MSCCH-04

VARDHMAN MAHAVEER OPEN UNIVERSITY

SPECTROSCOPIC TECHNIQUES, MATHEMATICS, BIOLOGY AND COMPUTER FOR CHEMIST

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Unit - 1 : Electromagnetic Radiation

Structure of Unit:

1.1 Objective

At the end of the unit learner will be able to

- To introduce general properties of all electromagnetic waves,
- Describe astronomical and artificial sources of electromagnetic radiation,
- To identify the position of each type of radiation in the electromagnetic spectrum according to its wavelength and frequency,
- Discuss methods used to detect and analyze different waves,
- Analyze the relation between the specific properties of waves, and their position in the electromagnetic spectrum,

- To highlight the idea of how knowledge about radiation helps scientists solve the mystery of the evolution of the Universe.

1.2 Introduction

Transmission of energy through a vacuum or using no medium is accomplished by electromagnetic waves, caused by the oscillation of electric and magnetic fields. They move at a constant speed of $3x10^8$ m/s. often, they are called electromagnetic radiation, light, or photons. An electromagnetic radiation, it has both electric and magnetic field components, which oscillate in a fixed relationship to one another, perpendicular to each other and perpendicular to the direction of propagation.

The two components making up an electromagnetic radiation are the:

a) Electric field B) Magnetic field

The two fields are always perpendicular to each other and both are perpendicular to the direction of propagation.

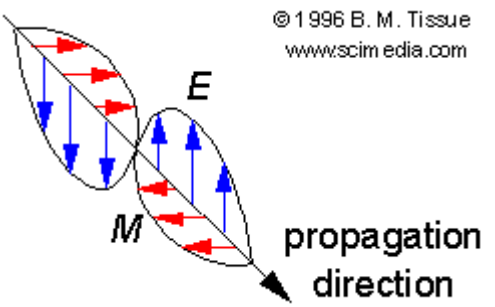


Fig. Electromagnetic wave

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$E = hc / \lambda$

where E is energy in kcal/mol, **λ** (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00 x 10^{8} m/s (the speed of light), and *h* is 9.537 x 10^{-14} kcal/s/mol^{-1}, a number known as Planck's constant.

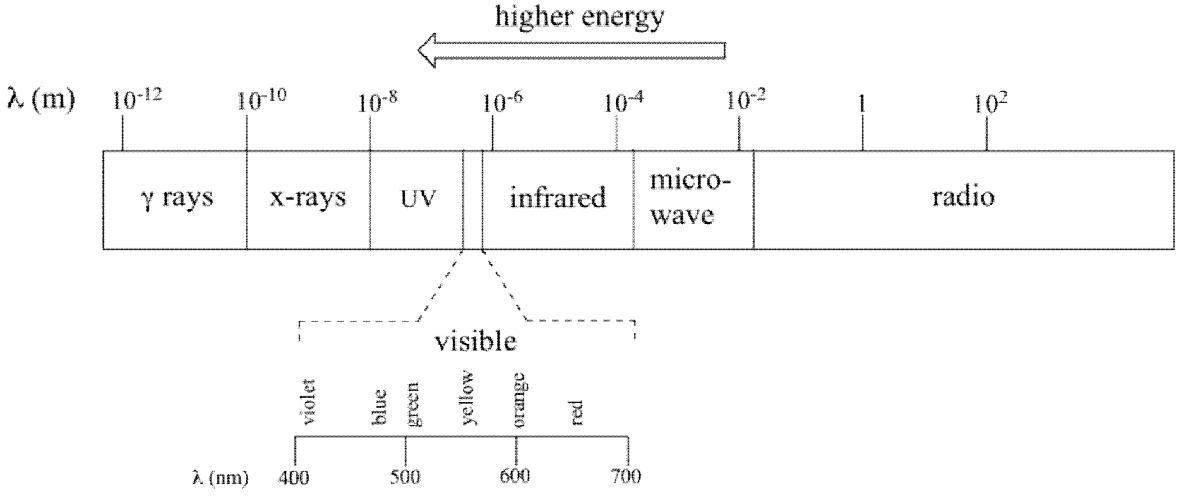
Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$\Rightarrow C = \vartheta\lambda$

where **ν** (the Greek letter '*nu'*) is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29 x 10^{14}Hz, and an energy of 40.9 kcal per mole of photons.

The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



1.3 Properties of Electromagnetic radiation

The radiated EM radiation has certain properties:

• EM waves travel at the speed of light c

• The electric and magnetic fields are perpendicular to each other.

• The electric and magnetic fields are in phase (both reach a maximum and minimum at the same time).

• The electric and magnetic fields are perpendicular to the direction of travel (transverse waves).

Terms Used

Wavelength - Is the distance between any two equivalent points on successive waves.

