-cm, Quartz: 5×10^{19} ohm-cm; Copper: 1.7×10^{-12} ohm-cm.
2. ***Dielectric Constant*** It is the quantitative measure of the ability of a material to store electric charge in presence of applied electric field. Dielectric constant is expressed as the ratio of the capacitance of a capacitor filled with dielectric material to the capacitance of same capacitor under vacuum. Dielectric constant should be low for a good insulator.
3. ***Dielectric Polarisation*** Charge separation of dielectrics under the electric field is called dielectric polarisation. If ‘Q’ is the charge collected in the presence of an applied voltage V, then the capacitance of material is

   $$C = Q/V$$
4. ***Dielectric Loss*** This is caused mainly by internal dipole fraction and by leakage of current through the material. Dielectric losses should be minimum for an ideal insulator.
5. ***Thermal Expansion and Contraction*** A good insulating material possesses least thermal expansion and contraction, which leads to gaps in the insulator.
6. ***Porosity*** Porosity of insulating materials causes increase of moisture holding capacity leading to adverse an effect on the electrical properties. Hence, dielectrics of high porosity are not used.

7. ***External Chemical Effects*** Insulating material should be chemically inert towards oils, acids, solvents and alkalis.
8. ***Dielectric Strength*** The ability to resist puncture or rupture of an insulating material with the applied electric field is called Dielectric Strength, expressed in volts/mm. Dielectric strength decreases with increase of thickness of material, humidity and temperature. In the case of liquid insulators, it increases with increase of viscosity. For ideal insulating material, it should have high dielectric strength.
9. ***Not Prone to Chemical Change Itself*** Chemical alteration may take place by some material during its use. But such changes should not deteriorate the properties of insulating materials.

4.9.2 Some Insulating Materials and their Applications

(a) Simple Gases Gases like air and nitrogen are considered as insulating materials.

- *(i) Air* It is considered as an important dielectric gas which provides insulation between the overhead transmission lines without any cost and maintenance charge.
- *(ii) Nitrogen* When chemical resistance or inert medium is needed, nitrogen is a very important gas in place of air since it causes oxidation. This is used in transformers. High pressure nitrogen is used as dielectric in electrical capacitors.
- *(iii) Electronegative gases* They have high dielectric strengths than normal gases such as air and nitrogen. For example, SF_6 is 2.35 times and CCl_4 is 6.33 times than that of air. Further, these are non-explosive and non-inflammable. SF_6 is used in electrical devices like capacitors and cables.

(b) Liquid Insulating Materials These are used mainly for pure dielectric purpose to eliminate air or other gases particularly as an insulating cum heat transfer medium. Some of the liquid insulating materials are mentioned below:

- *(i) Mineral oils* They have a better insulating property which is greatly influenced by the presence of non-hydrocarbon compounds nitrogen, oxygen, sulphur, etc. They have low dielectric constant (~2.5) and are used in the transformers.
- *(ii) Askarels* Askarels are non-inflammable and synthetic insulating liquids which do not decompose under the influence of electric arc. They are used as transformer fluids. Some of the examples are chlorinated diphenyl, pentachloro diphenyl and trichloro benzene.
- *(iii) Fluorinated fluids* They are non-inflammable, non-explosive and have very high chemical stability. These are better substitute of mineral and silicone fluids for heat transfer from the windings and magnetic circuits. They are used in small-sized electric and radio devices, electronic transformers, etc.

(iv) Silicone fluids For dielectric applications, combination of properties are required and fulfilled by silicone fluids and not found in other synthetic and natural materials. They are clear water-like liquid with a wide range of viscosity. Outstanding insulating properties are possessed by silicone fluids and they are stable at higher temperatures especially non-corrosive to metals up to 200°C. They are used as coolants for radio transformers, air crafts and radar pulse.

(v) Vegetable oils These are the oldest insulating liquids used, with a low price. They are drying oils such as linseed oil and tung oil used in the formation of insulating varnishes (used in the transformers and motor coils). The non-drying oils such as castor, coconut olive and peanut are known popular plasticisers in insulating resin components used in electrical equipment as structural and insulating materials.

Table 4.6 *Some insulating liquids and their operating temperatures*

S.No.	*Insulating liquid*	*Temperature range in which used*
1.	Mineral oil	– 50 to 110°C
2.	Askarels	– 50 to 110°C
3.	Fluorinated liquid	– 50 to 200°C
4.	Silicone fluids	– 90 to 220°C
5.	Synthetic hydrocarbons	– 50 to 110°C
6.	Organic esters	– 50 to 110°C
7.	Vegetable oils	– 20 to 100°C

(c) Solid Insulating Materials Most of the non-metals such as mica, paper, asbestos, polymers and silk are considered as solid insulators. All the materials are capable of retaining their insulating properties up to a definite temperature called limiting temperature.

Table 4.7 *Solid insulating materials with limiting temperature*

S. No.	*Insulating materials*	*Limiting temperature (°C)*
1.	Cellulose materials: cotton, silk and papers which are not impregnated	90
2.	Impregnated paper, silk, cotton, and polyamide resins with moderate heat resistance materials	105
3.	Fibrous materials like asbestos and fibre glass impregnated with varnish of ordinary heat resistance	130
4.	Mica, ceramics, glass, teflon, my clax and soapstone	> 180
5.	Enamelled wire insulation on polymer resin base	120
6.	Polymer resins bonded with high resistance varnish or compound	155
7.	Asbestos, mica, fibre glass impregnated with silicones and silicone rubbers etc.	180

Synthetic polymers are used as excellent insulators for low temperature operations but undergo softening at higher temperatures. They are used as thin films and in chokes, capacitors, electrical bushes and telephones. Teflon used as best insulator could withstand above 180°C with dielectric constant (2.0). For high voltage operations, epoxy resins possess excellent mechanical and electrical properties. Glass, ceramics and refractories are rigid insulators used in lightening systems and metal claddings. Zircon and alumina porcelains are used in spark plug cores.

Bitumen resins and drying oils are considered as insulating varnishes and also help in stopping ageing of cheaply available materials like paper and cotton.

4.10

THERMAL INSULATORS

Substances which possess extremely low thermal conductivities are known as thermal insulators. The principal purpose of thermal insulators is to reduce loss of heat in the form of convection, conduction or radiation. The thermal insulators are used, when (a) the flow of heat has to be stopped from the outside environment to the equipment or plant operating at low temperatures, and (b) the flow of heat has to be stopped from a furnace or heat generating plant to the outer environment.

Thermal insulators are used in refrigerators, cold storage rooms, steam carrying pipes, brine pipelines, ovens, boilers, etc.

4.10.1 Characteristics of an Ideal Thermal Insulator

Some important functions of thermal insulators are as follows:

1. It should be fireproof.
2. Thermal conductivity should be low.
3. It should have enough load bearing capacity under working conditions.
4. It should be chemically stable to surrounding environment at high temperature.
5. Its density should be low.
6. It should have very low or should resist moisture absorption.
7. Physically and mechanically, it should be stable at working temperature.

Thermal insulating materials are of two types. They are (i) organic such as wool, cotton, cattle hair, wood pulp, paper, charcoal, coke powder and cellular rubber suitable for low temperature work, and (ii) inorganic thermal insulator such as asbestos paper, fibrous-glass bonded with resin powder, laminated asbestos and glass-fibres suitable for higher temperature insulation works.

Table 4.8 *Thermal conductivities of organic thermal insulators at 20°C*

S. No.	*Insulating materials*	*Thermal conductivity (in Cal/Scm^3°C/cm)*	*Apparent sp.gr. (g.cm^{-3})*
1.	Wool	0.000086	0.110
2.	Cattle hair	0.000090	0.176
3.	Silk	0.000107	0.100
4.	Cork board	0.000103	0.160
5.	Wood pulp	0.000115	0.259
6.	Sawdust	0.000137	0.336
7.	Cotton wool	0.00009	0.080
8.	Leather	0.000038	0.998
9.	Coke powder	0.000456	–
10.	Charcoal powder	0.000128	0.248

Table 4.9 *Inorganic thermal insulators and their operating temperature*

S. No.	*Insulating materials*	*Maximum temperature (°C)*
1.	Asbestos paper	150
2.	Fibrous-glass bonded with resin powder	225
3.	85% magnesia + 15% asbestos	325
4.	Laminated asbestos sponge	375
5.	Asbestos fibre	400
6.	Glass-fibres	550
7.	Anhydrous calcium silicate	975
8.	Porous silica	1,100
9.	Clay bonded mineral wool	1,100
10.	Refractory insulating bricks	1,400

4.11

EXPLOSIVES

An explosive is defined as "a substance or mixture when subjected to thermal or mechanical shock, it gets very rapidly oxidised exothermically into products of potentially increased volume with a sudden release of potential energy".

The amount of power able to be produced from a given weight volume of explosive is called "power to weight/volume ratio". The power to volume ratio is small for gases while liquids and solids have better power ratio.

4.11.1 Characteristics of Explosives

(i) It should be cheap and stable under natural conditions.

(ii) It must have at least one chemical bond which can be easily broken or the molecule should have low dissociation energy.

(iii) The rate of decomposition should be fast to produce large volume of gaseous products exothermically.

(iv) It should have positive oxygen balance. The oxygen balance indicates oxygen, available in the molecule, which can be utilised to oxidise the carbon and hydrogen into CO_2 and water respectively.

4.11.2 Classification of Explosives

Normally explosives are classified into three broad groups as given below:

(a) Primary or initiating explosives
(b) Low explosives or propellants
(c) High explosives

(a) Primary or Initial Explosives or Detonators These are sensitive and explode on receiving even a slight shock or fire. Hence, they should be handled with utmost care. Detonators are used in small quantities in cartridges and shells to start or initiate the explosion of the main explosive which is relatively less sensitive. The explosion of a detonator is initiated by spark, flame or sharp blow and normally happens in two stages of deflagration and detonation. Deflagration is the actual process of burning with a flame, which further changes result into detonation on the basis of burning conditions.

Some of the examples of detonators and their uses including Lead azide (PbN_6), mercury fluminate ($Hg(CNO)_2$) and diazido dinitrophenol (DDNP). Lead azide has excellent initiating actioned storage stability and low cost. It is used for military purpose. DDNP is used mostly in commercial blasting caps as it can initiate explosion even in less sensitive high explosive.

(b) Low Explosives or Propellants These are basically explosives which normally burn and do not explode suddenly. The combustion reaction is relatively slow compared with detonators. The evolved gases in the combustion readily disperse without building high pressure, ultimately they can be controlled easily.

Examples of low explosives are: (i) Gun powder or Black powder, (ii) Cordilte, and (iii) Nitrocellulose or Smokeless powder.

Gun powder is a mixture of potassium nitrate (75%), charcoal (15%) and sulphur (10%). These are not explosives but on sparking, the mixture explodes due to redox reaction as follows:

$$10KNO_3 + 3S + 8C \rightarrow K_2SO_4 + 3K_2S_2 + 4CO_2\uparrow$$

$$4K_2CO_3 + 7S \rightarrow K_2SO_4 + 3K_2S_2 + 4CO_2\uparrow$$ (excess sulphur slow the reaction)

$$4K_2SO_4 + 7C \rightarrow 2K_2CO_3 + 2K_2S_2 + 5CO_2\uparrow$$ (excess carbon, more CO_2 slow the reaction)

The excess of carbon and sulphur leads to generation of more CO_2 gas by volume by using K_2CO_3 and K_2SO_4.

Nitrocellulose is a smokeless explosive called cordite giving off CO, CO_2, N_2 and water vapour.

(c) High Explosives These are more energetic than detonators and insensitive to mechanical shock and fire. High explosives are further subclassified into four groups (i) single compound explosives which contain only one chemical entity, (ii) binary explosives, (iii) plastic explosives, and (iv) dynamites.

(i) *Single compound explosives:* They contain only one chemical compound. For example, Ammonium nitrate, 2, 4, 6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), RDX or cyclonite, chemically known as cyclotrimethylenetrinitramines picric acid (Trinitrophenol), Tetryl (nitroaryl nitroamine).

(ii) *Binary explosives:* Basically they are a mixture of TNT with other explosives. TNT is an important ingredient.

For example, Amotol (a mixture TNT + Ammonium nitrate (50–80%))
Pentolite (a mixture of 50% TNT + 50% PETN)
Tetrytol (a mixture of 70% Tetryl + 30% TNT)
Tropex (a mixture of 40% RDX + 40% TNT + 20% Al powder)
Titronol (a mixture of 80% TNT + 20% Al flakes)

(iii) *Plastic explosives:* These are combination of explosives which in plastic state can be hand-moulded to various shapes without much risk. They are mainly used for industrial applications and military uses. For example, PETN or RDX mixed with oil/wax, moulded into desired shape such as flexible sheet or putty like mass without any rests.

(iv) *Dynamites:* Explosives containing nitroglycerene as the main ingredient are called dynamites.

$$4C_3H_5(NO_3)_3 \rightarrow 10H_2O\uparrow + 6N_2\uparrow + 12CO_2\uparrow + CO_2\uparrow$$

It is an oily liquid and detonates at 50°C or by shock. With the above reaction, one volume of dynamite will be converted into 10,000 volumes. Hence, it is always mixed with an inert absorbent such as starch, sawdust or wood pulp.

The strength of dynamites vary with % of absorbent. They are as follows:

(a) Straight dynamites: 50–60% nitroglycerine in wood + Na_2NO_3

(b) Blasting gelatin dynamites: 91.5%, nitroglycerine + 8% nitrocotton + 0.5 $CaCO_3$

(c) Gun cotton: Nitrating the cotton with conc. H_2SO_4 + conc. HNO_3

$$C_6H_7O_2(OH)_3 + 3HNO_3 \rightarrow C_6H_7O_2((NO_3))_2 + 3H_2O.$$

(d) Cordite: Gun cotton (65%) + nitro glycerine (30%) and petroleum jelly (5%) in acetone.

4.11.3 Precautions during Storage of Explosives

Explosives produce enormous amount of energy and hence, utmost care must be taken while storing. Some of the precautions are as follows:

(i) Different explosives should be stored in separate boxes.
(ii) Detonators and explosives should be stored in separate containers.
(iii) During power failure, any flammable source should not be used in any case.
(iv) In the storage place, electric fittings and wiring should be properly insulated and checked time to time.
(v) The explosive stores must be strictly prohibited from smoking/firing within a radius of 50 m.
(vi) Necessary caution on explosive related activities should be given on notice boards and watch men should guard round the clock.

4.11.4 Blasting Fuses

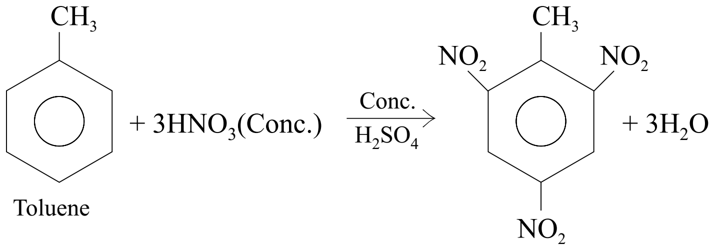
A fuse is defined as 'a thin water-proof canvas length of tube containing gun powder arranged to burn at a given speed for setting off charges of explosive'. They are of two types:

(i) Safety fuse: It is used in initiating caps where electrical firing is not used. For example. Black powder with wrapper of water proof fabrics (speed is 30–40 sec/ft.).
(ii) Detonating fuse: It has a speed of over 6,000 m per second and consists of a charge of high velocity explosive such as TNT in a small bent tube.

4.11.5 Important Explosives

Some of the most important explosives are as follows:

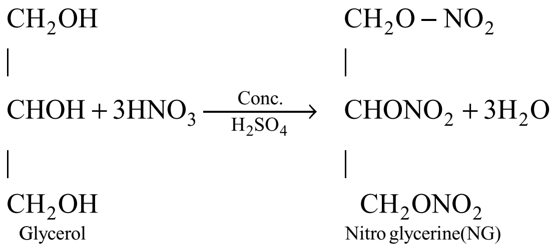
(a) Trinitrotoluene (TNT) It is prepared by the reaction between toluene and nitration mixture.



TNT is crystallised after washing with ammoniacal solution of Na_2SO_3 followed by cold water.

Uses Widely used in shell firing, under water explosions and military purpose.

(b) Nitro Glycerine It is prepared with the addition of glycerol to a cold mixture of 60% conc. H_2SO_4 and 40% conc. HNO_3 at 10°C by constant stirring.



$$\begin{array}{lcl} CH_2OH & & CH_2O-NO_2 \\ | & & | \\ CHOH + 3HNO_3 & \xrightarrow[H_2SO_4]{Conc.} & CHONO_2 + 3H_2O \\ | & & | \\ CH_2OH & & CH_2ONO_2 \\ \text{Glycerol} & & \text{Nitro glycerine(NG)} \end{array}$$

It is separated and washed with water then with dil. Na_2CO_3 (6%) to remove traces of acids. It is dangerous to handle and safety transport. It is mixed with inert absorbent (wood pulp, saw dust, etc.)

Uses Blasting of hard rocks, coal and other minerals and submarine blasting.

4.11.6 Uses of Explosives

Explosives can be used for constructive as well as destructive purpose. Some of the important usefulness of explosives are as follows:

(i) For breaking coal, quarrying limestone, bauxite, granite, etc.
(ii) In making of roads and tunnels particularly in hill zones
(iii) For blasting of ores of iron and other metal ores
(iv) To manufacture bombs, grenades, etc.
(v) As an ammunition in water
(vi) For launching of satellite with the help of rocket.

Short Answer Question

1. What is a Superconductor?

   Ans. A substance which offers no resistance to the passage of electricity

2. Give any two applications of superconductors.

   Ans. (i) Producing low power consuming super conducting Magnets,
   (ii) In Magnetic-hydrodynamic power generators to maintain plasma.

3. How does conductivity of a semiconductor vary with temperature?

   Ans. With increasing temperature, the density of hole-electron pairs increases and correspondingly the conductivity increases.

4. Differentiate between intrinsic and extrinsic semiconductor

   Ans. The conductivity of an intrinsic semiconductor is due to existence of vacant conduction band separated by a small energy gap filled valence band while conductivity of an extrinsic semiconductor is largely due to the presence of an acceptor or donor impurity with appropriate energy level.

5. Define portland cement

   Ans. Finely powdered mixture of calcium silicates and calcium aluminates of varying compositions.

6. What are Puzzolona cements

   Ans. Materials which when mixed lime form hydraulic cementing materials.

7. Which constituent of cement causes its initial setting.

Ans. Tri calcium aluminate (3CaO Al_2O_3)

8. Define refractoriness:

Ans. It is the ability of material to with stand high temperature, without appreciable deformation in shape or softening under particular operating condition.

9. Define cement

Ans. A material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks, etc.

10. What are the classification of Refractories

Ans. Based on the chemical properties, refractories are classified into 3 categories.

(i) Acidic refractories
(ii) Basic refractories
(iii) Neutral refractories

11. What are the characteristics of a good refractory?

Ans. A good refractory must posses:

(i) be infusible at the temperature to which it is to be exposed
(ii) be chemically inert by actions of corrosive gases, molten metals, slags etc produced in furnaces.
(iii) be resistant to the abrasing action of flue gases, flames, slages etc
(iv) no crack and suffer loss in size at operating temperature

12. Write short note on functions of lubricants

Ans. (i) It reduce frictional resistance
(ii) It reduce wear, tear and surface deformation
(iii) It act as coolant by reducing the loss of energy in the form of heat
(iv) Lubricant prevents rust and corrosion

13. What is neutralisation number?

Ans. The number of miligrams of KOH required to neutralise free acids in 1g of oil is called neutralisation number. It also called "acid number"

14. Define the Rocket Proplent.

Ans. Rocket proplents are the mixture of fuel and oxidant whose combustion takes place in a definite time and controlled manner with production of huge volume of gas.

15. Write the characteristics of good propellant

Ans. (i) They should produce low molecular weight products (H_2, CO, CO_2, N_2) during combustion
(ii) They should burn at low and steady rate producing high temperature
(iii) They should posses high density
(iv) They should not evolve toxic products during buring
(v) They should be non-hygroscopic and non corrosive

16. Define a lubricant

Ans. Any substance used between two moving or sliding surfaces to reduce frictional resistance between them is known as lubricant.

17. What are the properties of lubricant?

Ans. The properties of lubricants Viscosity, flash and fire points, cloud and pour point, aniline point, neutralisation number and mechanical strength. These are important for testing of lubricant.

18. What is meant by lubrication?

Ans. The process of reducing frictional resistance between moving or sliding surfaces by the introduction of lubricant in between them is called lubrication.

19. Define viscosity.

Ans. Viscosity is the property of the fluid by virtue of which it offers resistance to its own flow.

20. What is flash and fire point?

Ans. The lowest temperature at which the oils lubricant gives off enough vapours to ignite for a moment, when a tiny flame is brought near to it. Fire point is the lowest temperature at which the vapour of the oil burns continuously for at least five seconds, when a tiny flame is brought near to it.

Review Questions

Short Type Questions

1. Define the semi conductor? Give suitable example.
2. What is meant by conductivity materials? Write its few applications.
3. What are the magnetic materials? Give some examples.
4. Write short note on Ferromagnetic materials.
5. What is composition of cement?
6. Explain the mechanism of setting in cement?
7. What are refractories? Write their classification.
8. Define a lubricant?. What are its characteristics?
9. What are the important properties of Lubricants?
10. Write the characteristics of good propellant?
11. What is meant by rocket propellant? How it is useful.
12. Write short note on paramagnetic under load?
13. Explain briefly about refractoriness under load?
14. What is aniline point? Give its significance.
15. Define viscosity? What is its significance?
16. What is meant by lubrication process?
17. What are synthetic lubricants?
18. Distinguish between solid and liquid rocket propellants?

Essay Type Questions

1. What is portland cement? Explain the different ingredients of cement?
2. Give an account of
   (a) chemical composition of cement
   (b) chemical constitution of Portland cement.

3. By writing the various chemical reactions involved, explain the setting and hardening of cement.
4. Write a brief account on the following?
   (a) The raw materials and the ingredients of cement
   (b) Function of gypsum in cement.
5. Explain the analysis of cement.
6. Define refractories. What are the characteristics of a good refractory?
7. Give the classification of refractories with examples.
8. What is pyrometric cone equivalent? How it is determined for a refractory?
9. Define refractories? Write short note on the following
   (i) Refractoriness
   (ii) Refractoriness under load or strength
   (iii) Dimensional stability
   (iv) Thermal spalling
   (v) Thermal conductivity
   (vi) Porosity.
10. Write a note on the conditions leading to failure of a refractory material.
11. Explain the chemistry of the manufacture of cement by wet process.
12. What is cement? How do you classify the cement?
13. How is Portland cement manufactured by dry process?
14. (a) Define flash and fire points
    (b) Discuss the important functions of lubricants.
15. Write a note on lubricants with special reference to their classification, mode of action, examples and applications.
16. (a) Describe thick-film lubrication.
    (b) Write a note on semi-solid lubricants.
17. Write notes on: [16]
    (a) blended oils
    (b) petroleum oils
    (c) extreme pressure additives
    (d) antioxidants.
18. Define lubricant. Discuss the important properties of the lubricating oils.
19. Write notes on semi-solid lubricants.
20. (a) Explain the following terms:
    (i) cloud and pour points
    (ii) flash and fire points.
    (b) Explain how the following act as lubricants
    (i) graphite
    (ii) molybdenum disulphide.
    (c) Write an explanatory note on semi-solid lubricant.
21. (a) Explain calcium-base, soda-base and lithium based greases.
    (b) Write a note on solid lubricants.
22. Discuss the various types of liquid lubricants.
23. Discuss solid lubricants.
24. How to select lubricants for the following:
    (a) cutting tools
    (b) IC engines
    (c) steam engines
    (d) steam turbines
    (e) gears.

25. (a) Give the functions of lubricants.

(b) How is a viscous lubricant converted into grease?

26. Discuss the important properties of lubricating oils which are useful for their evaluation.

27. Discuss any four essential properties of a good refractory in detail.

28. Give the functions of lubricants.

29. (a) Explain calcium-base and lithium based greases.

(b) Write a note on solid lubricants.

30. Write notes on semi-solid lubricants.

31. Write notes on lubricants with special reference to their classification, mode of action, examples and applications.

32. How is a viscous lubricant converted into grease?

33. Define the term 'lubricant'. Mention their important functions. Explain and discuss the significance of any two properties of lubricants.

34. (a) What is a nano particle? How are they fabricated.

(b) Write an account on carbon nano tubes?

35. (a) What are fullerens and give an account of their applications.

(b) Write the application of carbon nano tubes.

36. (a) What is the effect of nanotechnology on food science.

(b) What are advancement of nanotechnology is referred to as nano medicine.

37. (a) How are lubricants classified? Give an examples.

(b) Explain the boundary film lubrication theory and mechanism of lubricants.

38. What are nano tubes? Give its properties.

39. What is meant by nanomaterials? Explain some of its important properties.

40. Write a brief note on the application of nanomaterials.

41. Define nanomaterials with suitable examples? How are nanomaterials classified? Give suitable examples.

42. What are nano particles? Explain their characteristic properties.

43. What are explosives? List out the important requirements of chemical explosives?

44. Define an explosive? How are explosives classified? What are the important requirements for a good explosive?

45. What is meant by deterioration? Explain with a suitable example.

46. Write short notes on (a) dynamites (b) TNT (c) cordite.

47. Write short notes on (i) high explosives (ii) detonators (iii) propellants.

48. What are rocket propellants? How are they classified? What is the criteria for the selection of a propellant?

49. What is meant by mono and bipropellants used in Rockets? Explain with an example.

50. Write short notes on:

(i) classification of propellants (ii) rocket propellants

(iii) liquid and solid propellants.

51. What is meant by an explosive? What are the different precautionary measures for storage of explosives?

52. What are fuses? Give examples.

53. What is meant by a lubricant? Explain its important functions.

54. What are lubricants? How are they classified on the basis of their physical state? Write a note on solid lubricants?

55. What are the characteristics required for a good lubricant?

56. Describe the following properties of lubricants and explain their significance.

(i) viscosity (ii) viscosity index

(iii) aniline point.

57. Write short notes on:

(i) cloud and pour point (ii) fire point and flash point.

58. What are solid lubricants? Where can they be used? Explain briefly about graphite.

59. What are greases? Give their characteristics.

60. Give an account of flash point and fire point of a lubricant ? Explain one method of determination of flash point and fire point.

61. (a) Define pour and cloud point? What are their significance?

(b) What is meant by neutralisation number? How is it relevant to lubrication oils?

62. What are the different types of greases? How are they prepared?

63. What are liquid lubricants? How are they classified? Give examples for each.

64. What are the important properties of a solid lubricant? Explain MoS_2 solid lubricant.

65. Write informative notes on:

(a) mineral oils (b) semisolid lubricants

(c) solid lubricants.

66. How do viscosity and viscosity index influence the selection of lubricants for a particular purpose?

67. What is the criteria for selection of lubricant in case of cutting tools and gears.

68. Write short note on the lubricant used in Internal Combustion Engine.

69. Write short notes on extreme-pressure lubrication.

70. Write short notes on (i) Hydrodynamic lubrication with its mechanism (ii) Fluid Film lubrication (iii) Boundary film lubrication.

71. What is lubrication? Explain any one type of lubrication mechanism in details.

72. Explain extreme-pressure lubrication and additives to improve the lubrication properties.

73. (a)What are thermal insulators? Give their characteristic properties.

(b) Differentiate between electrical insulators and dielectrics.

(c) Outline the important applications of thermal insulators.

74. Write briefly about the following:

(i) Silicone fluids and (ii) SF_6 in electrical industry.

75. (a) Differentiate between the different types of insulating materials.
(b) Explain the use of silicone fluids as insulating materials.

76. (a) Explain the importance of various gaseous insulators.
(b) Write briefly about liquid insulating materials

77. (a) Write a note on askarels.
(b) Write a note on electrical insulators.

78. (a) How do you classify insulators? Explain your answer with appropriate examples.
(b) Explain the importance of various gaseous insulators.
(c) Write briefly about liquid insulating materials.

79. (a) Differentiate between the different types of insulating materials.
(b) Explain the use of silicone fluids as insulating materials.

80. (a) Write a note on liquid insulating materials.
(b) Write a note on askarels.

81. (a) Write a note on askarels.
(b) Explain the difference between thermal and electrical insulators.
(c) Write briefly about the applications of these two types of insulators.

82. (a) Write a note on thermal insulators.
(b) Write a note on liquid insulating materials.
(c) Write an essay on the thermal insulators with special reference to its characteristics and engineering applications.

83. What are the characteristics of electrical insulators?

84. What are insulators? How are they classified? Give suitable examples to each.

85. Write briefly note on thermal insulators.

86. Define the terms
(i) Dielectric loss (ii) Dielectric constant
(iii) Dielectric strength.

87. (a) What are dielectrics? Discuss their important characteristics.
(b) Discuss the importance of gaseous insulators.

88. What are the important characteristics of thermal insulators?

Multiple Choice Questions

1. Major component of Portland cement is
(a) CaO (b) MgO
(c) $3CaO \cdot SiO_2$ (d) SiO_2.

2. Which of the following constituents of cement contain least heat of hydration
(a) C_2S (b) C_4AF
(c) C_3A (d) C_2A.

3. The main raw materials required for the manufacture of Portland cement are
(a) lime stone + clay
(b) lime stone + sand
(c) alumina + sand
(d) clay + sand.

4. When lime is exposed to air, it slowly absorbs
(a) nitrogen (b) oxygen
(c) carbon dioxide (d) sulphur.

5. Tobermonite gel is chemically
(a) hydrated tricalcium silicate
(b) hydrated tricalcium aluminate
(c) hydrated dicalcium silicate
(d) slaked lime.

6. Which of the following constituent of cement has least setting time?

(a) dicalcium silicate
(b) tricalcium silicate
(c) tricalcium aluminate
(d)tetracalcium aluminate.

7. The high percentage constituent in cement is

(a) tricalcium aluminate
(b)dicalcium aluminate
(c) dicalcium silicate
(d) tricalcium silicate.

8. The chemical formula for lime stone is

(a) $MgCO_3$ (b) $CaCO_3$
(c) Na_2CO_3 (d) Li_2CO_3.

9. The chemical formula for gypsum is

(a) $MgSO_4 \cdot H_2O$
(b) $CaSO_4 \cdot 2H_2O$
(c) $CaCl_2$
(d) $CaCO_3$.

10. An inorganic material that can withsand high temperatures without softening or suffering any deformation in shape is called

(a) cement (b) refractory
(c) glass (d) chalk.

11. Which of the following refractories is neutral?

(a) magnesite (b) silica
(c) dolomite (d) graphite.

12. A good refractory material must

(a) possess low softening temperature
(b) undergo spalling
(c) be chemically inactive
(d) contain high thermal expansion.

13. Refractoriness of a refractory can be measured by

(a) pyrometric cone test
(b) acid test
(c) penetration test
(d) none of these.

14. Silica is an example of

(a) basic refractory
(b) acidic refractroy
(c) neutral refractory
(d) fusion.

15. In basic environment, preferably refractory should not be

(a) basic
(b) acidic
(c) neutral
(d) none of these.

16. An example of basic refractory is

(a) dolomite (b) silica
(c) magnesite (d) chromite.

17. Most important characteristic of a refractory material is its

(a) strength
(b) refractoriness
(c) spalling
(d) none of these.

18. Higher the pyrometric cone equivalent (PCE), is the softening temperature of refractory

(a) lower (b) higher
(c) zero (d) moderate.

19. Breaking, cracking or fracturing of a refractory under high temperature is called

(a) thermal spalling
(b) thermal expansion
(c) fusion
(d) cracking.

20. Porosity of a refractory—the abrasion resistance

(a) increases
(b) no change
(c) decreases
(d) none of these.

21. In nanomaterials, atoms/molecules are fabricated in nano scale range _______

(a) 1–10 nm (b) 100–120 nm
(c) 10–20 nm (d) 1–10 μm.

22. The term ‘nano’ stands for _______

(a) 1 billionth of centimetre
(b) 1 billionth of metre

(c) 1 billionth of foot
(d) none of these.

23. Who is the father of nanomaterials sciences?
(a) Graham Bell
(b) Dalton
(c) Richard Feynmen
(d) Newton.

24. Nanomaterials are classified into _______ types
(a) 2 (b) 1
(c) 5 (d) 3.

25. Which of the following is considered as one-dimensional in the nano scale?
(a) quantum dots
(b) carbon nano tubes
(c) Fullerenes
(d) thin films.

26. Nano wires and nano tubes are ______ in nano scale
(a) one-dimensional
(b) three-dimensional
(c) two-dimensional
(d) none of these.

27. Fullerenes and dendrimers are considered as _______ in nano scale
(a) one-dimensional
(b) three-dimensional
(c) two-dimensional
(d) none of these.

28. Which of the following important properties of nanomaterials differ significantly from other materials?
(a) increase surface area
(b) decrease surface area
(c) increase constant size
(d) none of these.

29. A nano crystal of 10 nm in size has approximately _______ of atoms on the surface.
(a) 80% (b) 20%
(c) 15% (d) 5%.

30. Which of the following materials are useful in catalyst for hydrogenation of olefins?
(a) Rani Ni
(b) Rhodium hydrosols
(c) Palladium
(d) Silica.

31. Which of the following nano materials show effective catalytic activity for methenation of CO + H_2 at low temperature?
(a) Palladium (10 nm)
(b) Palladium colloids
(c) MoS_2
(d) Rhodium hydrosols.

32. Zinc oxide nano wire exhibits at room temperature _______
(a) magnetic material
(b) ultraviolet laser
(c) storage device
(d) superconductor.

33. Which of the following nano wires show photoluminescence?
(a) zinc oxide
(b) semiconductor
(c) silicone
(d) carbon.

34. The nano tubes of MoS_2 and CoS_2 are used as _______
(a) semiconductors
(b) insulators
(c) storage device
(d) solid lubricants.

35. Which of the following nano-materials act as sensors of gases like NO_2 and NH_3 on the basis of increase in electrical conductivity?
(a) Carbon nano tubes
(b) thin film
(c) zinc oxide
(d) palladium.

36. Dynamite is the nitro compound of _______

(a) benzene (b) toluene

(c) glycol (d) glycerol.

37. TNT is the nitro compound of _______

(a) toluene (b) benzene

(c) cellulose (d) phenol.

38. Smokeless powder is an example of _______

(a) primary explosive

(b) high explosive

(c) low explosive

(d) initiating explosive.

39. TNT is used in making _______

(a) detonating fuses

(b) rocket propellant

(c) cordite

(d) safety fuse.

40. An example of primary explosive

(a) lead azide (b) dynamite

(c) TNT (d) cellulose.

41. A good propellant should

(a) have high specific impulse

(b) leave solid residue after impulsions.

(c) possess low density

(d) burn rapidly.

42. A propellant used in rocket engine is

(a) fuel

(b) oxidant

(c) both (a) and (b)

(d) none of these.

43. Low explosives are called

(a) propellants

(b) detonators

(c) primary explosives

(d) fuel.

44. Machines operating under high temperature and loads are lubricated by _______

(a) synthetic oil

(b) mineral oil

(c) grease

(d) solid lubricant.

45. Greases are not suitable for _______

(a) watches

(b) engine parts

(c) gear boxes

(d) instruments with bearings.

46. Lubricants are mainly employed to reduce _______

(a) abrasion (b) corrosion

(c) wearing (d) all of these.

47. Lubricant used in machines working at low temperature should have ____

(a) high pour point

(b) low pour point

(c) high flash point

(d) low flash point.

48. Graphite dispersed in oil is called _______

(a) dispersion lubricant

(b) graoil

(c) grease

(d) oildag.

49. Generally for liquid lubricants, _____

(a) flash and fire points are identical
(b)flash point > pour point

(c) flash point < fire point
(d)flash point > fire point.

50. A lubricant is a chemical substance used to _______

(a) reduce viscosity

(b) reduce frictional resistance

(c) increase thermal stability
(d)inverse dimensional stability.

51. The most suitable lubricant for watches and clocks is

(a) Bazel nut oil (b) grease

(c) palm oil (d) tallow oil.

52. Animal and vegetable oils _______

(a) are not oxidised easily

(b) have good oiliness
(c) are very cheap
(d) do not change viscosity in use.

53. The foremost important property of lubricating oil is its _______
(a) oiliness (b) cloud point
(c) viscosity index (d) fire-point.

54. The viscosity of liquids changes with respect to the temperature, which is expressed in terms of _______
(a) flash point (b) fire point
(c) viscosity index (d) pour point.

55. The possible deterioration of rubber sealings and packings in contact of lubricating oils is indicated by _______
(a) pour point (b) aniline point
(c) cloud point (d) flash point.

56. Which of the following exhibit ultra violet laser action at RT?
(a) MoS (b) ZnO
(c) WS_2 (d) NbS_2

57. Nano tubes of $NbSe_2$ is metallic in nature and act as _______
(a) Semiconductor
(b) magnetic material
(c) super conductor
(d) laser

58. The nano tubes of MoS_2 and WS_2 used as _______
(a) solid lubricants
(b) super conductors
(c) semi conductors
(d) catalyst.

59. A chemical substance which can act fuel as well or oxidiser is called _______
(a) bipropellant
(b) mono propellant
(c) low explosive
(d) high explosive.

60. Explosive containing nitroglycerine as principle ingradient it is called
(a) dynamite (b) TNT
(c) cordite (d) RDX

61. Amatol is mixture of _______
(a) TNT + RDX
(b) TNT + NH_4NO_3
(c) RDX + NH_4NO_3
(d) $N_2H_4 + N_2O_4$

62. Gun-cotton is a mixture of _______
(a) $N_2H_4 + N_2O_4$
(b) TNT + NH_4NO_3
(c) Cotton steeped in cold conc. HNO_3 + conc. H_2SO_4
(d) TNT + $NaNO_3$

63. Cyclomethylene trinitroamine is called _______
(a) TNT
(b) RDX
(c) Amatol
(d) Dynamite

64. Which of the following oil is suitable for thick film lubrication
(a) Petroleum oils
(b) Mineral oils
(c) Vegetable oils
(d) None of these

65. _______ type of lubrication is involved in delicate machines like watches, sewing machines, etc.
(a) Fluid film
(b) Thin film
(c) Extreme pressure
(d) None of these

66. Which of the following possess least oiliness
(a) Mineral oil
(b) animal oils
(c) vegetable oils
(d) greases.

67. Property of an oil to sticky onto the surfaces of machine parts under conditions of heavy load is called _______

(a) pour point
(b) oiliness
(c) viscosity
(d) emulsification.

68. Lubricants for internal combustion Engines should have _______

(a) low viscosity
(b) high viscosity index
(c) low viscosity index
(d) low pour point

69. For light cutting operations, _______ are used.

(a) ordinary mineral oil
(b) heavy oils
(c) lard oil
(d) vegetable oil.

70. Neutralisation number is also called _______

(a) Acid number
(b) Saponification number
(c) base number
(b) none of these

71. For determination of viscosity of thin lubricating oils _______ is used.

(a) Redwood viscometer-2
(b) Redwood viscometer-1
(c) viscometer
(d) Able apparatus

72. The _______ reveal the suitability of lubricating oil at low temperature

(a) Flash and fire points
(b) Cloud and pour points
(c) Neutralisation number
(d) Aniline point

73. _______ is commercially available as "MolyKotes"

(a) graphite
(b) tungston
(c) Molybdenum disulphide
(d) none of these

74. The suspension of graphite in oil is termed as _______

(a) aqua dag (b) oil dag
(c) emulsion (d) molyKotes

75. The oils with additives are called _______

(a) Mixed oils
(b) Mineral oils
(c) Blended oils
(d) none of these

76. A good electrical insulator should possess ________.

(a) high porosity
(b) high dielectric loss
(c) low dielectric constant
(d)high dielectric constant.

77. Sulphur hexachloride is ________

(a) inflammable
(b) non-toxic
(c) decomposes at 100 – 150°C
(d) is chemically, unstable.

78. Which of the following is inert gas to act as insulator?

(a) O_2 (b) CO_2
(c) N_2 (d) CO

79. Outstanding insulating properties of silicone oil is due to their ________.

(a) stability of high temperature
(b) oily consistency
(c) wide range of viscosity
(d) all of these.

80. A good thermal insulator should possess

(a) good thermal conductivity
(b) absorption of moisture capacity
(c) high density
(d) low thermal conductivity.

Answers

1. (a)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (a)
6. (c)	**7.** (d)	**8.** (b)	**9.** (b)	**10.** (b)
11. (d)	**12.** (c)	**13.** (a)	**14.** (b)	**15.** (b)
16. (a) or (c)	**17.** (b)	**18.** (b)	**19.** (a)	**20.** (c)
21. (a)	**22.** (b)	**23.** (c)	**24.** (d)	**25.** (d)
26. (c)	**27.** (b)	**28.** (a)	**29.** (c)	**30.** (b)
31. (c)	**32.** (b)	**33.** (c)	**34.** (d)	**35.** (a)
36. (d)	**37.** (a)	**38.** (c)	**39.** (a)	**40.** (a)
41. (a)	**42.** (c)	**43.** (b)	**44.** (d)	**45.** (a)
46. (d)	**47.** (a)	**48.** (d)	**49.** (c)	**50.** (b)
51. (a)	**52.** (b)	**53.** (c)	**54.** (c)	**55.** (b)
56. (b)	**57.** (c)	**58.** (a)	**59.** (b)	**60.** (a)
61. (b)	**62.** (c)	**63.** (b)	**64.** (a)	**65.** (a)
66. (a)	**67.** (b)	**68.** (b)	**69.** (a)	**70.** (a)
71. (b)	**72.** (b)	**73.** (c)	**74.** (b)	**75.** (c)
76. (c)	**77.** (b)	**78.** (c)	**79.** (d)	**80.** (d)

Fill Up the Blanks Questions

1. In Portland cement, weight of insoluble residue should not exceed ________.

2. ________ acts as a retarding agent for early setting of cement.

3. The process of solidification of cement consists ________ and ________.

4. Calcareous materials are rich in ________.

5. Argillaceous materials is rich in ________.

6. The chemical formulae of gypsum is ________.

7. ________ bricks are the most widely used refractories.

8. A refractory lining in a muffle furnace should possess ________ thermal conductivity.

9. High alumina bricks contain about 50–80% Al_2O_3 and 40–45% ________.

10. Refractories should have ________ electrical conductivity.

11. A good refractory should have ________ thermal expansion.

12. A good refractory should show ________ resistance to thermal spalling.

13. Refractories are chemically ________.

14. The refractoriness is measured in terms of ________.

15. Pyrometric cone equivalent (PCE) number of silica brick is________.

16. Zinc oxide nano wires show ________ at room temperature.

17. The two principal factors for the properties of nanomaterials ________.

18. Biopolymers and nano tubes come under ________.

19. The high electrical conductivity of nano tubes is mainly due to ________.

20. ________ are the stiffest and strongest fibres known.

21. The amount of power able to produce from a given weight of volume of explosive is called ________.

22. Initial explosives also called are ________.

23. Explosives containing nitroglycerine as the main ingredient are called ________.

24. The thickness of the film in thick film lubrication is ________.

25. The coefficient of friction for thin film lubrication is

26. Graphite act a solid lubricant mainly due to ________.

27. Cup-greases are also called as ________.

28. Pensky-Martin apparatus is useful for the determination of ________.

29. Capacity of stick on the surface of moving/rolling bodies is called ________.

30. Four ball extreme pressure test is for ________.

31. Extreme pressure additives are used for ________.

32. Lubricants for refrigeration is used ________ oils.

33. Possible detercoration of oil when in contact with rubber can be known with the help of ________.

34. Molybdenum disulphide act as solid lubricant due to ________.

35. Viscosity Index (VI) of Pensylvannian oil is ________.

36. Dielectric constant should be ________ for a good insulator.

37. Askarels are ________ which do not decompose under the influence of electric arc.

38. ________ are clear water like liquid with a wide range of viscosity.

39. ________ are the oldest insulating liquids.

40. For high voltage operations ________ are excellent mechanical and electrical properties.

41. Thermal insulators should have ________.

Answers

1. 2%

2. Gypsum

3. setting and hardening

4. lime

5. silica

6. $CaSO_4 \cdot 2H_2O$

7. Fireclay

8. high

9. SiO_2

10. low

11. less

12. high

13. inert

14. pyrometric cone equivalent (PCE)

15. 32

16. Ultraviolet laser

17. To increase relative surface area and quantum effect

18. Two dimensions is ratio scale

19. negligible amount of defects

20. carbon nano tubes

21. power to weight/volume ratio

22. detonators

23. Dynamites

24. 1000Å

25. 0.05–0.15

26. layered structure

27. calcium based greases

28. Flash and five points

29. oiliness
30. Mechanical stability
31. Heavy cutting
32. Naphthalene
33. Aniline point
34. Sandwich-like structure
35. 100
36. low
37. Synthetic insulating liquids
38. silicone fluids
39. vegetable oils
40. Epoxy resins
41. Low thermal conductivity

5

Water Treatment

5.1

INTRODUCTION

Water is an essential compound for survival. One can survive for weeks without food, but one can survive only for a few days without water. Water is an indispensable natural resource on this earth on which all life depends. It is not only essential for the lives of animals and plants but also occupies a unique position in many industrial processes. Most animals and plants contain a large portion of water (for example, the human body 70%, land plants 50–75% and aquatic plants 95–99%). Hydrated salts also contain water as 'water of crystallisation'. Water is required in large quantities for various industries like textiles, chemicals, pharmaceuticals, paper, food processing, leather and fertilizer industry. Its most important use as the engineering material is steam generation. It is also used as a coolant in power and chemical plants. Being a universal solvent, it is the important factor in determining the structure, function and distribution of an ecosystem.

5.2

SOURCES OF WATER

Surface water and ground water are the main sources of water from which it may be drawn for domestic, agricultural and industrial requirements.

5.2.1 Surface Water

The surface water can be classified into four types:

(i) Rain water is the purest form of natural water. However, it dissolves considerable amount of gases (CO_2, SO_2, NO, NO_2, etc.) and suspended solid particles from atmosphere during its journey through it and becomes polluted.

(ii) River water: Rivers are formed by rain and spring waters. During its flow over the surface of land, it dissolves minerals of the soil such as chlorides, sulfates, bicarbonates of sodium, calcium, magnesium and iron. It also contains the organic matters formed by the decomposition of plants and other impurities.

(iii) Lake water has constant chemical composition. It contains less of dissolved minerals but quite a high quantity of organic matter.

(iv) Sea water is the most impure form of natural water. It contains larger percentage of the dissolved salts (above 3.5%) out of which about 2.6% is sodium chloride. On evaporation of sea water using sunlight, sodium chloride crystals can be obtained. Sulphates of sodium, bicarbonates of potassium, magnesium, calcium, bromides of potassium, magnesium, etc. are other salts present in sea water.

5.2.2 Underground Water

Spring and well waters are the underground water sources. They are in general clearer in appearance due to the filtering action of the soil. They contain more of the dissolved salts. Generally, underground water is of high organic purity.

5.3

TYPES OF IMPURITIES IN WATER

The impurities present in water may be classified as follows:

(i) ***Dissolved impurities:***

Inorganic: The carbonates, bicarbonates, sulphates, chlorides of calcium, magnesium, iron, potassium and aluminium.

Organic: Organic water products, amino acids, proteins, etc.

Gases: Oxygen, carbon dioxide, oxides of nitrogen and sulphur, hydrogen sulphide, etc.

(ii) ***Suspended impurities:***

Inorganic: Sand and clay

Organic: Vegetable and animal matter

(iii) ***Biological impurities:*** Micro-organisms like pathogenic bacteria, fungi, algae, etc.

Note: When water is associated with such impurities, it may have objectionable colour, taste, odours, turbidites, etc.

5.4
HARDNESS OF WATER

The water which gives lather easily with soap is called soft water (e.g. distilled water and rain water) while the water which does not gives lather easily with soap but produces a white precipitate or scum is called hard water (e.g. sea water, well water).

Hardness is the property present in water which prevents lathering with soap. Hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium, magnesium and to a minor extent of certain heavy metals such as strontium and iron. Soap is the sodium or potassium salt of fatty acids such as steric acid, palmitic acid, etc. If soap is added to hard water, a white precipitate is formed due to the formation of calcium or magnesium soap.

$$M^{2+} + 2C_{17}H_{35}COONa \rightarrow (C_{17}H_{35}COO)_2M + 2Na^+ \text{ (M = Ca (or) Mg)}$$

e.g.,

$$C_{17}H_{35}COONa + MgCl_2 \rightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$$

5.4.1 Types of Hardness

Hardness of water is of two types:

(i) Temporary hardness
(ii) Permanent hardness

(i) Temporary hardness or Carbonate hardness

This is due to presence of bicarbonates of calcium and magnesium in water. This can be removed by boiling the water. When water is boiled, the soluble bicarbonates calcium and magnesium are decomposed to insoluble carbonates or hydroxides.

$$\underset{\text{(soluble)}}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{(insoluble)}}{CaCO_3}\downarrow + H_2O + CO_2\uparrow$$

$$\underset{\text{(soluble)}}{Mg(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{(insoluble)}}{Mg(OH)_2}\downarrow + 2CO_2\uparrow$$

(ii) Permanent hardness or Non-Carbonate hardness

This is due to the presence of chlorides and sulphates of calcium and magnesium in water. This cannot be removed just by boiling the water.

5.4.2 Disadvantages of Hard Water

The following are the disadvantages when hard water is used for various purposes.

(i) ***Domestic use:***

(a) *Washing and Bathing:* Hard water does not form lather easily with soap. As a result, a large amount of soap is wasted.

   (b) *Drinking:* Hard water causes bad effects on our digestive system. Sometimes, stone formation takes place in kidneys.
   (c) *Cooking:* The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking.

(ii) ***Industrial use:***
   (a) *Textile industry:* Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
   (b) *Paper industry:* Calcium and magnesium salts in water may affect the quality of paper.
   (c) *Sugar industry:* Water containing sulphates, carbonates, nitrates affects the crystallisation of sugar.
   (d) *Dyeing industry:* The salts of calcium and magnesium in hard water react with dyes and spoil the desired shade.
   (e) *Pharmaceutical industry:* Hard water may form some undesirable products while preparation of pharmaceutical products.
   (f) *Concrete making:* Chloride and sulphates present in hard water will affect the hydration of cement and the final strength of the hardened concrete.

(iii) ***Steam generation in boilers:*** For steam generation, boilers are employed. If hard water is used in boilers, it may lead to the following troubles:
   (a) Corrosion (b) Scale and sludge formation (c) Priming and foaming (d) Caustic embrittlement.

5.4.3 Units of Hardness

The following are the general units used in measurement of hardness:

(i) *Parts per million (ppm):* It is defined as the number of parts by weight of $CaCO_3$ equivalent hardness present per million (10^6) parts by weight of water.

i.e. 1 ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water

(ii) *Milligrams per litre (mg/L):* It is defined as the number of milligrams of calcium carbonate equivalent hardness present per litre of water.

$$1\text{mg/L} = 1 \text{ mg of } CaCO_3 \text{ equivalent hardness per litre of water}$$

But, 1 litre of water by weight = 1 kg = 1000 g

$$= 1000 \text{ mg} \times 1000 \text{ g} = 10^6 \text{ mg}$$

$$\begin{aligned} 1 \text{ mg/L} &= 1 \text{ mg of } CaCO_3 \text{ equivalent hardness per } 10^6 \text{ mg of water} \\ &= 1 \text{ part of } CaCO_3 \text{ equivalent per } 10^6 \text{ parts of water} \\ &= 1 \text{ ppm} \end{aligned}$$

$$\therefore \quad \mathbf{1\ mg/L = 1\ ppm}$$

(iii) *Degree clark (°Cl):* It is defined as the number of parts of calcium carbonate equivalent hardness per 70,000 parts of water.

1° Cl = 1 part of $CaCO_3$ equivalent hardness per 70,000 parts of water

1 ppm = 0.07° Cl

(iv) *Degree French (° Fr):* It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1° Fr = 1 part of $CaCO_3$ hardness per 10^5 parts of water.

1 ppm = 0.1° Fr

5.4.4 Problems Relating to Hardness of Water

Hardness is always expressed as equivalents of calcium carbonate. The choice of calcium carbonate in particular is due to its molecular weight being 100 and equivalent weight being 50 which is found to be convenient for calculation and also it is the most insoluble salt that can be precipitated in water treatment. The conversion of other hard salts to $CaCO_3$ equivalent can be achieved by the following formula.

$$\text{Calcium carbonate equivalent} = \frac{\text{Weight of the salt}}{\text{Equivalent weight of that salt}} \times 50$$

$$= \frac{\text{Weight of the salt}}{\text{Molecular weight of that salt}} \times 100$$

Hard salt	*Molecular weight*	*Equivalent weight*
$Mg(HCO_3)_2$	146	73
$Ca(HCO_3)_2$	162	81
$MgCl_2$	95	47.5
$MgSO_4$	120	60
$CaCl_2$	111	55.5
$CaSO_4$	136	68
$Mg(NO_3)_2$	148	74

Solved Problems

1. **Calculate temporary, permanent and total hardness of a sample of water containing $Ca(HCO_3)_2$ = 40.5 mg/L; $Mg(HCO_3)_2$ = 46.5 mg/L; $MgSO_4$ = 27.6 mg/L; $CaCl_2$ = 22.4 mg/L, $CaSO_4$ = 32.1 mg/L.**

Solution Calculation of $CaCO_3$ equivalents

Hard salt	*Weight (mg/L)*	*Molecular weight*	*$CaCO_3$ equivalent = $\frac{Weight}{M.W} \times 100$ (mg/L)*
$Ca(HCO_3)_2$	40.5	162	$\frac{40.5}{162} \times 100 = 25$

(*Contd*)

Table (*Contd*)

$Mg(HCO_3)_2$	46.5	146	$\frac{46.5}{146} \times 100 = 31.8$
$MgSO_4$	27.6	120	$\frac{27.6}{120} \times 100 = 23$
$CaCl_2$	22.4	111	$\frac{22.4}{111} \times 100 = 20.1$
$CaSO_4$	32.1	136	$\frac{32.1}{136} \times 100 = 23.6$

Temporary hardness = Hardness due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$
= 25 + 31.8 = 56.8 mg/L
Permanent hardness = Hardness due to $MgSO_4$, $CaCl_2$ and $CaSO_4$
= 23 + 20.1 + 23.6
= 66.7 mg/L
Total hardness = Temporary hardness + Permanent hardness
= 56.8 + 66.7 = 123.5 mg/L

2. **A sample of water on analysis has been found to contain the following in ppm $Ca(HCO_3)_2 = 4.86$; $Mg(HCO_3)_2 = 5.84$; $CaSO_4 = 6.80$; $MgSO_4 = 8.40$. Calculate the temporary hardness and permanent hardness of water.**

Solution Calculation of calcium carbonate equivalents.

Hard salt	***Weight (ppm)***	***Molecular weight***	***$CaCO_3$ equivalent = $\frac{Weight}{M.W} \times 100$ (ppm)***
$Ca(HCO_3)_2$	4.86	162	$\frac{4.86}{162} \times 100 = 3$
$Mg(HCO_3)_2$	5.84	146	$\frac{5.84}{146} \times 100 = 4$
$CaSO_4$	6.80	136	$\frac{6.80}{136} \times 100 = 5$
$MgSO_4$	8.40	120	$\frac{8.40}{120} \times 100 = 7$

Temporary hardness = Hardness due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$
= 3 + 4 = 7 ppm
Permanent hardness = Hardness due to $CaSO_4$ and $MgSO_4$
= 5 + 7 = 12 ppm

3. **A sample of water on analysis has been found to contain the following: $Ca(HCO_3)_2$ = 10.5 ppm; $Mg(HCO_3)_2$ = 12.5 ppm; $CaSO_4$ = 7.5 ppm; $CaCl_2$ = 8.2 ppm; $MgSO_4$ = 2.6 ppm. Calculate temporary hardness and permanent hardness in degree clark.**

Solution Calculation of calcium carbonate equivalents.

Hard salt	*Weight (ppm)*	*Molecular weight*	*$CaCO_3$ equivalent = $\frac{Weight}{M.W} \times 100$ (ppm)*
$Ca(HCO_3)_2$	10.5	162	$\frac{10.5}{162} \times 100 = 6.48$
$Mg(HCO_3)_2$	12.5	146	$\frac{12.5}{146} \times 100 = 8.56$
$CaSO_4$	7.5	136	$\frac{7.5}{136} \times 100 = 5.51$
$CaCl_2$	8.2	111	$\frac{8.2}{111} \times 100 = 7.38$
$MgSO_4$	2.6	120	$\frac{2.6}{120} \times 100 = 2.16$

Temporary hardness = Hardness due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$
= 6.48 + 8.56 = 15.04 ppm
= 15.04 × 0.07°Cl
= 1.05°Cl

Permanent hardness = Hardness due to $CaSO_4$, $CaCl_2$ and $MgSO_4$
= 5.51 + 7.38 + 2.16
= 15.05 ppm
= 15.05 × 0.07°Cl
= 1.05°Cl

Exercise Problems

1. Calculate temporary hardness and permanent hardness of a sample of water containing $Mg(HCO_3)_2$ = 7.3 mg/L, $Ca(HCO_3)_2$ = 16.2 mg/L; $MgCl_2$ = 9.5 mg/L; $CaSO_4$ = 13.6 mg/L.

   [*Ans*: Temp. 15 mg/L; Perm. 20 mg/L]

2. A sample of water on analysis gives the following: $MgCl_2$ = 9.5 ppm; $CaSO_4$ = 3.4 ppm; $Mg(HCO_3)_2$ = 7.3 ppm; $MgSO_4$ = 6.0 ppm. Calculate temporary and permanent hardness of the sample.

   [*Ans*: Temp. 5 ppm; Perm. 17.5 ppm]

3. A sample of water on analysis has been found to contain the following: $Ca(HCO_3)_2$ = 32.4 ppm: $CaSO_4$ = 13.6 ppm; $MgCl_2$ = 19.0 ppm; $Mg(HCO_3)_2$ = 14.6 ppm. Calculate the carbonate hardness and non-carbonate hardness of the sample in degree French.

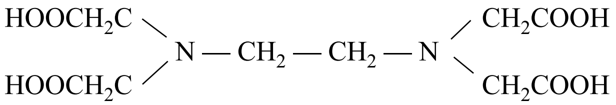
[*Ans*: Carbonate hardness. 3°Fr; non-carbonate hardness 3°Fr]

5.5

ESTIMATION OF HARDNESS BY EDTA METHOD

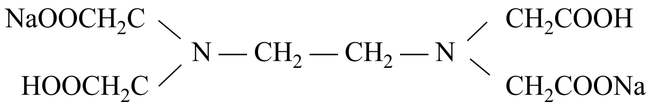
Principle Disodium salt of Ethylenediaminetetraacetic acid [EDTA] forms stable complex with Ca^{+2} and Mg^{+2} ions in aqueous solution. The amount of EDTA consumed in the reaction gives the amount of calcium and magnesium salts present in the hard water.

Structure of EDTA



Since EDTA is insoluble in water, the disodium salt of EDTA is used as complexing agent with Ca^{2+} and Mg^{2+} ions.

Structure of EDTA (Disodium salt)



When Eriochrome Black-T (EBT) indicator is added to the hard water sample, it forms wine red colour, unstable complex at pH_{10} with Ca^{2+} and Mg^{2+} ions. When this solution is titrated against EDTA solution, the colour of the complex changes from wine red to deep blue which indicates the end point, i.e., EDTA formed stable complex with Ca^{2+} and Mg^{2+} ions.

$$\underset{(Ca^{2+}\text{ or }Mg^{2+})}{M^{2+}} + EBT \rightarrow \underset{\text{unstable complex (wine red)}}{M - EBT}$$

$$M - EBT + EDTA \rightarrow \underset{\text{Stable Complex blue}}{M - EDTA + EBT}$$

Preparation of Solutions

EDTA Solution Dissolve 3.72 g of disodium salt of EDTA in one litre of distilled water.

Standard Hard Water Dissolve 1.0 g of pure dry $CaCO_3$ in small quantity of dil. HCl and then evaporate the solution to dryness on water bath. Dissolve the residue in distilled water to make one litre solution. 1 ml of the solution contains 1 mg $CaCO_3$ equivalent hardness.

Indicator Dissolve 0.5 g of EBT in 100 ml of alcohol.

Buffer Solution Add 67.5 g of NH_4Cl to 570 ml of concentrated ammonia solution and then dilute with distilled water to 1 litre.

Procedure

Standardisation of EDTA Solution The burette is rinsed and filled with EDTA solution. 50 ml of standard hard water is pipetted out into a clean conical flask. 5 ml of ammonical buffer and few drops of EBT indicator are added and then titrated against EDTA solution until the wine red colour changes to deep blue colour which indicates the end point.

Let the volume of EDTA used be V_1 ml.

Estimation of Total Hardness 50 ml of a given sample of hard water is pipetted out into a clean conical flask. 5 ml of ammonical buffer and few drops of EBT indicator are added and then titrated against EDTA solution until the wine red colour changes to deep blue colour. Let the volume of EDTA used be V_2 ml.

Estimation of Permanent Hardness 250 ml of the hard water sample is taken in a beaker and evaporated to nearly 50 ml (when all the bicarbonates are decomposed to insoluble $CaCO_3$ and $Mg(OH)_2$). Filter and wash and make up the filtrate to 250 ml with distilled water. 50 ml of made up solution is pipetted out into a conical flask. 5 ml of ammonical buffer and few drops of EBT are added and then titrated against EDTA until the wine red colour changes to deep blue. Let the volume of EDTA used be V_3 ml.

Calculations

Standardisation of EDTA

$$\begin{aligned}
\text{1 ml of standard hard water} &= \text{1 mg of } CaCO_3 \\
\text{50 ml of standard hard water} &= V_1 \text{ ml EDTA} \\
\text{50 mg of } CaCO_3 \text{ eq.} &= V_1 \text{ ml of EDTA} \\
\therefore \quad \text{1 ml EDTA} &= \frac{50}{V_1} \text{ mg of } CaCO_3 \text{ eq.}
\end{aligned}$$

Estimation of Total Hardness

$$\begin{aligned}
\text{50 ml of given hard water} &= V_2 \text{ ml of EDTA} \\
&= V_2 \times \frac{50}{V_1} \text{ mg of } CaCO_3 \text{ eq.} \\
\text{1 ml of hard water} &= \frac{V_2}{\cancel{50}} \times \frac{\cancel{50}}{V_1} \text{ mg of } CaCO_3 \text{ eq.} \\
\therefore \quad \text{1 litre of given hard water} &= \frac{V_2}{V_1} \times 1000 \text{ mg of } CaCO_3 \text{ eq.} \\
\therefore \quad \text{Total hardness} &= \frac{V_2}{V_1} \times 1000 \text{ mg/L}
\end{aligned}$$

Estimation of Permanent Hardness

$$50 \text{ ml of boiled water} = V_3 \text{ ml of EDTA}$$

$$= V_3 \times \frac{50}{V_1} \text{ mg of } CaCO_3 \text{ eq.}$$

$$1 \text{ ml of boiled water} = \frac{V_3}{\cancel{50}} \times \frac{\cancel{50}}{V_1} \text{ mg of } CaCO_3 \text{ eq.}$$

$$1 \text{ litre of boiled water} = \frac{V_3}{V_1} \times 1000 \text{ mg of } CaCO_3 \text{ eq.}$$

$$\therefore \quad \text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L}$$

Temporary Hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

$$= \left(\frac{V_2}{V_1} \times 1000\right) - \left(\frac{V_3}{V_1} \times 1000\right)$$

$$= 1000\left[\frac{V_2}{V_1} - \frac{V_3}{V_1}\right]$$

$$= 1000\left[\frac{V_2 - V_3}{V_1}\right] \text{ppm}$$

Solved Problem

1. **0.5 g of $CaCO_3$ was dissolved in dil. HCl and diluted to 1000 ml. 50 ml of this solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution for titration. 50 ml of same water sample on boiling, filtering, etc. required 10 ml of EDTA solution. Calculate the different kinds of hardness in ppm.**

Solution

Volume of EDTA consumed for 50 ml of standard hard water (V_1) = 48 ml

Volume of EDTA consumed for 50 ml of given sample of hard water (V_2) = 15 ml

Volume of EDTA consumed for 50 ml of boiled water (V_3) = 10 ml

$$\text{Total hardness} = \frac{V_2}{V_1} \times 1000 \text{ mg/L}$$

$$= \frac{15}{48} \times 1000 = 312.5 \text{ mg/L}$$

$$\text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L}$$

$$= \frac{10}{48} \times 1000 = 208.3 \text{ mg/L}$$

$$\begin{aligned} \text{Temporary hardness} &= \text{Total hardness} - \text{permanent hardness} \\ &= 312.5 - 208.3 \\ &= 104.2\ \text{mg/L} \end{aligned}$$

Exercise Problem

1. 0.28 g of $CaCO_3$ was dissolved in dil. HCl and the solution made up to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution for titration. 100 ml of the water sample required 33 ml of EDTA solution for titration. After boiling 100 ml of this water, cooling, filtering required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water.

[*Ans*: Total 1178.5 mg/L; Perm. 357.1 mg/L; Temp. 821.4 mg/L]

5.6
ALKALINITY

The alkalinity of a solution is a measure of its capacity to neutralize acids. It is due to presence of OH^-, CO_3^{2-} and HCO_3^- ions. These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators. The determination is based on the following reactions

$$\left.\begin{array}{l} \left.\begin{array}{rl} \text{(i)} & [OH^-] + [H^+] \rightarrow H_2O \\ \text{(ii)} & [CO_3^{2-}] + [H^+] \rightarrow [HCO_3^-] \end{array}\right\} P \\ \begin{array}{rl} \text{(iii)} & [HCO_3^-] + [H^+] \rightarrow H_2O + CO_2 \end{array} \end{array}\right\} M$$

The titration of the water sample against a standard acid up to phenolphthalein end point gives the completion of (i) and (ii) reactions only. The amount of acid consumed thus corrosponds to hydroxide plus one half of the carbonate present. On the other hand titration of the water sample against a standard acid up to methyl orange end point makes the completion of reactions (i), (ii), and (iii). Hence the amount of acid used after the phenolphthalein end point corrosponds to half of carbonate plus all the bicarbonates, while the total amount of acid used represents the total alkalinity due to OH^-, CO_3^{2-} and HCO_3^- ions.

The possible combinations of ions causing alkalinity in water are OH^- only or CO_3^{2-} only or HCO_3^- only or OH^- and CO_3^{2-} ions together or CO_3^{2-} and HCO_3^- together. But OH^- and HCO_3^- can not exist together because they combine instantaneously to form carbonate ions.

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$$

Procedure

Pipette out 100 ml of water sample in to a clean conical flask and add 2 to 3 drops of phenolphthalein indicator. Titrate with N/50 H_2SO_4 solution till the pink color just disappears note down the titre value. Then add 2 to 3 drops of methyl orange indicator to the same solution continue the titration till the pink color reappears and note down the titre value.

Calculations

Volume of water sample taken = 100 ml

Concentration of the standard sulphuric acid = $\frac{N}{50}$

Volume of acid consumed for phenolphthalein end point = V_1 ml
Extra volume of acid consumed for methyl orange end point = V_2 ml
Phenolphthalein alkalinity interms of $CaCO_3$ equivalents

$$(P) = \frac{V_1 \times 50 \times 10^6}{50 \times 100 \times 1000} \text{ PP m}$$

$$= 10\, V_1 \text{ PP m}$$

Methyl orange alkalinity interms of $CaCO_3$ equivalents

$$(M) = \frac{(V_1 + V_2) \times 50 \times 10^6}{50 \times 100 \times 1000}$$

$$= 10\,(V_1 + V_2) \text{ PP m}$$

Note:

(i) When P = O, both OH^- and CO_3^{2-} are absent and the alkalinity is only due to HCO_3^-

(ii) When P = 1/2 H, only CO_3^{2-} is present, since half of carbon neutralization reaction takes place with phenolphthalein indicator, while complete carbonate neutralization takes place when methyl orange indicator is used there fore, alkalinity due to carbonate = 2p

(iii) When P = M, only OH^- is present. Thus alkalinity due to OH^- = P = M

(iv) When P > 1/2 H, both OH^- and C CO_3^{2-} are present. Now half of carbonate is equal to M–P. There fore, alkalinity due to carbonate = 2 (M–P) and alkalinity due to OH^- = M–2 (M–P)
= 2 P–M

(v) When P < 1/2 M, Carbonates and bicarbonates are present. Now alkalinity due to carbonate = 2P. There fore alkalinity due to bicarbonate = M–2P.

5.7

CHLORIDES

Chloride ions present in water are due to chlorides of calcium, magnesium, sodium etc.

Principle

Chloride content in water is determined by titrating a known volume of the water sample with standard silver nitrate solution using potassium chromate as indicator. Silver nitrate precipitates chloride as silver chloride. When all the chloride ions are precipitated as silver chloride, the excess drop of silver nitrate solution reacts with the chromate ions to form brick red coloured precipitate at end point.

$$AgNO_3 + C\bar{l} \rightarrow Agcl \downarrow + N\bar{O}_3$$

$$2\,AgNO_3 + Cro_4^{2-} \rightarrow \underset{\text{(Brick red)}}{Ag_2\,Cro_4} \downarrow + 2N\bar{O}_3$$

Procedure

Pipette out 100 ml of the water sample in to a clean conical flask. Add 2 to 3 drops of potassium chromate indicator and titrate with sandard silver nitrate solution till the colour changes from yellow to brick red. Note down the titre value.

Note: If the water sample is acidic, it has to be neutralized by adding about 1g of $CaCO_3$ powder before the titration is carried out. In such cases, a blank titration has to be carried out. For this pipette out 100 ml of distilled water in to a conical flask. Add 1g of $CaCO_3$ powder, 2 to 4 drops of potassium chromate indicator and titrate with silver nitrate solution as before. The volume of silver nitrate consumed by blank has to be subtracted from the titre value obtained for the water sample.

Calculation

Normality of silvernitrate solution = N_1

Volume of silvernitrate consumed by water = V_1 ml

Normality of chloride in the solution = $\frac{N_1V_1}{100}$

Chloride content in water interms of $CaCo_3$

equivalents = $\frac{N_1 \times V_1 \times 50 \times 10^6}{100 \times 1000}$ PP m

5.8

ACIDITY

Pure water has a neutral P^H, although drinking water may be slightly acidic or basic depending on dissolved mineral content and other trace chemicals. Water with P^H less than 6.5 is considered as acidic. This water typically is corrosive. " Acidity is a measure of capacity of water to neutralise bases." Acidity is due to the presence of mineral acids like H_2SO_4, HCl, HNO_3 and dissolved CO_2 in the form of H_2CO_3. According to the method of determination, acidity is important because acid contributes to corrosiveness and influences certain chemical and biological processes. These acids can be estimated by titration against standard strong base using methyl orange and phenolphthalein indicators.

Procedure

Pipette out 100 ml of water sample in to a clean conical flask and add 2 to 3 drops of methyl orange indicator. Tirate this solution against N/50 NaoH solution till the colour changes from faint orange to yellow. Note down the volume of NaOH solution consumed ($v_1$ml). Then add 2 to 3 drops of phenolphthalein indicator to the same solution in the conical flask. Continue the titration till the appearance of faint pink colour. Note down the extra volume of NaoH solution consumed (V_2 ml). V_1 ml will indicate the neutralization of mineral acids. V_2 ml will indicate the neutralization of Co_2 in the form of $CaCo_3$. While ($V_1 + V_2$) ml will indicate the total acidity ie., complete neutralization of mineral acids and dissolved CO_2

Calculations

Methyl orange acidity interms of $CaCO_3$ equivalents
(Mineral acidity)

$$= \frac{V_1 \times 50 \times 10^6}{50 \times 100 \times 1000}$$

$$= 10\,V_1 \text{ PP m}$$

Total acidity interms of $CaCO_3$ equivalents

$$= \frac{(V_1 + V_2) \times 50 \times 10^6}{50 \times 100 \times 1000} \text{ PP m}$$

$$= 10\,(V_1 + V_2) \text{ PP m}$$

5.9

TREATMENT OF WATER FOR DOMESTIC PURPOSE

The water obtained from natural sources like rivers, lakes and ponds does not fulfil the required characteristics of water. Water for drinking and other domestic uses should be free from disease producing bacteria, chemicals or other substances. Hence, water should be treated before being used for drinking and other domestic purposes.

The following are different steps in treatment of water.

A. Removal of Suspended Impurities

1. *Screening* The process of removing floating matter from water is known as screening. In this process, water is passed through a screen. The floating matter is arrested by the screen and the water is free from the floating matter.
2. *Plain sedimentation* The process of removing big sized suspended solid particles from water is called plain sedimentation. In this process, water is stored in big tanks for several hours. 70% of solid particles settle down due to the force of gravity.

3. *Sedimentation by coagulation* This is the process of removing fine suspended and colloidal impurities by adding coagulants like alum ($K_2SO_4 Al_2(SO_4)_3 24H_2O$), ferrous sulphate ($FeSO_4$) and Sodium aluminate ($NaAlO_2$). When coagulant is added to water, floc formation takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.
4. *Filtration* The process of passing a liquid containing suspended impurities through a suitable porous material so as to effectively remove suspended impurities and some microorganisms is called filtration. It is a mechanical process. When water flows through a filter bed, many suspended particles are unable to pass through the gaps and settle in the bed.

B. Disinfection or Sterilisation

The process of killing pathogenic bacteria and other microorganisms is called disinfection or sterilisation. The water which is free from pathogenic bacteria and safe for drinking is called potable water. The chemicals used for killing bacteria are called disinfectants.

1. By adding Bleaching Powder Water is mixed with required amount of bleaching powder, and the mixture is allowed to stand for several hours.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \rightarrow \underset{\text{Hypochlorous acid}}{HOCl} + HCl$$

$$\text{Germs} + HOCl \rightarrow \text{Germs are killed.}$$

The disinfection action of bleaching powder is due to available chlorine in it. It forms hypochlorous acid which acts as a powerful germicide (disinfectant).

2. Chlorination Chlorine is mixed with water in a chlorinator; which is a high tower having a number of baffle plates (Fig. 5.1). Water and required quantity of concentrated chlorine solution are introduced from its top during their passage through the tower. They get thoroughly mixed and then sterilised water is taken out from the bottom.

Advantages

(i) Storage requires less space
(ii) Effective and economical
(iii) Stable and does not deteriorate
(iv) Produces no salts
(v) Ideal disinfectant

Disadvantages

(i) Excess of chlorine causes unpleasant taste and odour.
(ii) More effective at below pH 6.5 and less effective at higher pH values.

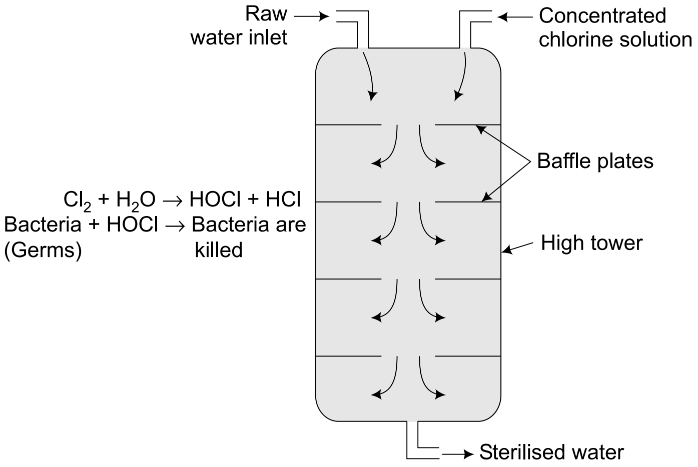


Fig. 5.1 *Chlorinator*

*3. **Ozonisation*** Ozone is an excellent, disinfectant which can be prepared by passing silent electric discharge through pure and dry oxygen. Ozone is highly unstable and breaks down, liberating nascent oxygen.

$$3O_2 \rightarrow 2O_3$$
$$O_3 \rightarrow O_2 + (O) \text{ Nascent oxygen}$$

This nascent oxygen kills bacteria as well as oxidises the organic matter present in water.

Advantages Removes colour, odour and taste.

Disadvantages The method is costly.

5.10
WATER FOR STEAM MAKING

Water used for making steam should be free from dissolved salts, gases, suspended impurities, oil and silica. In very big boilers, soft water is used for producing steam. The boilers are heated with fuels such as coal, and the steam produced rotates the blades of turbines in a fast manner (the turbine is a magnet wounded by coil wire). Any magnet wounded by coil wire will produce electricity. This electricity is produced by making use of water in boilers.

5.11
BOILER TROUBLES

Boilers are used for steam generation. The troubles that arise in the boilers due to presence of impurities in the boiler feed water are called boiler troubles.

The major boiler troubles are

(i) Priming and foaming
(ii) Boiler corrosion
(iii) Sludges and scales
(iv) Caustic Embrittlement.

(i) Priming and Foaming This is also known as wet steam or carry over.

Priming Production of wet steam by rapid boiling of water in boilers is called priming. It may be caused due to

(a) very high steam velocity
(b) high water level
(c) improper boiler design
(d) sudden boiling, etc.

It can be avoided by

(a) maintaining low water level
(b) using softened water
(c) fitting mechanical steam purifiers
(d) using a well-designed boiler.

Foaming The production of persistent bubbles or foam in boiler water surface is called foaming

It may be caused due to

(a) the presence of oil or soapy substances
(b) certain dissolved salts.

It can be avoided by

(a) adding antifoaming agents like cotton seed oil and castor oil.
(b) adding sodium aluminate which coagulates the oily or soapy substances.

(ii) Boiler Corrosion The decay of boiler material by a chemical or electrochemical attack by its environment is called boiler corrosion. It is due to

(a) dissolved oxygen
(b) dissolved carbon dioxide
(c) acids from dissolved salts.

(a) Dissolved oxygen Water usually contains 8 mg/L of dissolved oxygen at room temperature. It attacks boiler material causing rust formation.

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \downarrow$$
$$4Fe(OH)_2 + O_2 \rightarrow \underset{\text{rust}}{2(Fe_2O_3 . 2H_2O)} \downarrow$$

Removal of dissolved oxygen By adding calculated quantity of sodium sulphide or sodium sulphate or hydrazine

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$
$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$
$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

(b) Dissolved carbon dioxide It gives carbonic acid which has a slow corrosive effect on the boiler material.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Removal of dissolved carbon dioxide By adding calculated quantity of ammonia

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2\,CO_3 + H_2O$$

(c) Acids from dissolved salts The magnesium salts present water, liberates acids on hydrolysis

$$MgCl_2 + H_2O \rightarrow Mg(OH)_2 \downarrow + 2HCl$$

The liberated HCl reacts with iron in chain reactions producing HCl again and again.

$$Fe + HCl \rightarrow FeCl_2 + H_2 \uparrow$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 \downarrow + 2HCl$$

Presence of even a small amount of $MgCl_2$ can cause corrosion of iron to a large extent. This type of corrosion may be avoided by neutralisation with alkali.

(iii) Sludges and Scales The water evaporates continuously in boilers. As the concentration of dissolved salts increases progressively, when the concentration reaches saturation point, they are thrown out in the form of precipitates (sludge or scale).

Sludge A loose and slimy precipitate formed within the boiler is called sludge. Sludges can be formed by substances which have greater solubilities in hot water than in cold water.

Salts like $MgCO_3$, $MgSO_4$, $MgCl_2$, $CaCl_2$, etc., are responsible for sludge formation in boilers.

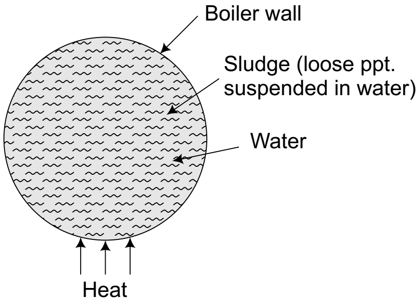


Fig. 5.2 *Boiler*

Disadvantages

(a) Sludge is a bad conductor of heat, hence it wastes a portion of heat generated.
(b) Excessive sludge formation reduces the efficiency of the boiler.

Prevention

(a) Frequent blow-down operation should be carried out.
(b) By using well-softened water.

Scale A hard, adhering coating on the inner walls of the boiler is called scale. Salts like $CaSO_4$ and $Ca(HCO_3)_2$ are responsible for scale formation in boilers.

Disadvantages

(a) Scale acts as a bad conductor of heat.
(b) Scale formation can reduce the efficiency of a boiler.
(c) At high temperatures, cracks may be formed on scale, leading to explosion.

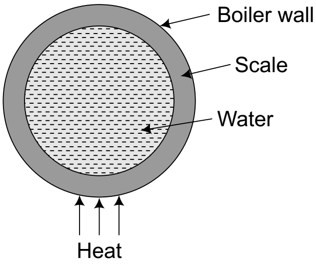


Fig. 5.3 *Boiler*

Removal of Scales

(a) By thermal shocks.
(b) With the help of a wire brush, wood piece or scraper.
(c) Carbonate scales can be removed by 5–10% HCl.

Prevention

(a) *External treatment:* Ion-exchange process or zeolite process or Lime–Soda process has to be applied for softening boiler water.
(b) *Internal treatment:* Water is treated within the boiler either by converting scale forming substance into sludge forming substances followed by blow down operation or by keeping the scale forming substances in soluble state by means of complexation.
    1. Colloidal conditioning: Organic substances like kerosene and agar–agar are added to the water to avoid scale formation.
    2. Phosphate conditioning: Phosphates react with water and a loose sludge is formed which can be easily removed by blow-down operation.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl.$$

    3. Carbonate conditioning: In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water

$$CaSO_4 + Na_2CO_3 \rightarrow \underset{\text{(sludge)}}{CaCO_3} + Na_2SO_4$$

    4. Calgon conditioning: Sodium hexa meta phosphate (Calgon) is added to boiler water which can prevent the scale formation by the formation of soluble complex

$$2CaSO_4 + Na_2(Na_4(PO_3)_6) \rightarrow Na_2(Ca_2(PO_3)_6) + 2Na_2SO_4$$

    5. Sodium aluminate conditioning: Sodium aluminate gets hydrolysed yielding NaOH and aluminium hydroxide precipitate. The sodium hydroxide reacts with magnesium salts to magnesium hydroxide. These hydroxides entrap finely divided particles and neutralise the charge on colloidal particles, and the loose precipitate can be removed by blow-down operation.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$$
$$2NaOH + MgCl_2 \rightarrow Mg(OH)_2 \downarrow + 2NaCl$$

(iv) Caustic Embrittlement This is a type of corrosion caused by the formation of sodium hydroxide in boiler. Sources of formation of sodium hydroxide are generally by using highly alkaline water or Na_2CO_3 present in water softened by lime soda process.

Sodium carbonate decomposes to give NaOH and CO_2 and this makes the boiler water caustic.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow$$

This sodium hydroxide passes into the minute hair cracks present on the boiler by capillary action and attacks the surrounding area dissolving iron of boiler as Sodium ferroate (Na_2FeO_2).

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2$$

This causes the embrittlement of boiler parts particularly at bends, rivets, joints, etc. causing failure of boiler.

Prevention

(a) By adding Na_2SO_4, tannin, etc. to the boiler water which blocks hair cracks.

(b) By using sodium phosphate as the softening agent instead of sodium carbonate.

5.12
SOFTENING OF WATER

The removal of hardness causing salts from water is called softening of water. The three important industrial methods employed for softening of water are:

1. Lime–soda process
2. Zeolite or permutit process
3. Ion-exchange (or) demineralization process

1. Lime–soda Process This process is based on converting the soluble calcium and magnesium salts into insoluble calcium carbonate and magnesium hydroxide precipitates by addition of calculated amount of lime [$Ca(OH)_2$] and soda [Na_2CO_3]. The precipitates are removed by filtration. Any free dissolved CO_2 and acids are also removed by this process. The various chemical reactions involved in this process are

(a) For calcium and magnesium bicarbonates, only lime is required

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

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

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

$$\overline{\underline{Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow\ Mg(OH)_2\downarrow + 2H_2O}}$$

(b) For $MgSO_4$ and $MgCl_2$, both lime and soda are required.

(iii) $MgSO_4 + Na_2CO_3 \rightarrow MgCO_3 + Na_2SO_4$

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

$$\overline{\underline{MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4}}$$

(iv)

$$\begin{array}{rcl} MgCl_2 + Na_2CO_3 & \rightarrow & MgCO_3 + 2NaCl \\ MgCO_3 + Ca(OH)_2 & \rightarrow & Mg(OH)_2 \downarrow CaCO_3\downarrow \\ \hline MgCl_2 + Na_2CO_3 + Ca(OH)_2 & \rightarrow & Mg(OH)_2 \downarrow + CaCO_3\downarrow + 2NaCl \\ \hline \end{array}$$

(c) For $CaSO_4$ and $CaCl_2$, only soda is required

(v) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$

(vi) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$

(d) Other reactions: Free acids, CO_2, H_2S, dissolved iron and aluminium salts, etc. are also removed in this process.

$$\begin{array}{rcl} 2HCl + Na_2CO_3 & \rightarrow & 2NaCl + H_2O + CO_2\uparrow \\ H_2SO_4 + Na_2CO_3 & \rightarrow & Na_2SO_4 + H_2O + CO_2\uparrow \\ CO_2 + Ca(OH)_2 & \rightarrow & CaCO_3 \downarrow + H_2O \\ H_2S + Ca(OH)_2 & \rightarrow & CaS \downarrow + H_2O \\ Fe^{+2} + Ca(OH)_2 & \rightarrow & Fe(OH)_2 \downarrow + Ca^{+2} \\ Al^{+3} + 3Ca(OH)_2 & \rightarrow & 2Al(OH)_3 \downarrow + 3Ca^{+2} \end{array}$$

Calculation: 100 parts by mass of $CaCO_3$ are equivalent to 74 parts of $Ca(OH)_2$ and 106 parts of Na_2CO_3.

(a) Amount of lime required for softening

$$= \frac{74}{100}\left[\begin{array}{l} \text{Temp. } Ca^{2+} + 2\times \text{Temp. } Mg^{2+} + \text{Perm. } (Mg^{2+} + Fe^{2+} + Al^{3+}) \\ + CO_2 + H^+ (\text{HCl or } H_2SO_4) + HCO_3^- \\ \text{all in terms of } CaCO_3 \text{ eq.} \end{array}\right]$$

(b) Amount of soda required for softening

$$= \frac{106}{100}\left[\begin{array}{r} \text{Perm. } (Ca^{2+} + Mg^{2+} + Fe^{2+} + Al^{3+}) + H^+ (\text{HCl or } H_2SO_4) \\ -HCO_3^- \text{ all in terms of } CaCO_3 \text{ eq.} \end{array}\right]$$

(i) Cold lime–soda process: In this method the lime and soda are mixed with hard water at room temperature with constant stirring. Generally the precipitates formed by this process are finely divided and in order to settle the precipitates, coagulants like alum, ferrous sulphate, etc. are added.

The hard water to be softened is mixed with calculated quantity of chemicals (lime + soda + coagulant) from the top into the inner chamber (Fig. 5.4) on vigorous stirring. The chemical reactions take place and the hardness producing salts get converted into insoluble precipitates (sludge). The sludge is removed from the bottom of the outer chamber while the softened water passes through a wood fibre filter to ensure the complete removal of any residual sludge particles. The clear softened water is withdrawn from the top of the outer chamber. The softened water from this process contains a residual hardness of 50–60 ppm.

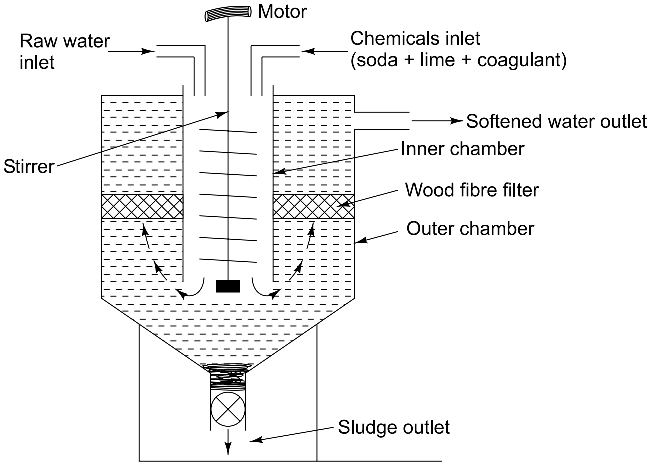


Fig. 5.4 *Continuous cold lime soda process*

(ii) Hot lime–soda process: This process is similar to the cold lime–soda process but no coagulant is needed. Here the process is carried at a temperature of 80 to 150°C. Since the reaction carried out at high temperature

(a) The reaction takes place faster.
(b) The sludge settles rapidly.
(c) Viscosity of soft water is lower, hence filtered easily.
(d) The dissolved gases such as CO_2, air, etc. driven out of the water.
(e) The residual hardness is low compared to the cold lime–soda process.

Hot lime soda process consists of three parts (Fig. 5.5).

(a) "Reaction tank" in which complete mixing of water, chemicals and steam takes place and water gets softened.
(b) "Conical sedimentation vessel" where the sludge settle down.
(c) "Sand filter" where sludge is completely removed.

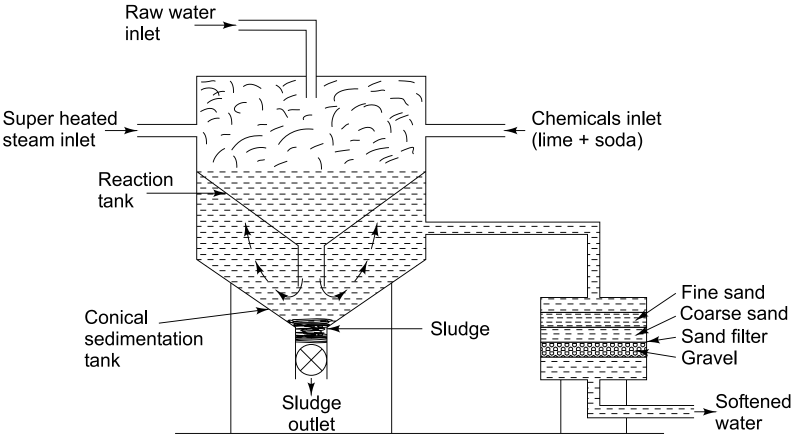


Fig. 5.5 *Hot lime–soda process*

The softened water from this process contains a residual hardness of 15–30 ppm.

Advantages of lime–soda process

(i) This process is economical.
(ii) Mineral content of the water is reduced.
(iii) The process increases the pH value of the water, which reduces the content of pathogenic bacteria.
(iv) Manganese and iron salts are also removed by this process.
(v) The process improves the corrosion resistance of the water.

Disadvantages of lime–soda process

(i) Due to residual hardness, water is not useful for high pressure boilers.
(ii) Large amount of sludge is formed which create disposal problem.

Solved Problems

1. Calculate the quantities of lime and soda required to soften 5000 litres of water containing the following salts:

$MgCl_2$ = 15.5 ppm; $Ca(HCO_{3v})_2$ = 32.5 ppm
$CaSO_4$ = 22.4 ppm; $Mg(HCO_3)_2$ = 14.6 ppm
NaCl = 50 ppm

Solution Calculation of calcium carbonate equivalents

Hard Salt	***Weight (ppm)***	***Molecular Weight (MW)***	***$CaCO_3$ eq. = $\frac{Weight}{MW} \times 100$ (ppm)***
$MgCl_2$	15.5	95	$\frac{15.5}{95} \times 100 = 16.31$
$Ca(HCO_3)_2$	32.5	162	$\frac{32.5}{162} \times 100 = 20.06$
$CaSO_4$	22.4	136	$\frac{22.4}{136} \times 100 = 16.47$
$Mg(HCO_3)_2$	14.6	146	$\frac{14.6}{146} \times 100 = 10.00$

Lime required for litre of water

$$= \frac{74}{100}\left[Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + MgCl_2 \text{ as } CaCO_3 \text{ eq.}\right]$$

$$= \frac{74}{100}\left[20.06 + 2 \times 10 + 16.31\right]$$

$$= \frac{74}{100} \times 56.37 = 41.71 \text{ mg}$$

Lime required for 5000 litres of water = $\dfrac{41.71 \times 5000}{1000}$ = 208.55 g = 0.208 kg.

$$\text{Soda required for litre of water} = \frac{106}{100}\left[\text{MgCl}_2 + \text{CaSO}_4\right] \text{as CaCO}_3 \text{ eq.}$$

$$= \frac{106}{100}\left[16.31 + 16.47\right]$$

$$= \frac{106}{100} \times 32.78 = 34.74 \text{ mg}$$

Soda required for 500 litres of water = $\dfrac{34.74}{1000} \times 5000 = 173.7$ g = 0.173 kg

2. **Calculate the amount of lime and soda required to soften 30,000 litres of water containing the following salts**

$Mg(HCO_3)_2$ = 73 Mg/L; $MgSO_4$ = 120 mg/L
$MgCl_2$ = 95 mg/L; $CaSO_4$ = 13.6 mg/L;

Purity of lime is 80% and that of soda is 95%.

Solution Calculation of calcium carbonate equivalents

Hard salt	***Weight (mg/L)***	***Molecular weight (MW)***	***$CaCO_3$ eq. = $\frac{Weight}{M \cdot W} \times 100$ mg/L***
$Mg(HCO_3)^2$	73	146	$\frac{73}{146} \times 100 = 50$
$MgSO_4$	120	120	$\frac{120}{120} \times 100 = 100$
$MgCl_2$	95	95	$\frac{95}{95} \times 100 = 100$
$CaSO_4$	13.6	136	$\frac{13.6}{136} \times 100 = 10$

$$\text{Lime required for softening} = \frac{74}{100}\left[\begin{array}{r} 2 \times \text{Mg(HCO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2 \\ \text{as CaCO}_3 \text{ eq.} \end{array}\right] \times 100\% \text{ purity} \times \text{vol. of water}$$

$$= \frac{74}{100}\left[2 \times 50 + 100 + 100\right] \times \frac{100}{80} \times 30000$$

$$= \frac{74}{100} \times 300 \times \frac{100}{80} \times 30000 = 8.325 \times 10^6 \text{ mg}$$

$$= 8.325 \text{ kg}$$

$$\text{Soda required for softening} = \frac{106}{100}\left[\begin{array}{r} \text{MgSO}_4 + \text{MgCl}_2 + \text{CaSO}_4 \\ \text{as CaCO}_3 \text{ eq.} \end{array}\right] \times 100\% \text{ purity} \times \text{vol. of water}$$

$$= \frac{106}{100}[100+100+10]\times\frac{100}{95}\times 30000$$

$$= \frac{106}{100}\times 210\times\frac{100}{95}\times 30000 = 7.02 \times 10^6 \text{ mg}$$

$$= 7.02 \text{ kg}$$

Exercise Problems

1. Calculate the quantity of lime and soda required to soften 50,000 litres of water containing the following salts

   $Ca(HCO_3)_2$ = 8.1 mg/L; $Mg(HCO_3)_2$ = 7.5 mg/L; $CaSO_4$ = 13.6 mg/L

   $MgSO_4$ = 12.0 mg/L; $MgCl_2$ = 2.0 mg/L; NaCl = 4.7 mg/L

   [*Ans:* Lime = 1.01 kg; Soda = 1.17 kg]

2. Calculate the quantity of lime (74% purity) and soda (90% purity) to soften 5000 litres of water containing the following impurities

   $Mg(HCO_3)_2$ = 73 mg/L; $CaCl_2$ = 222 mg/L; $MgSO_4$ = 120 mg/L

   $Ca(NO_3)_2$ = 164 mg/L.

   [*Ans:* Lime = 1 kg; Soda = 2.35 kg]

2. Zeolite or Permutit Process Zeolite is hydrated sodium alumino silicate. Its general formula is $Na_2O \cdot Al_2O_3 \cdot x\, SiO_2 \cdot y\, H_2O$.

Here $x = 2 - 10$ $y = 2 - 6$.

eg: Natrolite $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$.

Natural zeolites are generally non-porous. The artificial zeolite is called permutit. They are prepared by heating together with china clay, feldspar and soda ash. These are porous and have greater softening capacity than natural zeolite. They exchange Na^+ ions with the hardness producing ions (Ca^{2+}, Mg^{2+}, etc.) in water. Sodium zeolite is denoted as Na_2Ze.

Process In this process hard water is passed through a bed of zeolite (as shown in Fig. 5.6) at ordinary temperature. The hard water percolates, Ca^{2+} and Mg^{2+} present in hard water are exchanged with Na^+ ions. The following reactions are taking place.

$$\begin{aligned} MgCl_2 + Na_2Ze &\rightarrow MgZe + 2NaCl \\ MgSO_4 + Na_2Ze &\rightarrow MgZe + Na_2SO_4 \\ CaCl_2 + Na_2Ze &\rightarrow CaZe + 2NaCl \\ CaSO_4 + Na_2Ze &\rightarrow CaZe + Na_2SO_4 \\ Mg(HCO_3)_2 + Na_2Ze &\rightarrow MgZe + 2NaHCO_3 \\ Ca(HCO_3)_2 + Na_2Ze &\rightarrow CaZe + 2NaHCO_3 \end{aligned}$$

Regeneration of zeolite On continuous passing of hard water through sodium zeolite bed. It is converted to calcium and magnesium zeolite which is known as exhausted bed. Hence it must be regenerated. This can be done by washing the zeolite bed with 10% sodium chloride solution.

$$\begin{aligned} CaZe + 2NaCl &\rightarrow Na_2Ze + CaCl_2 \\ MgZe + 2NaCl &\rightarrow \underset{\text{(Regenerated zeolite)}}{Na_2Ze} + MgCl_2 \end{aligned}$$

Advantages

(i) The equipment is small and easy to handle.
(ii) It requires less time for softening.
(iii) Water obtained from this process contains a residual hardness up to 10 ppm.
(iv) Easy to regenerate.
(v) No sludge is formed in this process.

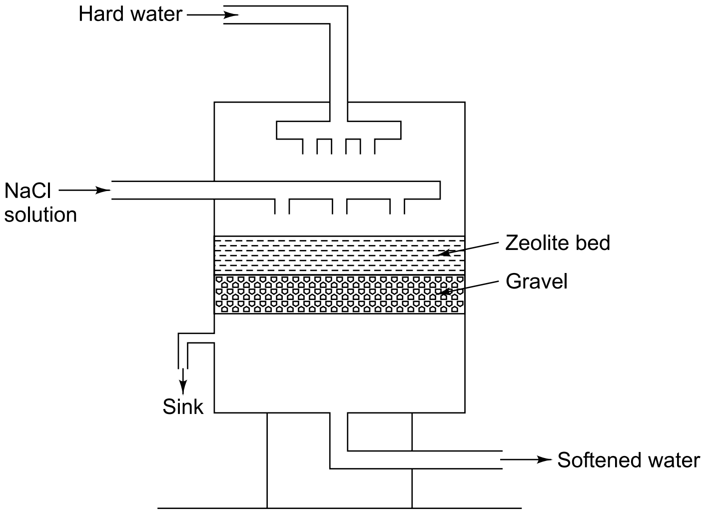


Fig. 5.6 *Zeolite softener*

Disadvantages

(i) Highly turbid water cannot be treated by this process.
(ii) The process exchanges only Ca^{2+} and Mg^{2+} ions by sodium ions and hence the softened water contains more sodium salts.
(iii) All the acidic ions like HCO_3^-, CO_3^{2-}, etc. are not removed by this process. Sodium bicarbonate decomposes in the boiler releasing CO_2 which leads to corrosion while Na_2CO_3 is hydrolysed to NaOH which creates caustic embrittlement of the boiler.

3. Ion-Exchange Process This is also known as De-mineralisation process. Ion-exchange resins are insoluble, cross-linked, long chain organic polymers. The functional groups attached to the chains can exchange hardness producing cations and anions present in water.

Process The process involves the following steps.

1. The first chamber is packed with cation exchange resin (RH^+). When the hard water is passed through a bed of cation exchange resin it exchanges hydrogen ions with Ca^{+2}, Mg^{+2}, K^+, Na^+, etc. of hard water (Fig. 5.7).

$$RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$$
$$RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$$

Thus hardness producing cations (Ca^{2+}, Mg^{2+}, etc.) are removed.

2. The second chamber is packed with anion exchange resin ($R'OH^-$). The water coming out of the first chamber contains H^+, Cl^-, SO_4^{2-} and CO_3^- ions. It is now passed through anion exchange resin bed which can exchange OH^- ions with anions like Cl^-, SO_4^{2-} and HCO_3^-,

$$R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-$$
$$2R'OH^- + SO_4^2 \rightarrow R_2'SO_4^{2-} + 2OH^-$$
$$R'OH^- + HCO_3^- \rightarrow R'HCO_3^- + OH^-$$

Thus, hardness producing anions like Cl^-, SO_4^{2-} and HCO_3^- are removed (Fig 5.7).

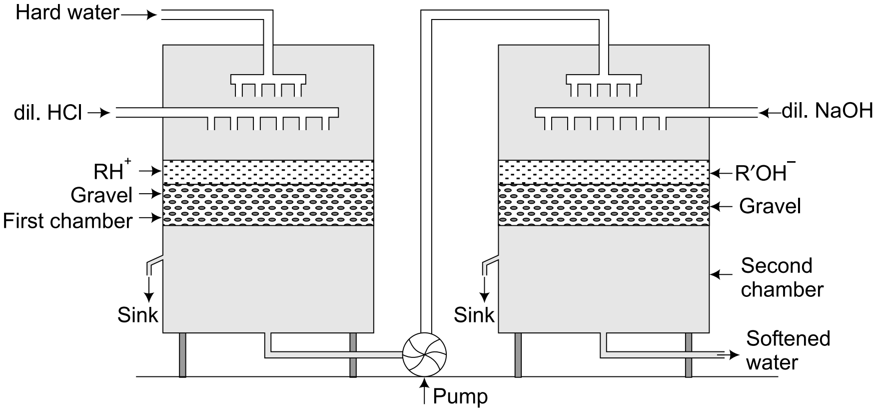


Fig. 5.7 *Demineralisation of water*

3. The H^+ ions produced from first chamber combine with OH^- ions produced from second chamber to form water

$$H^+ + OH^- \rightarrow H_2O$$

Hence, the water produced from ion-exchange process is completely free from all cations and anions of salts.

Regeneration of Resins The resin beds gets exhausted, when used for a long period and can be regenerated;

(a) The exhausted cation exchange resin can be regenerated by passing dil. HCl.

$$R_2Mg^{2+} + 2H^+ \rightarrow 2RH^+ + Mg^{2+}$$
$$R_2Ca^{2+} + 2H^+ \rightarrow 2RH^+ + Ca^{2+}$$

(b) The exhausted anion exchange resin can be regenerated by passing dil. NaOH.

$$R'Cl^- + OH^- \rightarrow R'OH^- + Cl^-$$
$$R_2'SO_4^{2-} + 2OH^- \rightarrow 2R'OH^- + SO_4^{2-}$$
$$R'HCO_3^- + OH^- \rightarrow R'OH^- + HCO_3^-$$

Advantages

1. The softened water by this method is completely free from all salts and fit for use in boilers.
2. It produces very low hardness nearly 2 ppm.
3. Highly acidic or alkaline water can be treated by this process.

Disadvantages

1. The equipment is costly.
2. More expensive chemicals are required for regeneration.
3. Turbid water cannot be treated by this method.

5.13

ANALYSIS OF WATER

Estimation of Dissolved Oxygen A good amount of dissolved oxygen in water at room temperature and pressure is about 8 mg/L. It is essential for sustaining aquatic life and also serves as an indicator of the extent of water pollution by impurities. Hence, determination of dissolved oxygen content is of significance both from environmental as well as from the industrial points of view. Dissolved oxygen content in water is determined by Winkler's method.

Principle The determination of dissolved oxygen is based on the oxidation of potassium iodide by dissolved oxygen. The liberated iodine is titrated against a standarded solution of sodium thiosulphate (Hypo) using starch as indicator. The dissolved molecular oxygen in water is unable to react with KI. So an oxygen carrier like Manganese hydroxide is used to bring about the reaction between KI and Oxygen. Action of potassium hydroxide on manganous sulphate gives manganese hydroxide.

$$\begin{aligned}
MnSO_4 + 2KOH &\rightarrow Mn(OH)_2 + K_2SO_4 \\
2Mn(OH)_2 + O_2 &\rightarrow \underset{\text{Basic manganic oxide}}{2MnO(OH)_2} \\
2MnO(OH)_2 + H_2SO_4 &\rightarrow MnSO_4 + 2H_2O + (O) \\
2KI + H_2SO_4 + (O) &\rightarrow K_2SO_4 + I_2 + H_2O \\
Na_2S_2O_3 + I_2 &\rightarrow Na_2S_4O_6 + 2NaI
\end{aligned}$$

Procedure 2 ml of Manganese sulphate solution and 2 ml of alkaline potassium iodide solution are added to 250 ml of water sample. The bottle is stoppered and shaken well for 10–15 minutes and allowed to stand for few minutes to settle the precipitate. Then 2–3 ml of concentrated sulphuric acid is added, stoppered and shaken to dissolve the precipitate. 100 ml of the solution is pipetted out from the bottle into a clean conical flask and titrated against standard hypo solution using starch as indicator. End point is disappearance of blue colour.

Calculation

$$\text{Volume of hypo solution consumed} = V_1 \text{ ml}$$

$$\text{Normality of hypo solution} = N_1$$

$$\text{Normality of the dissolved oxygen} = \frac{V_1 N_1}{100}$$

$$\text{Weight of dissolved oxygen per litre of water} = \frac{V_1 \times N_1 \times 8}{100} \text{ g}$$

$$= \frac{V_1 \times N_1 \times 8 \times 10^6}{100 \times 1000} \text{ ppm}$$

5.14

DEMINERALISATION OF BRAKISH WATER

This is also known as desalination of brakish water. It involves the removal of salts from water. The salinity of water is mostly due to dissolved sodium chloride and to a smaller extent of other inorganic salts. Sea water containing an average of about 3.5% salts comes under this category (Brakish water). This water is totally unfit for drinking and other domestic purposes. Reverse osmosis method is commonly used for desalination of Brakish water.

Reverse Osmosis Method When a semipermeable membrane saparates two solutions of different concentrations, the flow of solvent takes place from 'less concentrated' to a region of 'more concentrated' due to osmosis. The semipermeable membrane are cellulose acetate, polymethys methaacrylate and polyamide polymers. Semipermeable membrane can allow only solvent (water) but not solute (salts) particles. If more pressure, which is higher than osmotic pressure, is applied then reverse osmosis takes place, i.e., flow of solvent from higher concentration to less concentration (Fig. 5.8). Using this principle drinking water is obtained from brakish (sea water/saltish water). In this method, a pressure in the range of 15–40 kg/cm^2 is applied on the brakish water. The water molecules pass through the membrane while the salts get concentrated in the effluent stream which can be removed.

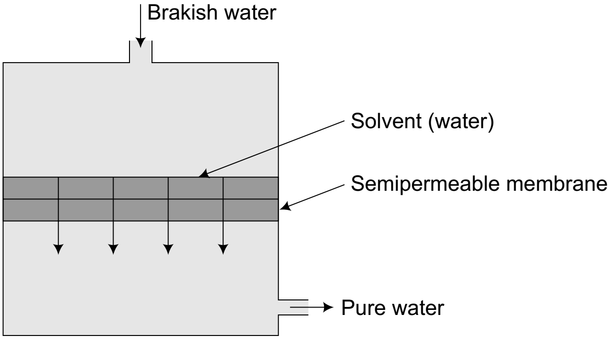


Fig. 5.8 *Reverse osmosis cell*

Electrodialysis This method is another efficient method used for the desalination of water. It is based on the principle that the ions migrate towards oppositely charged electrodes by passing direct current using ion selective permeable membranes. The cation membranes are permeable to only cations while anion membranes are permeable to only anions the process gives pure water by decreasing salt concentration.

"The process of decreasing the concentration of salts in saline water using ion selective membranes under the influence of a direct current is called electro- dialysis."

As shown in Fig. 5.9 an electrodialysis cell consists of a series of alternative cation permeable membranes (C) and anion permeable membranes (A). Saline water is passed under pressure of about 5–6 kg m^{-2} between membrane pairs and electic field is applied across the two electrodes immersed in saline water (brine). The sodium ions (Na^+) move through the 'C' while anions (Cl^-) move through 'A' from each compartment of 'CA'. Therefore the salt content in the 'CA' decreases and an increase salt concentration in AC compartments. The fresh water produced in 'CA' is collected while the concentrated brine from 'AC' compartments is discharged.

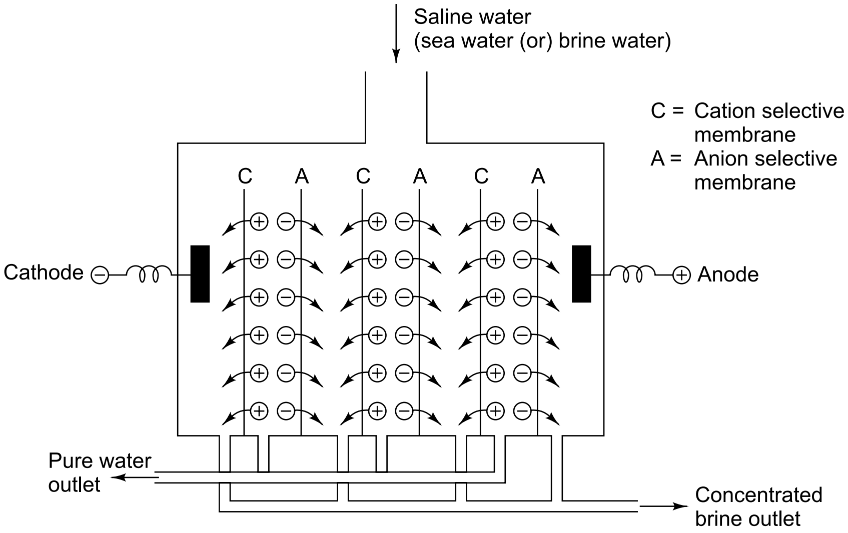


Fig. 5.9 *Electrodialysis cell*

Short Answer Question

1. Define Hardness of water.

   Ans. The water which does not gives lather easily with soap but produces a white precipitate or scum is called hard water hardness of water is due to the presence of bicarbonates and chiorides and sulphates of calcium, magnesium ions. If soap is added to hard water, a white precipitate is formed due to the formation of calcium or magnesion soap.

$$M^{2+} + 2C_{17}H_{35}COONa \rightarrow (C_{17}H_{35}COO)_2M + 2Na^{+}\ (M = Ca(or)Mg)$$

$$C_{17}H_{35}COONa + Mgcl_2 \rightarrow (C_{17}H_{35}COO)_2Mg + 2Nacl$$

2. What are the disadvantages of hard water

Ans. (i) Hard water does not form lather easily with soap.

(ii) Hard water causes bad effects on our digestive system

(iii) Calcium and magnesium salts in water may effect the quality of paper

(iv) Water containing sulphates, carbonates, nitrates effects the crystallization of sugar

(v) Due to the hard water corrosion, scale and sludge formation primary and foaming takesplaces in boilers

3. Which salts caused to temporary and permanent hardness.

Ans. Temporary hardness is due to presence of bicarbonates of calcium and magnesium in water. This can be removed by boiling the water

$$Mg(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

Permanent hardness due to the presence of chloride and sulphates of calucium and megnesium in water this cannot be removed just by boiling the water

4. Why do we express hardness of water in terms of $CaCo_3$ equivalent.

Ans. Hardness is always expressed as equivalents of calcium carbonate. The choice of $CaCo_3$ in particular is due to its Molecular weight being 100 and equivalent weight being 50 which is found to be coinvent for calculation and also insoluble salt that can be precipitated in treatment.

5. Calculate temporary and permanent and total hardness of sample of water containing $Ca(HCO_3)_2 = 40.5$ mg/L: $mg(HCO_3)_2 = 465$ $MgSO_4 = 27.6$ mg/L: $Cacl_2 = 22.4$ mg/L, $CaSo_4 = 32.1$ mg/L

Ans. Calculation of $CaCo_3$ equivalent $= \dfrac{\text{Weight}}{\text{M.w}} \times 100$ mg/L

$$Ca(HCO_3)_2 = \frac{40}{162} \times 100 = 25$$

$$Mg(HCO_3)_2 = \frac{46.5}{146} \times 100 = 31.8$$

$$MgSO_4 = \frac{27.6}{120} \times 100 = 23$$

$$Cacl_2 = \frac{27.4}{111} \times 100 = 20.1$$

$$CaSo_4 = \frac{32.1}{136} \times 100 = 23.6$$

$$\begin{aligned}\text{Temporary hardness} &= Ca(HCO_3)_2 \text{ and } mg(HCO_3)_2\\ &= 25 + 31.8\\ &= 56.8 \text{ mg/L}\end{aligned}$$

Permanent hardness = $CaCl_2$, $CaSO_4$ and $MgSO_4$

= 20.1 + 23.6 + 23

= 66.7 mg/L

Total hardness = Temporary hardness + Permanent hardness

= 56.8 + 66.7 mg/L

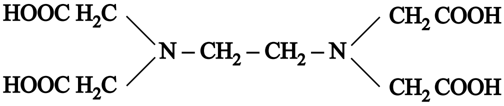
= 123.5 mg/L

6. Why do we add buffer Solution in estimation of hardness of water

Ans. The indicator shows colour change at P^H value of about 10. So We add Alkaline buffer. This is maitain P^H 10.

7. Write Structure of EDTA.

Ans. Ethylene diamine tetra acetic acid (EDTA) is a complexing agent used for estimation of hardness of water



Structure of EDTA

8. What are the industrials methods used for softening of water

Ans. The removal of hardness causing salts from water is called softening of water. The Three important industrial methods employed for softening of water

1. Lime-Soda process
2. Zeolite or Permutit process
3. Ion-exchange or demineralization process

9. Write briefly on Chlorination of water.

Ans. Chlorine produces hypochlorous acid, which is a powerful Germicide.

$$Cl_2 + H_2O \rightarrow \underset{\text{Hypochlorous acid}}{HOCl} + HCl$$

$$\text{Germs} + HOCl \rightarrow \text{Germs are killed}$$

10. Explain the role of nascent oxygen in ozonisation.

Ans. Ozone is an excellent disinfectant. Ozone is highly unstable and breaks down liberating nascent oxygen

$$3O_2 \rightarrow 2O_3$$

$$O_3 \rightarrow O_2 + (O) \text{ Nascent oxygen}$$

nascent oxygen kills becteria as well as oxidise the organic matter

11. Define sterilization and name three methods

Ans. The process of killing pathgenic bacteria and other micro organisms is called sterilization. They are three chemical process for sterilization of water

(i) By adding Bleaching powder

(ii) Chlorination

(iii) Ozonisation

12. Differentiate between scale and sludge.

Ans. Sludge is a soft, loose, slimy deposit formed inside the boiler, salts like $MgCO_3$, $MgSO_4$, $Mgcl_2$, $Cacl_2$ etc are responsible for sludge formation in boilers.

A hard, adhering coating on the inner walls of the boiler is called scale. Salts like $CaSO_4$ and $Ca(HCO_3)_2$ are responsible for scale formation in boilers

13. Define priming and foaming

Ans. Priming: This is also known as wet steam or carry over production of wet steam by rapid boiling water in boilers is called Priming.

Foaming: The production of persistent bubbles or foam in boiler water surface is called foaming

14. Write a short note on any two methods for scale prevention in internal treatment.

Ans. Water is treated within the boiler by converting scale forming substances into sludge forming substances followed by blow down operation.

1. Colloidal conditioning

   Organic Substances like Kerosene and agar agar are added to the water to avoid scale formation.

2. Phosphate conditioning: Phosphates react with water and loose sludge is formed which can be easily removed by blow-down operation

$$3CaCl_2 + 3Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl$$

15. What are the advantages and disadvantages of ion-Exchange process?

Ans. *Advantages:*

1. The softened water by this method completely free from all salts and fit for use in boilers.
2. It produces very low hardness nearly 2 PPM
3. Highly acidic or alkaline water can be treated by this process.

Disadvantages:

1. The equipment is costly
2. More expensive chemicals are required for regeneration.
3. Turbid water cannot be treated by this method.

16. Write the chemical formula of Zeolite

Ans. Zeolite is hydrated sodium alumino Silicate.

Its general formula is $Na_2O.\ Al_2O_3.\ x\,SiO_2.\ y\,H_2O$

17. What are the advantages of zeolite or Permutit process

Ans. *Advantages:*

1. The equipment is small and easy to handle
2. It requires less time for softing
3. Water obtained form this process contains a residual hardness upto 10 PPm
4. Easy to regenerate
5. No sludge is formed in this process.

18. What is the principle involved in reverse osmosis method.

Ans. A semipermeable membrane separates two solutions of different concentrations, the flow of solvent takes place from less concentrated to a region of "more concentrated" called osmosis.

Semipermeable membrane can allow only solvent (water) but not solute (salts) particles. If more pressure, which is higher than osmotic pressure is applied then reverse osmosis takes place. Solvent moves from higher concentration to less concentration

Ex. This Principle used in to obtained drinking water from brakish (Sea water or Salt water).

19. Define the electrodialysis

Ans. The process of decreasing the concentration of Salts in Saline water using ion Selective membranes under the influence of a direct Current is called "Electrodialysis"

20. What is main advantage of reverse osmosis.

Ans. Reverse Osmosis eliminates all ionic, non-ionic, colloidal and organic mater. This process can be easily done and low cost.

Review Questions

Short Type Questions

1. What is mean by Hardness? What are its units to express Hardness?
2. What are the disadvantages of Hard water?
3. Expand EDTA? Write the structure of EDTA
4. What are the water treatments for Domestic purpose
5. Define alkalinity and acidity
6. Define Scale and Sludge
7. What is priming and Foaming
8. Explain Caustic Embrittlement
9. What is Boiler corrosion
10. Write Short note on any one internal treatment of Boiler feed water
11. What is the Chemical formula of Zeolite?
12. What is reverse Osmosis
13. Define Electro dialysis
14. What is meant by chlorination? give its draw backs.
15. Define ppm
16. Why EDTA used in estimation of hardness?
17. What are the important parameters for water quality?
18. Write the chemical Equation for the determination of D.O by Wrinkler's method
19. Define Brakish water? What type of method used its purification?
20. Write the principle for Osmosis? How it is used in water purification?

Essay Type Questions

1. Discuss the impurities in water and their effects.
2. What is meant by hardness of water? Give its units?
3. What are the major disadvantages of hard water used for
    (i) domestic purposes
    (ii) industrial purposes
    (iii) steam generation in boilers.

4. What is meant by carbonate and non-carbonate hardness of water? Explain with examples?
5. Describe the estimation of hardness by EDTA method?
6. What is meant by sterilisation of water? Explain how sterilisation of water is carried out by using chlorine and ozone?
7. Write short note on
   (i) Priming and foaming (ii) Phosphate conditioning
   (iii) Caustic embrittlement
8. (i) Explain the process of scale and sludge formation in boilers.
   (ii) Describe the internal treatment of boiler water.
9. Describe the ion-exchange process for softening of water? What are its advantages and limitations?
10. (i) What are the important sources of water?
    (ii) How do you estimate dissolved oxygen in water?
11. Discuss briefly boiler troubles and their treatment?
12. What are scales and sludges? How do they effect the boiler? How can they be prevented?
13. Write a short note on boiler corrosion?
14. Describe the desalination of brakish water by Reverse osmosis method?
15. Describe the desalination of brakish water by electrodialysis.
16. Describe the permutit process for softening of water.
17. Describe the methods for the conditioning of boiler feed water.
18. Explain the lime–soda process for softening of water used for steam generation in industrial boilers mentioning clearly the reactions and conditions employed?

Multiple Choice Questions

1. Temporary hardness of water can be removed by
   (a) Filtration
   (b) Screening
   (c) Boiling
   (d) Sedimentation.
2. Purest form of natural water is
   (a) Sea water (b) River water
   (c) Rain water (d) Lake water.
3. Calgon is a trade name given to
   (a) Sodium hexametaphosphate
   (b) Magnesium phosphate
   (c) Calcium silicate
   (d) Sodium sulphate.
4. Blow down operation causes the removal of
   (a) Sludges (b) Scales
   (c) Both of them (d) Cold water.
5. Brakish water mostly contains dissolved
   (a) K salts (b) Mg salts
   (c) Ca salts (d) NaCl.
6. Water can be sterilised by using
   (a) Cl_2 (b) O_3
   (c) Both of them (d) NaOH.
7. pH of alkaline water is
   (a) 7 (b) more than 7
   (c) Less than 7 (d) 0.
8. Brakish water can be purified by using

(a) Lime–Soda process
(b) Permutit process
(c) Filtration
(d) Reverse osmosis method.

9. Hard water is water containing
(a) Ca^{2+} and Mg^{2+}
(b) K^+ and Li^+
(c) CO_2 and O_2
(d) NO_3^- and NO_2^-.

10. Water containing calcium chloride and magnesium sulphate is
(a) Temporary hard only
(b) Permanent hard only
(c) Both of them
(d) Soft only.

11. Best method of removing hardness of water is
(a) Ion-exchange (b) Permutit
(c) Lime-soda (d) Boiling.

12. Hardness of water is expressed in terms of equivalents of
(a) $MgCO_3$ (b) $CaCO_3$
(c) Na_2CO_3 (d) K_2CO_3.

13. Caustic embrittlement causes due presence of residual in boiler water
(a) NaCl (b) NaOH
(c) $MgCO_3$ (d) KNO_3.

14. Priming and foaming in boilers produce steam of
(a) Wet (b) Dry
(c) Soft water (d) none of these.

15. The exhausted cation exchange resin can be regenerated by washing with
(a) dil. NaOH
(b) dil. HCl
(c) Distilled water
(d) Brakish water

16. A hard sticky precipitate formed on the inner surface of the boiler is called
(a) Sludge (b) Oil
(c) Grease (d) Scale.

17. Which of the following is responsible for temporary hardness?
(a) $MgCl_2$ (b) $CaSO_4$
(c) $MgSO_4$ (d) $Mg(HCO_3)_2$.

18. The water which is fit for drink is called
(a) Hard water
(b) Brakish water
(c) Potable water
(d) Moderately hardness.

19. Which of the following is a powerful disinfectant?
(a) O_2 (b) Cl_2
(c) $CaOCl_2$ (d) N_2.

20. ______ indicator is used for determination of hardness by EDTA method
(a) Methyl orange
(b) Methyl red
(c) EBT
(d) FSB – F.

21. Anion exchange resin is regenerated by using
(a) dil. NaOH (b) dil. HCl
(c) dil. NaCl (d) dil. KCl.

22. pH of neutral water is
(a) 7 (b) More than 7
(c) Less than 7 (d) 14.

23. Water is hard, when it contains
(a) alkalinity
(b) acidity
(c) dissolved potassium salts
(d) dissolved Ca and Mg salts.

24. Loose and slimy precipitate formed within the boiler is called
(a) scale (b) sludge
(c) priming (d) corrosion.

25. Dissolved CO_2 in water can be removed by adding
(a) ammonia
(b) sodium chloride
(c) HCl
(d) H_2SO_4.

Answers

1. (c)
2. (c)
3. (a)
4. (a)
5. (d)
6. (c)
7. (b)
8. (d)
9. (a)
10. (b)
11. (a)
12. (b)
13. (b)
14. (a)
15. (b)
16. (d)
17. (d)
18. (c)
19. (b)
20. (c)
21. (a)
22. (a)
23. (d)
24. (b)
25. (a)

Fill Up the Blanks Questions

1. Soft water give ________ with soap.
2. $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ salts present in water produces ________ hardness.
3. $MgCl_2$ and $MgSO_4$ salts present in water produces ________ hardness.
4. $Ca(HCO_3)_2$ and $CaCl_2$ salts present in water produce ______and______hardness.
5. The full name of EDTA is ________.
6. The common units used for expressing hardness of water ________.
7. The process of removing hardness producing salts from water is called ________.
8. The most important method for softening of water is ________.
9. The process of killing pathogenic bacteria is called ________.
10. The percentage of NaCl present in sea water is ________.
11. The production of persistent bubbles or foam in boiler water surface is called ________.
12. The loose and slimy precipitate formed within the boiler is called ________.
13. A good amount of dissolved oxygen in water at room temperature and pressure is about ________.
14. The process of removing common salt from water is called ________.
15. The chemical formula for Calgon is ________.

Answers

1. Lather
2. Temporary
3. Permanent
4. Temporary and permanent
5. Ethylene diamine tetra acetic acid
6. Parts per million (ppm) (or) milligrams per litre (mg/L)
7. Softening
8. ion-exchange
9. Sterilization
10. about 2.6%
11. foaming
12. sludge
13. 8 mg/L
14. desalination
15. $Na_2[Na_4(PO_3)_6]$

6

Phase Rule

6.1

INTRODUCTION

The phase rule is an important generalisation dealing with the behaviour of a heterogeneous system. This relationship governing all heterogeneous equilibria was first discovered by an American physicist, JW Gibbs in 1874. It is possible to predict phase rule qualitatively by means of a diagram, showing the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium.

The derivation of phase rule is general relation between the number of degrees of freedom F, the number of components C, and the number of phases at equilibrium P, for a system of any composition. The mathematical equation of phase rule is given by

$$F = C - P + 2$$

Phase may be defined as any homogeneous part of a system having all physical and chemical properties the same throughout. In this, the system consists of one or more than one phases.

The component C in the phase rule equation, may be defined as "the least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation".

1. One-phase or 1-phase system ($p = 1$) system containing only liquid water system.
2. Two phase or 2-phase system ($p = 2$) liquid water and water vapour (a gas) system.
3. The system containing liquid water, water vapour and solid ice is a three-phase or 3-phase system.

Homogeneous system consisting of only one phase.

Heterogeneous system consisting of two or more phases.

Ordinarily, three states of matter gas, liquid, and solid are known as phases. In this phase rule, a uniform part of a system in equilibrium is termed a phase. Thus, a liquid or solid mixture could have two or more phases.

Few examples of phase of phase rule are given below.

1. *Pure Substances* A pure substance (solid, liquid or gas) made up of one chemical species only is considered as one phase. For example, Oxygen (O_2), Benzene (C_6H_6) and Ice are all 1-phase systems. It must be remembered that a phase may or may not be continuous. Thus, whether ice is present in one block or many pieces, it is considered as one phase.
2. *Mixtures of Gases* All gases mix freely to form homogeneous mixtures. Mixtures of gases, say N_2 and O_2 are 1-phase system.
3. *Miscible Liquids* Two completely miscible liquids yield a uniform solution, thus a solution of water and ethanol is a 1-phase system.
4. *Non-Miscible Liquids* A mixture of two non-miscible liquids on standing forms two separate layers. A mixture of water and chloroform ($CHCl_3$) constitutes a 2-phase system.
5. *Aqueous Solutions* An aqueous solution of a solid substance such as sodium chloride (or sugars) is uniform throughout. Hence, it is a 1-phase system. A saturated solution of sodium chloride in contact with excess solid sodium chloride is a 2-phase system.
6. *Mixtures of Solids*
   (i) From the definition, phase must have the same physical and chemical properties throughout, ordinary sulphur as it occurs in nature is a mixture of monoclinic and rhombic sulphur. These allotropes of sulphur consist of the same chemical species, but differ in physical properties. Thus, a mixture of two allotropes is a 2-phase system.
   (ii) A mixture of two or more chemical substances contains as many phases.

6.1.1 Phase Diagrams

The phase diagram of a substance is a map showing the conditions of pressure and temperature at which its various phases are thermodynamically most stable. For example: At point ‘A’ in Fig. 6.1, the various phases of a substance are thermodynamically most stable, but at ‘C’, the liquid phase is the most stable.

The boundaries between regions in a phase diagram are called ‘phase boundaries’. In this, they show the values of *P* and *T* at which the two neighbouring phases are in equilibrium. For example, a system is arranged to have a pressure and temperature represented by a point ‘B’. Then, the liquid and its vapour are in equilibrium (liquid water and water vapour at 1 atm and 100°C). If the temperature is reduced at constant pressure, the system moves to point ‘C’, where the liquid is stable (water at 1 atm and at temperature between 0°C and 100°C). If the temperature is reduced still further to ‘D’, then the solid and the liquid phases are in equilibrium (ice and water at 1 atm and 0°C). A further reduction in temperature takes the system into the region where the solid is the stable phase.

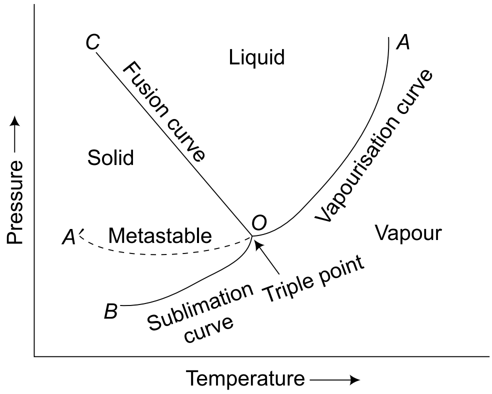


Fig. 6.1 *A typical phase diagram of one component system*

6.2

PHASE DIAGRAM FOR 1-COMPONENT SYSTEM (WATER SYSTEM)

Under normal conditions, the system water is in three phases, one-component system. The three phases involved are liquid water, ice and water vapour. All these phases can be represented by one chemical entity H_2O and hence, one component of the system. The number of phases which can exist in equilibrium any time depends on the conditions of temperature and pressure. The phase diagram or *PT-graph* of the system/water/ice/vapour are shown in Fig. 6.2. The salient features of the phase diagram are given in the next page:

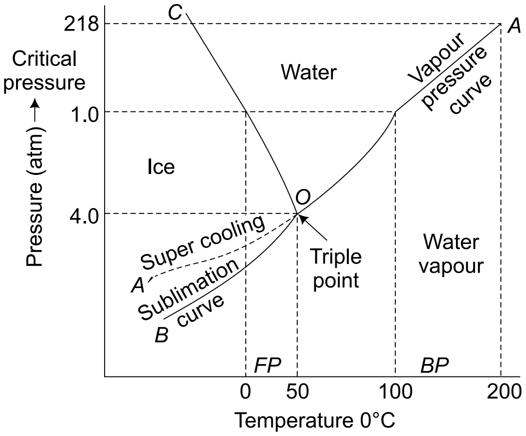


Fig. 6.2 *The phase diagram of the system 'water'.*

1. The curves *OA*, *OB*, *OC*
2. The triple point *O*
3. The areas *AOC*, *AOB*, *BOC*

1. The Curves OA, OB, OC Here, these three curves meet at the point *O* and divide the diagram into three regions or areas.

I. The curve *OA* is the vapour pressure curve of water. It represents the vapour pressure of liquid water at different temperatures. The two phases, water and water vapour, coexist in an equilibrium along this curve. The curve *OA* terminates at *A*, the critical point (218 atm, temperature 374°C). When the liquid and vapour are indistinguishable from each other, one phase is left only. When the vapour pressure is equal to one-atmosphere, the corresponding temperature, as indicated on the phase diagram is the boiling point (100°C) of water.

II. The curve *OB* is the sublimation curve of ice. It shows the vapour pressure of solid ice at different temperatures. The two phases, solid ice and vapour, coexist in equilibrium along this curve. At the lower limit, the curve *OB* terminates at absolute zero (–273°C) where no vapour exists.

The curve *OC* is the fusion curve of ice. It depicts the effect of pressure on the melting point of ice. Here, ice and water coexists in equilibrium. The fact that *OC* slopes to the left indicates that the melting point of ice decreases with increase of pressure. Since ice melts with decrease in volume by Le Chatelier's principle, the melting point is lowered by an increase of pressure. It may be noted that the 1.0 atmosphere line meets the fusion curve at 0°C which is the normal melting point of ice.

Along the curves *OA*, *OB*, *OC*, there are two phases in equilibrium and one component. Therefore,

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

Hence, each two phase system:

Water/water vapour represented by *OA*
Ice/water vapour represented by *OB*
Ice/water represented by *OC*

has one degree of freedom, i.e. is monovariant.

2. The Triple Point 'O' The curves *OA*, *OB* and *OC* meet at a triple point '*O*' where all the three phases liquid water/ice/vapour are in equilibrium. The curves at 0.0076°C and vapour pressure 4.58 mmHg. Since there are three phases and one component, we have

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

i.e., the system at the triple point is non-variant. Thus, if either pressure or temperature is changed, the three phases would not exist and one of the phases would disappear.

3. Area AOC, AOB, BOC The areas or regions between the curves show the conditions of temperature and pressure under which a single phase—ice, water or vapour is capable of stable existence. Thus, Area *AOC* represents conditions for the one-phase system water.

Area *AOB* represents conditions for the one-phase system water vapour.

Area *BOC* represents conditions for the one-phase system ice.

In all the three areas, there being one-phase and one-component, we have

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

Thus, each system water, water vapour or ice has 2 degrees of freedom, i.e. the system is bi-variant.

6.3
TWO-COMPONENT SYSTEM

When a single phase is present in a two component system, the degrees of freedom are three.

$$F = 2 - 1 + 2 = 3$$

This means, the three variables must be specified in order to describe the condition of the phase.

6.3.1 Lead–Silver System

This system has two components and four phases. The phases are (i) solid silver, (ii) solid lead, (iii) solution of molten silver and lead, and (iv) vapour.

Lead and silver considerably having high boiling points, so the vapour phase is practically absent. Thus, Ag/Pb is a condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore, we need to consider only the two remaining variables, namely the temperature (*T*) and concentration (*C*). The complete PC diagram of the system Ag/Pb is in Fig. 6.3.

The salient features of the diagram are

(a) Two curves *AC* and *BC*
(b) Eutectic point, *C*
(c) Three areas (i) above *ACB*, (ii) below *AC*, (iii) below *BC*

Curve AC Is the freezing point curve of Ag. *A* represents the freezing point or melting point of solid silver (961°C) and the curve *AC* shows that the addition of lead, lowers the melting point along it. The phases in equilibrium along *AC* are solid silver and solution of silver and lead. Applying the reduced phase rule equation,

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

Thus, the system Ag/solution is mono-variant.

Curve BC Is the freezing point curve of Pb. *B* represents the melting point of solid lead (327°C) and the curve *BC* shows that the melting point is lowered by addition of silver. The phases in equilibrium along *BC* are solid lead and solution. The system is mono-variant.

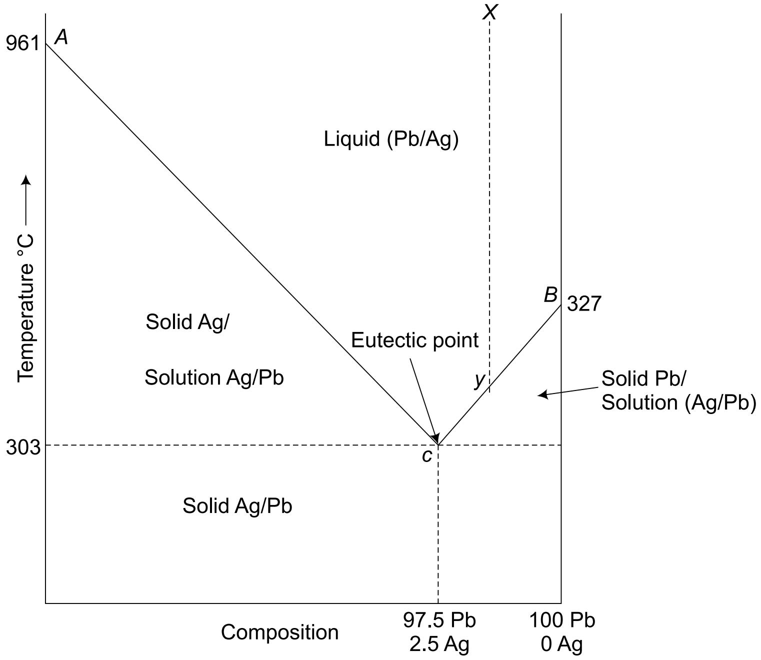


Fig. 6.3 *The phase diagram of Ag/Pb system*

The Eutectic Point C The curves *AC* and *BC* intersect at *C*, which is called Eutectic point. Here, three phases solid Ag, solid Pb and solution are in equilibrium. Applying the reduced phase rule equation,

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

Thus, the system Ag/Pb/solution at *C* is non-variant. Both the variables, temperature (303°C) and composition (97.5% Pb, 2.5% Ag) are fixed. If you raise the temperature above the eutectic temperature, the solid phases Ag and Pb disappear, and if you cool it below the eutectic temperature, you will land in the solid Ag/Pb area, where solution phase is non-existent.

The area above *AOC*—this region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule equation, we have,

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

Thus, the system solution Ag/Pb is bi-variant.

The area below *AC*, represents the phases Ag + solution, while that below *BC*, represents the phases Pb + solution. The area below the temperature 303°C, represents solid Ag + solid Pb. All these areas have two phases and one degree of freedom,

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

6.3.2 Eutectic System

A binary system consisting of two substances which are miscible in all proportions in the liquid phase, but which do not react chemically is known as the Eutectic (easy to melt) system, e.g. a mixture lead and silver comprises such a system.

Applications of Eutectics Low melting alloys are used as safety devices (e.g. as plugs in automobiles), fire sprinklers and as 'fail safe' device in boilers. By suitable choice of metals very low melting alloys can be obtained, e.g., wood's metal (alloy containing 50% Bi, 25% Pb, 12.5% Sn and 12.5% Cd) melts at 65°C only.

6.3.3 Iron–Carbon Alloy System

Pure iron (molten) freezes into the δ-ferrite at 1537°C. Solid iron exists in three different states.

1. δ-ferrite from 1537 to 1404°C—a body face-centred cubic lattice.
2. ρ-ferrite from 1404°C to 906°C—a face-centred cubic lattice.
3. Below 906°C, α-ferrite—a body centred cubic lattice.

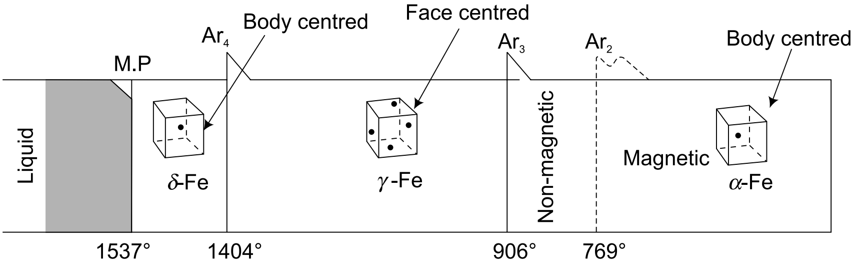


Fig. 6.4 *Different states of solid iron*

Phase Diagram It is a case of the formation of solid solution, where one of the components is a metal and the other a non-metal (viz. carbon). Another important feature in this case is that the point of interest extends up to 6.7% of carbon only. Beyond this, there will be no discussion.

The equilibrium relationship in alloys of iron and carbon are given in Fig. 6.5. The diagram is divided into a number of phases fields, each occupied either by a single phase or a mixture of two phases.

1. The curve *ABCD* is the liquidus line above which there is an only one liquid phase consisting of iron and dissolved carbon. The melting point of iron–carbon system can be found with the help of this line.
2. The curve *AEPGCH* is the solidus line below which various iron–carbon compositions are completely solid. Evidently, the regions between the liquidus line and solidus line represent mixture of solids and liquid.
3. It will be noted here that with increasing carbon content, the melting point of iron–carbon alloy is progressively depressed until alloy with 4.3%C

melts at 1130°C (as compared with 1537°C for pure iron). As the *C* content increases further up to 6.67%, when only cementite (Fe_3C) is present, the melting point again rises.

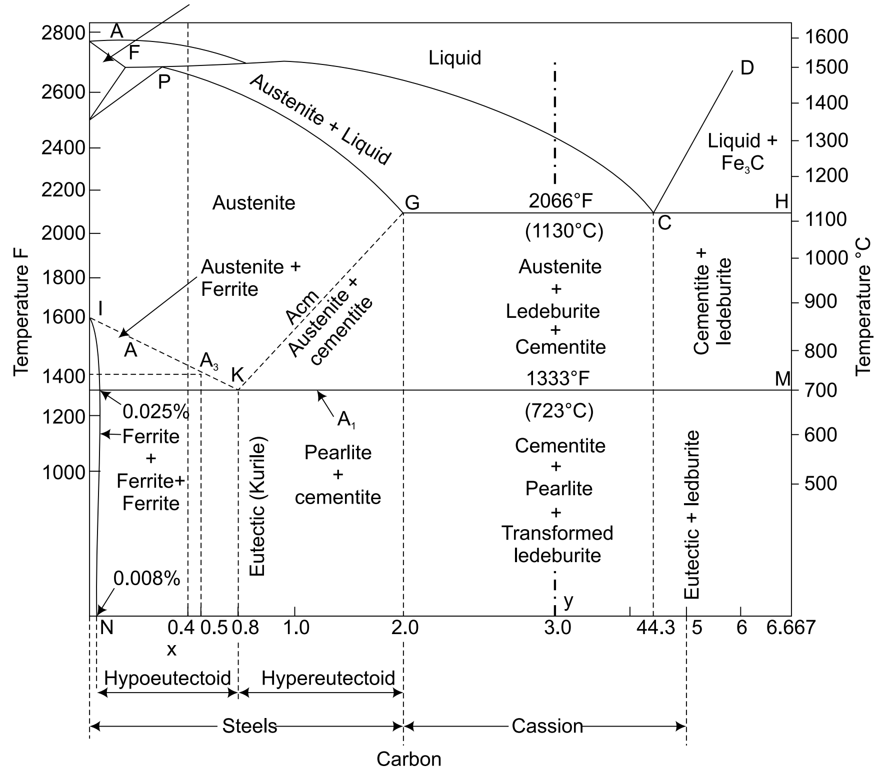


Fig. 6.5 *Equilibrium diagram for Fe–C system*

4. Within the area *AEB*, the alloy exists as δ-iron plus liquid. The region *DCH* consists of cementite (Fe_3C) plus liquid. The region *BCGP* consists of austenite plus liquid; whilst the region *PGKI* consist wholly of ρ-iron (i.e. austenite).
5. The transformation of one solid phase into another, as from austenite (or ρ-iron) to ferrite (or α-iron) or to cementite (Fe_3C) occurs at certain critical temperatures indicated on the diagram by lines *LKM*; *IK* and *GK*. These lines are usually referred to respectively as A_1, called the lower critical temperature line, and A_3 and A_{cm}, called the upper critical temperature lines.
6. The diagram also indicates the ranges of composition for iron, steel and cast iron. Thus, compositions (α) up to 0.088%C are regarded as commercially pure iron; (b) those from 0.088 to 2%C represent steel; and (c) those above 2%C represent cast iron. Steels are further subdivided into hypoeutectoid steel (i.e. up to 0.8%C) and hypereutoid (i.e. from 0.8 to 2%C).

7. From the diagram, it is clear that austenite is not stable below the upper critical lines A_3 (IK) and A_{cm} (GK).
   (a) For compositions containing less than 0.8%C, austenite on cooling begins to transform into ferrite and the carbon content of the remaining austenite increases along the line A_3 until point *K* (10.8%C) is reached.
   (b) For composition between 0.8% to 2%, cooling results in separation of cementile and the composition of remaining austenite varies along the lines A_3 (*GK*) until again the point *K* is reached.
   (c) At point *K* (called the eutectoid), austenite is transformed into pearlite (an intimate mixture of ferrite and cementite). This is called the eutectoid transformation. At the eutectoid point, three-phases—austenite, ferrite and cementite—co-exist in equilibrium and the point in invariant.
8. At a temperature of 1130°C (2066°F), the eutectic transformation point *C* takes place. The eutectic liquid with 4.3%C on cooling freezes to ledeburite, an eutectic mixture of austenite and cementite. On further cooling, the eutectic austenite gradually transforms to cementite and its composition varies along line *GK* until again the eutectoid point *K* is reached, where all the remaining austenite is transformed into pearlite.
9. Changes taking place on cooling hypoeutectoid steel (i.e., containing less than 0.8%C) can be illustrated by discussing cooling of steel containing say 0.4% C. This is represented in the diagram by the line *xx*. When this steel is cooled from point "1" along *xx*, freezing begins at point "2", which is the point of intersection of the *xx* line with the liquids line *ABC*. Complete solidification of an alloy occurs at point "3". As cooling proceeds, no change occurs until the point "4" on line A_3 is reached, where the precipitation of ferrite (from the solid phase of austenite) begins. Further cooling results in simultaneous increase of ferrite and decrease of austenite content along line *IK*. The composition of ferrite varies along the line *IL*. It may be pointed out that at any point in the regions *ILK*, the percentage of ferrite and austenite can be computed from the lever rule. For example, at 1380°F (see the horizontal dashed line in Fig. 6.5) the austenite contains 0.5% C and ferrite contains 0.02% C. Consequently, the amount of austenite in the alloy will be

$$\frac{0.4\% - 0.02\%}{0.5\% - 0.02\%} = \frac{0.38\%}{0.48\%} * 100\% = 79\%$$

   And the corresponding percentage of ferrite will be 100% – 79% = 21%
10. At the eutectoid temperature of 723°C (1333°F), the remaining austenite undergoes transformation to pearlite. On further cooling below this temperature, practically no change occurs in the micro-structure of the steel, since the solubility of C in ferrite (indicated by line *LN*) varies relatively very little.

11. It can also be seen that a steel of the eutectoid composition (i.e., with 0.8%C) will consist of pearlite only; whereas a steel with a C content greater than 0.8% will consist of pearlite plus cementite.
12. Now consider the cooling of an iron-carbon alloy corresponding to the composition of cast iron. Let an alloy under consideration containing 3%C, represented on the diagram by the line *yy*. On cooling this alloy, freezing begins at about 1,270°C, the point of intersection of *yy* with *ABC*. On further cooling, austenite begins to separate out of the liquid. As cooling proceeds further, the amount of solid increases and its composition varies along the liquidus line *PG*; whereas the amount of liquid decreases and its composition varies along the liquids line *BC*. When the temperature 1130°C (2066°F) is reached, the mixture will consist of austenite containing 2%C and a liquid of eutectic composition. Further removal of heat causes no drop in temperature until all liquid solidifies to ledeburite, an autistic mixture of austenite and cementite. At this point, cast iron will consist of primary austenite plus ledeburite. Still further cooling causes both primary and eutectic austenite to decompose to cementite along the line *GK*. When eutectic temperature (723°C) is reached, the residual austenite will transform to pearlite. At temperatures below 723°C, all ledeburite will be transformed into a pearlite and cementite mixture which will thus be the final micro-structure of cast iron.

6.4

HEAT TREATMENT OF ALLOYS

The alloys can be heat treated by a number of methods such as annealing, precipitation hardening and Martensite hardening, etc.

(a) Annealing When alloy is cold worked, some properties such as tensile strength, hardness, electrical resistance, coefficient of expansion and electrode potential increase, and some properties such as ductility, cold workability, density and resistance to notches decrease. When temperature of the alloy is increased, all the properties tend to return to normal values and this heating of the alloy for softening is generally known as annealing.

(b) Precipitation Hardening This is the heat treatment given to an alloy in order to increase its strength and the latter increases on account of the appearance and growth of a second phase in a super saturate solid solution. For example, when 4% copper alloy is cooled slowly from 520°C, there is an appearance of theta crystals, when the temperature falls below the saturation curve. During continuous slow cooling to room temperature, the size of such theta crystals increases and content of copper in the solid solution decreases. The appearance of theta crystal phase is nothing but precipitation hardening.

(c) Martensite Hardening This type of heat treatment is carried out by suppressing the eutectoid phase transformation by rapid cooling or quenching. As a result, a hard unstable phase is obtained. For example, martensite, a hard unstable phase is formed by quenching austenite (a solid solution of carbon in face centred cubic iron in steel) from the temperature above the iron–iron carbide eutectoid at 720°C.

Short Answer Questions

1. Define the term phase

   Ans. A homogenous part of a system which is having the same physical and chemical properties through out is called a phase. A system may consist of one phase or more than one phases.

2. What is meant by components?

   Ans. The least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation.

3. How many phases are present in Mixture of gases?

   Ans. All gases mix freely to form homogeneous mixtures. Therefore any mixture of gases say O_2 and N_2, is a one phase system.

4. How many phases are present in Decomposition of calcium carbonate.

   Ans. When $CaCO_3$ is heated in a closed vessel, we have

   $$\underset{\text{(solid)}}{CaCO_3} \rightleftharpoons \underset{\text{(solid)}}{CaO} + \underset{\text{(gas)}}{CO_2}$$

   There are two solid phases and one gas phase.

   Hence it is a 3-phase system

5. Define the degree of freedom.

   Ans. The least number of variable factors (temperature, pressure and concentration) which most be specified so that the remaining variables are fixed automatically and the system is completely defined. If a system with F = 0 is known as nonvariant.

6. Write a note on eutectic point.

   Ans. The mixture of components A and B at point C melts at lowest temperature indicated on the graph. The point C is therefore, called the Eutectic point.

7. Define Phase role.

   Ans. The derivation of phase rule is general relation between the number of degrees of freedom F, the number of components C, and number of phase at equilibrium P, for a system of only composition.

   The mathematical equation of phase role is given by

   $$F = C - P + 2$$

8. What is an variant system (non variant)?

   Ans. The system in which the degree of freedom to zero i.e., no condition is required to be specified to define the system.

9. What is triple point?

   Ans. A point at which the gaseous, liquid and solid phases of the system co-exist in equilibrium

   $$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{gaseous}$$

10. What are the applications of Eutectics?

Ans. 1. Low melting alloys are used as safety devices (e.g. plugs in auto mobiles)

2. Fire sprinklers and as 'fail safe' device in boilers.

3. By suitable choice of metals very low melting alloys can be obtained e.g. wood's metal.

11. What is condensed system?

Ans. The vapour phase practically absent so pressure can have no effect on the system. Such system called condensed system.

12. What are the limitation of phase role?

Ans. 1. Phase role can be applied only for system in equilibrium

2. Phase role conditions that all phases of the system must be present, simultaneously under identical conditions.

13. What is eutectic composition of lead-silver system?

Ans. The eutectic composition of lead-silver system is 97.4% Pb and 2.6% Ag.

14. How many components present in water system?

Ans. The water consist three phases i.e., solid (ice), liquid, gaseous containing same molecular formula (H_2O). Hence it is one component system.

15. What is the difference between critical point and triple point?

Ans. Critical point refers to the temperature and pressure where a liquid and its vapour become identical. While triple point is the condition of temperature and pressure under which three phases of substance co-exist in equilibrium.

Review Questions

Short Type Questions

1. State and Explain the phase rule.
2. What is reduced phase rule?
3. A system consists chloroform and water. What is the number of phases.
4. Give an example of bivariant system.
5. What is metastable equilibrium?
6. How many number of phases and components are present in the following system?

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

7. What is hypoeutectoid steel?
8. Define the Ferrite and cementite.
9. What are the different states of solid iron?
10. Write short note on significance of triple point.
11. What are the applications of phase diagrams?

Essay Type Questions

1. Define or explain the following terms.

(a) Phase rule (b) Degrees of freedom

(c) Phase (d) Components.

2. Explain the term ‘component’. How many components are present in the following system?

$$\text{Water} \rightleftharpoons \text{Water Vapour}$$

3. Draw a phase diagram for such a component system which contains more than one solid phase. Explain the following terms with the help of diagrams.
   (a) Triple point
   (b) Invariant system
   (c) Metastable system.
4. (a) Explain the following terms
      (i) Phase
      (ii) Component
      (iii) Degree of freedom.

   Explain their relation.

   (b) Define Eutectic point.
   (c) Discuss the phase diagram of water system.
5. For one component system, the triple point is an invariant system. Discuss.
6. Explain why the fusion curve of ice has a negative slope whereas the sublimation curve has a positive slope in the phase diagram.
7. (a) State and explain the phase rule. Explain various terms involved.
   (b) Draw and explain the phase diagram of one-component three-phase systems.
8. Explain the following terms:
   (a) Eutectic point
   (b) Eutectic mixture
   (c) Condensed system
   (d) Triple point.
9. Draw and explain the phase diagram of water system, i.e. one-component system.
10. Discuss the phase diagram of two-component system, i.e. Lead-silver system.
11. Discuss the salient features of phase diagram of Lead-Silver system.
12. Apply phase rule to water system.
    (a) What is condensed system? Write the reduced phase rule equation.
    (b) Discuss the salient features of Lead-Silver system.
13. Discuss the main features of the phase diagram of the water system, explaining especially why the slope solid-liquid line is negative for water.
14. Write short notes on the following:
    (a) Phase rule for condensed system.
    (b) Functioning of freezing mixtures.
15. Determine the number of phases, components and degrees of freedom in the system: ice, water and water vapour in equilibrium.
16. Describe an experimental method for determining a phase diagram of two-component system.
17. (a) State the phase rule and explain the terms involved.
    (b) Is there any difference between an eutectic point temperature and melting point temperature? If there is any difference, how will you distinguish between the two by thermal analysis.
18. Draw the phase diagram for two-component system forming a simple eutectic. Apply the phase rule to discuss the diagram completely.

19. Explain the terms involved in the phase rule equation with examples. Explain the water system.

20. Write a short note on phase diagram.

21. With the help of iron-carbon diagram, define clearly the following terms:

(a) Ferrite
(b) Pearlite
(c) Cementite
(d) Ledeburite.

Multiple Choice Questions

1. The phase rule was first discovered by

(a) Nernst
(b) Gibbs
(c) Arrhenius
(d) Lechatelier.

2. Mathematically, the phase rule can be expressed by

(a) $F + P = C - 2$
(b) $F = C - P + 2$
(c) $P = C - F + 2$
(d) All of the above.

3. A system containing liquid water and water vapour has the number of phases equal to

(a) 0
(b) 1
(c) 2
(d) 3.

4. Water system has three phases—ice, water and vapour. The number of components in the system are

(a) One
(b) Two
(c) Three
(d) Four.

5. For one component system, the phases are

(a) $F = 3 - P$
(b) $F = 2 - P$
(c) $F = 1 - P$
(d) None of the above.

6. At a triple point

(a) Both the temperature and pressure are fixed
(b) Only the temperature is fixed
(c) Only the pressure is fixed
(d) Sometimes pressure and sometimes temperature is fixed.

7. The occurrence of a substance in more than one crystalline form is known as

(a) Isomerism
(b) Racemisation
(c) Polymorphism
(d) None of the above.

8. For one phase and one component system, the degrees of freedom are equal to

(a) 1
(b) 2
(c) 3
(d) 4.

9. When a single phase is present in a two-component system, the degrees of freedom are

(a) Zero
(b) Bivariant
(c) Invariant
(d) None of the above.

10. A system with zero degree of freedom is known as

(a) Mono-variant
(b) Bivariant
(c) Invariant
(d) None of the above.

11. The number of components present in the following systems

$$\text{Water} \rightleftharpoons \text{Water vapour}$$

(a) 1 and 1
(b) 1 and 2
(c) 2 and 1
(d) 2 and 3.

12. The phase rule is applicable to

(a) Homogeneous system
(b) Reversible systems

(c) Irreversible systems

(d) Heterogeneous system whether physical or chemical.

13. For a bivariant system, the degrees of freedom are

(a) One (b) Two

(c) Three (d) Four.

14. For a two-component system in a single phase, the degrees of freedom are

(a) Zero (b) One

(c) Two (d) Three.

15. A one-component system has four phases. Can four phases co-exist in equilibrium?

(a) No

(b) Yes

(c) Sometimes

(d) None of the above.

16. For one component system, at triple point, the number of degrees of freedom are

(a) Zero (b) One

(c) Two (d) Three.

17. For one component system, there does not exist quadruple point as the number of degrees of freedom cannot be

(a) Zero (b) –1

(c) 1 (d) 2.

Answers

1. (b) **2.** (d) **3.** (c) **4.** (a) **5.** (a)

6. (a) **7.** (c) **8.** (b) **9.** (d) **10.** (c)

11. (b) **12.** (d) **13.** (c) **14.** (d) **15.** (a)

16. (b) **17.** (b)

Appendix

Fuel Cells

The galvanic cells can only produce electrical energy for a limited time because the electrode reactants are eventually depleted. Fuel cells are different; they are electrochemical cells in which electrode reactants are supplied continuously and are able to operate without theoretical limit as long as the supply of reactants is maintained. This makes fuel cells an attractive source of power where long-term generation of electrical energy is needed.

In a fuel cell, an electrical energy is obtained without combustion from oxygen and a gas that can be oxidized. A fuel cell converts the chemical energy of the fuels directly to electricity. On the basis of kind of electrolyte being used in fuel cells, they are classified into three types, namely, hydrogen–oxygen fuel cell, methanol fuel cell, and solid oxide fuel cell.

1.3.3 Solid Oxide Fuel Cell (SOFC)

SOFC is a single fuel-cell unit consisting of two electrodes, namely, an anode and cathode separated by the electrolyte. For a solid oxide fuel cell, the electrolyte is a solid ceramic compound of metal oxides such as Ce/Zr. Fuel (usually hydrogen, H_2, or methane, CH_4, or carbon monoxide, CO) arrives at the anode, where it reacts with oxide ions from the electrolyte, thereby releasing electrons (e^-) to the external circuit. On the other side of the fuel cell, the oxidant (usually oxygen or air) is fed to the cathode, where it supplies the oxide ions (O^{2-}) for the electrolyte by accepting electrons from the external circuit. The electrolyte conducts these ions between the electrodes, maintaining overall electrical charge balance. The block diagram of the SOFC is shown in Fig. 1.

The cathode is made up of (Ca, Sr) MnO_3/(La, Sr)(Co.Fe) O_3/(La, Sr) CoO_3 and the anode is typically formed from an electronically conducting nickel/yttria-stabilised zirconia (Ni/YSZ) cermets, i.e., a ceramic/metal composite.

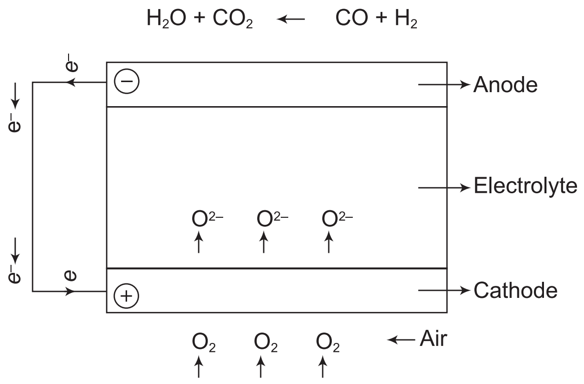


Fig. 1 *Block diagram of SOFC*

Cathodic reaction

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

Anodic reaction

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$
$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

Net cell reaction

$$O_2 + 2H_2 \rightarrow 2H_2O$$
$$O_2 + 2CO \rightarrow 2CO_2$$

Applications

1. Suitable for decentralised electricity production.
2. The major applications of SOFCs are in stationary plants, auxiliary power units in
   a. Transportation vehicles
   b. On-board power for aircraft
   c. Power packs small enough to be carried by soldiers

Drawbacks

1. The high temperature limits applications of SOFC units and they tend to be rather large.
2. Solid electrolytes can't leak, but they can crack.
3. Complex materials are required.

1.15.3 Electroplating of Copper

There are two main ways to electroplate an object with copper. The first method uses a copper anode to transfer copper to a non-copper cathode, coating it in a thin layer of copper. Alternatively, anodes and cathodes of other metals can be used in a copper sulphate solution to take copper from the solution and plate the cathode. Copper electroplating is used in a variety of practical and ornamental applications.

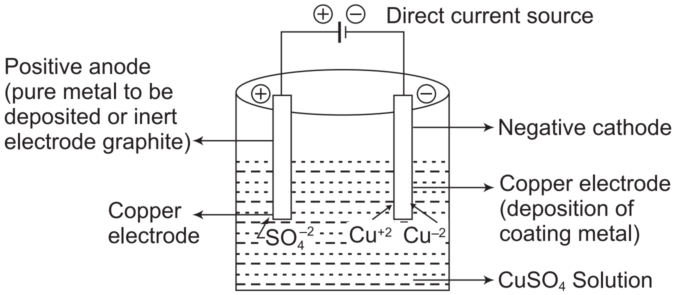


Fig. 2 *Copper electroplating*

In its most basic form, copper electroplating uses electrical current to transfer copper from a copper cathode via electrolysis to the anode, made of another metal. This requires an electrolyte solution to function efficiently, such as salt water or a copper sulphate solution. The following are the electroplating bathing conditions for effective electroplating.

1. *Plating-bath composition:* Copper sulphate solution (200 g/L) + H_2SO_4 (50 g/L) + water
2. *Additives*: Geltain or dextrin, sulphur containing brightener, sulphonic acid
3. *Current density*: 20–50 $mAcm^{-2}$
4. *Anode*: P containing rolled Cu
5. *Current efficiency*: 95–98%
6. *Optimum temperature*: 20–40°C
7. *Throwing-power applications*: Low

The above conditions are suitable for printed circuit boards (not suitable for iron and its alloys).

Copper Electroplating by using Cyanide Bath

The following procedure is adopted for copper electroplating using cyanide bath. The details are as follows:

1. *Plating-bath composition*: Copper cyanide solution (40–50g/L), and KCN (20–30 g/L).K_2CO_3 (10 g/L) water.
2. *Additives:* Sodium thiosulphate ($Na_2S_2O_3$)
3. *Current density*: 10–40 $mAcm^{-2}$
4. *Anode*: Oxygen-free high-conducting Cu
5. *Current efficiency*: 60–90%
6. *Optimum temperature*: 40–70°C
7. *Throwing power*: Good
8. *Applications*: As an undercoat for chromium plating and printed circuit boards, particularly suitable for iron and its alloys.

1.16.1 Electroless Plating of Copper

The surface to be plated is first degreased using an organic solvent or alkali, followed by acid treatment subjected to the following:

1. The surfaces of the metals like Fe, Co, Ni, etc., can be directly copper plated without any pretreatment.
2. Non-metallic materials (glass, plastics, printed circuit boards) are activated by dipping them in solution containing tin chloride ($SnCl_2$) with acidic medium (HCl), followed by palladium chloride solution ($PdCl_2$). On drying, a thin layer is formed on the surface which is ready for electroless plating.

1.16.2 Various Parameters for Electroless Plating

1. *Coating solution*: Copper sulphate solution (12 g/L)
2. *Reducing agent*: Formaldehyde (8 g/L)
3. *Buffer solution*: Sodium hydroxide solution (15 g/L) + Rochelle agent (14 g/L)
4. *Complexing agent cum exhalant*: EDTA
5. *Optimum pH*: 11.0
6. *Optimum temperature*: 25°C

Maintain the above conditions for copper electroless plating in which redox reaction takes place.

At cathode $Cu^{2+} + 2e^- \rightarrow Cu$

At anode $2HCHO + 4OH^- \rightarrow 2HCHO^- + 2H_2O + H_2 + 2e^-$

Net reaction $Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCHO^- + 2H_2O + H_2$

1.16.3 Procedure

The process is known as substantive method. A thin layer of copper (5 to 10 μm) is first electroplated over the PCB (printed circuit board) made of either glass-reinforced rubber like GR-P or epoxy phenolic polymer. Then, selected areas are protected by applying electroplated image (or photo resist) and the remaining areas are etched away so as to get the required type of circuit pattern (or track).

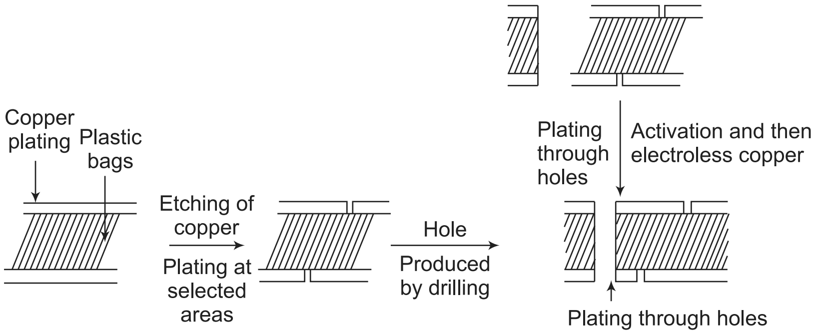


Fig. 3 *Electroless plating of copper*

In order to pack more number of components in a small space, double-sided tracks are prepared. Finally, the connection between the two sides of the PCB is made by drilling holes, followed by electroless copper plating through the holes. Thus, the holes provide electrical contact in both sides.

Applications Used in double or multilayered boards (PCB) in which plating through holes is required.

3.8

DIESEL

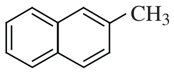
Diesel is an important liquid fuel among the three liquid fuels which are derived from petroleum. The fraction is obtained by fractional distillation between 250–320°C and is a mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbons. Its density is 8.6 to 0.95 kg/m^3. The calorific value of diesel is 11,000 kcal/kg. This oil is used for diesel engine fuel.

The combustion of a fuel in a diesel engine is not instantaneous and the interval between the start of fuel injection and its ignition is called *ignition delay* and is an important quality of the diesel fuel. This delay is due to time taken for the vaporization of individual droplets and rising of the vapour to its ignition temperature. Long ignition delay leads to accumulation of more vapours in the engine and, when ignited, an explosion results as the combined effects of increased temperature and pressure. This is responsible for *diesel knock*. The following is the preferred composition for diesel with minimum knocking.

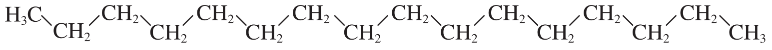
Straight-chain paraffins > Cycloparaffins > Olefins > Branched paraffins > Aromatics

Cetane Number

The knocking characteristics of diesel oil are expressed in terms of cetane number. The *cetane rating* for diesel fuels is equivalent to octane rating for gasoline. Two hydrocarbons, namely, α-methyl naphthalene (aromatic) and *n*-hexadecane (aliphatic straight chain) are specified as standards. Since *n*-hexadecane (*n*-cetane) has low ignition lag, its cetane number is arbitrarily fixed as 100, while since α-methyl naphthalene has long ignition lag, its cetane number is fixed as zero. The cetane number of diesel oil is defined as "The percentage of *n*-cetane in a mixture of *n*-cetane and α-methyl naphthalene giving the same performance as that of diesel oil under tests". The cetane number of diesel may be increased by the addition of ethylnitrate or amylnitrate.



α-methylnapthalene (cetane number = 0)



n-hexadecane (cetane number = 100)

A good diesel fuel should contain as many as possible straight chains, with a minimum mixture of side chains and aromatic hydrocarbon molecules, which will give least knocking property.

Emulsions

The ability of an oil to get intimately mixed with water forming an emulsion is called *emulsification.* A good lubricant must be capable of forming an emulsion with water which can be broken off quickly. In various machining operations such as cutting, sawing, and drilling, the tool employed gets heated up to a very high temperature, particularly at the cutting edge. Due to this overheating, the tool may lose its temper and hardness. In order to prevent this, efficient cooling and lubrication have to be provided. This can be done by employing emulsions. An emulsion is a two-phase system consisting of a fairly coarse dispersion and two immiscible liquids—one being dispersed as fine droplets in the other. It is stabilized by adding a third component called the *emulsifying agent.* Emulsifiers, or emulsifying agents, are the substances which exhibit both polar and non-polar character. Hence, an emulsifier is absorbed at the interface of the two immiscible phases (oil and water), resulting in the form of a protective film. There are two types of emulsions.

(a) Oil-in-Water Emulsions They are obtained by adding an oil to a suitable quantity of water in the presence of 3–20% of a water-soluble emulsifying agent, such as sodium soaps and sodium and potassium salts of sulphuric acids. These types of emulsions are used as coolant cum lubricants for cutting tools, in diesel motor pistons and internal combustion engines.

(b) Water-in-Oil Emulsions They are prepared by mixing water containing 1–10% water-soluble emulsifier to the oil. Alkaline earth-metal soaps like calcium stearate are used as emulsifiers. These emulsions have high viscosity compared to the oil from which they are derived. They are used to lubricate steam cylinders and compressor handling fuel gases.

Model University Question Paper-I
I Year B.Tech(R13) Regular Examinations, June.2014.
ENGINEERING CHEMISTRY
(Common to all branches)

Time: 3 hours **Max Marks: 70**

Answer to all the questions from Part A and each question carry two marks.
Answer to all the questions from Part B. Each question carry 10 marks

PART-A

Unit-1

1. Differentiate between the primary and Secondary Batteries.
2. Define electrochemical sensor? Give suitable examples.

Unit-2

3. What kind of compounds is used in Addition polymerization?
4. What are conducting polymers? How are they classified

Unit-3

5. What are different types of fuels?
6. What is meant by calorific value of fuel?

Unit-4

7. What are Puzzolona cements?
8. Write the characteristics of good propellant?

Unit-5

9. What is mean by Hardness? What are its units to express Hardness?
10. Define Electro dialysis.

PART-B

Unit-1

1. (a) What is oxidation corrosion and how does it take place? Describe the mechanism of oxidation corrosion?

(b) Describe the various factors influencing the rate of chemical corrosion. [8+8]

OR

What is meant by electrochemical sensors? Discuss any one of the electrochemical sensor.

Unit-2

2. Write a note on

(a) Teflon **(b)** Silicone rubber

OR

What are liquid crystal polymers? How are they produced? Explain the characteristics and applications (uses) of liquid crystals.

Unit-3

3. Write short notes on

(a) Coal gas **(b)** Bio gas

(c) Water gas **(d)** Producer gas

(e) Natural gas

OR

Discuss the ultimate analysis of coal with its significance.

Unit-4

4. Write a brief account on the following?

(a) The raw materials and the ingredients of cement

(b) Function of gypsum in cement.

OR

(a) Explain the following terms:

(i) cloud and pour points **(ii)** flash and fire points.

(b) Explain how the following act as lubricants

(i) graphite **(ii)** molybdenum disulphide.

(c) Write an explanatory note on semi-solid lubricant.

Unit-5

5. (a) What are the major disadvantages of hard water used for
   - **(i)** domestic purposes
   - **(ii)** industrial purposes
   - **(iii)** steam generation in boilers.

(b) How do you estimate dissolved oxygen in water?

OR

(a) Write short note on
   - **(i)** Priming and foaming
   - **(ii)** Phosphate conditioning
   - **(iii)** Caustic embrittlemen

(b) What is Boiler corrosion?

Model University Question Paper-II
I Year B.Tech(R13) Regular Examinations, June.2014.
ENGINEERING CHEMISTRY
(Common to all branches)

Time: 3 hours **Max Marks: 70**

Answer to all the questions from Part A and each question carries two marks.
Answer to all the questions from Part B. Each question carries ten marks

PART-A

Unit-1

1. Explain the basic principle involved in Methanol fuel Cell.
2. What is oxidation Corrosion? Give an example?

Unit-2

3. What is functionality of monomer?
4. What is meant by tacticity?

Unit-3

5. Give four characteristics of a good fuel.
6. What do you mean by refining of petroleum?

Unit-4

7. Define the Semi conductor? Give suitable example
8. What are magnetic materials? Give some examples.

Unit-5

9. What is priming and Foaming?
10. Define Brakish water? What type of method used its purification?

PART-B

Unit-1

1. **(a)** Describe the cathodic protection of corrosion control.
   (b) Write a note on electroplating.

OR

Explain the mechanism of corrosion when

(a) Two dissimilar metals are connected and exposed to electrolyte
(b) A metal is exposed to varying aeration.

Unit-2

2. Give an account of preparation, properties and uses of the following.

(a) Polyethylene
(b) PVC
(c) Polystyrene

OR

Write brief notes on

(a) Vulcanisation
(b) Compounding of rubber.

Unit-3

3. **(a)** Define calorific value of a fuel. Distinguish gross and net calorific value.
(b) How do you synthesise petrol by Fisher–Tropsch process?

OR

(i) Explain the significance of the following constituents present in coal

(a) Moisture
(b) Volatile matter
(c) Ash
(d) Fixed carbon

(ii) What are the characteristics of metallurgical coke?

Unit-4

4. **(a)** Define refractories. What are the characteristics of a good refractory?
(b) Give the classification of refractories with examples.

OR

Define refractories? Write short note on the following

(i) Refractoriness
(ii) Refractoriness under load or strength

(iii) Dimensional stability
(iv) Thermal spalling
(v) Thermal conductivity
(vi) Porosity

Unit-5

5. **(a)** Discuss briefly boiler troubles and their treatment?
(b) Describe the permutit process for softening of water.

OR

(a) Explain the process of scale and sludge formation in boilers.
(b) Describe the internal treatment of boiler water.