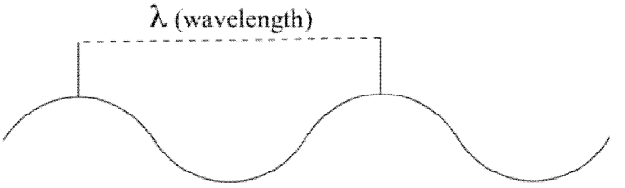
Wavenumber - Is the reciprocal of the wavelength in centimeters.

Frequency - Is the number of oscillations of the field which occur each second.

Velocity - In a vacuum, the velocity of electromagnetic radiation is 2.9979 x 10^8 m/s

Amplitude - The height of the wave.

Their wavelengths and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*



PROBLEM: Calculate wavelength and frequency of waves.

(a) A local radio station broadcasts at a frequency of 91.7 MHz (91.7 x 10^6 Hz). What is the Wavelength of these radio waves?
b) What is the frequency of blue light with a wavelength of 435 nm?

SOLUTION:
You are asked to calculate the wavelength or frequency of electromagnetic radiation.
You are given the frequency or wavelength of the radiation.
(a) First rearrange Equation 6.1 to solve for wavelength (λ). Then substitute the known values into the equation and solve for wavelength.

$\upsilon = c / \lambda$ or $\lambda = c / \upsilon$

$$\frac{2.998 \text{ x } 10^8 \text{ m/s}}{91.7 \text{ x } 10^6 \text{ 1/s}}$$

$\lambda = 3.27$ m

(b) First rearrange Equation 6.1 to solve for frequency (υ). Then substitute the known values into the equation and solve for frequency. Notice that wavelength must be converted to units of meters before using it in Equation ($c = \lambda\upsilon$)

$435nm \Rightarrow 435 \times 10 - 9m$
= 4.35 x 10^{-7} m

1.4 Interaction of electromagnetic radiation with matter

It is well known that all matter is comprised of atoms. But subatomically, matter is made up of mostly empty space. For example, consider the hydrogen atom with its one proton, and one electron. The diameter of a single proton has been measured to be about 10^{-15} meters. The diameter of a single hydrogen atom has been determined to be 10^{-10} meters; therefore the ratio of the size of a hydrogen atom to the size of the proton is 100,000:1. Consider this in terms of something more easily pictured in your mind. If the nucleus of the atom could be enlarged to the size of a softball (about 10 cm), its electron would be approximately 10 kilometers away. Therefore, when electromagnetic waves pass through a material, they primarily move through free space, but may have a chance to encounter with the nucleus or an electron of an atom.

Because the encounters of photons with sub atomic particles are by chance, a given photon has a finite probability of passing completely through the medium it is traversing. The probability that a photon will pass completely through a medium depends on numerous factors including the photon's energy and the composition and thickness of the medium. The more densely packed a medium's atoms, the more likely the photon will encounter an atomic particle. In other words, the more subatomic particles in a material (higher Z number), the greater the likelihood that interactions will occur Similarly, the more material a photon must cross through, the more likely the chance of an encounter.

When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be reemitted back the way it came (reflected), scattered in a different direction or transmitted forward into the material. Let us first consider the interaction of visible light. Reflection and transmission of light waves occur because the light waves transfer energy to the electrons of the material and cause them to vibrate. If the

material is transparent, then the vibrations of the electrons are passed on to neighboring atoms through the bulk of the material and reemitted on the opposite side of the object. If the material is opaque, then the vibrations of the electrons are not passed from atom to atom through the bulk of the material, but rather the electrons vibrate for short periods of time and then reemit the energy as a reflected light wave. The light may be reemitted from the surface of the material at a different wavelength, thus changing its color.

The interactions between electromagnetic radiation and matter cause changes in the energy states of the electrons in matter.

Electrons can be transferred from one energy level to another, while absorbing or emitting a certain amount of energy. This amount of energy is equal to the energy difference between these two energy levels (E_2-E_1).

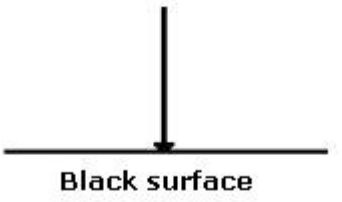
When this energy is absorbed or emitted in a form of electromagnetic radiation, the energy difference between these two energy levels (E_2-E_1) determines uniquely the frequency (λ) of the electromagnetic radiation:

$(\Delta E) = E_2\text{-}E_1 = h\vartheta$

1.4.1 Absorption

Absorption of electromagnetic radiation is the way in which the energy of a photon is taken up by matter, typically the electrons of an atom. Atoms or molecules absorb light, the incoming energy excites a quantized structure to a higher energy level. The type of excitation depends on the wavelength of the light. Electrons are promoted to higher orbitals by ultraviolet or visible light, vibrations are excited by infrared light, and rotations are excited by microwaves.

An absorption spectrum is the absorption of light as a function of wavelength. The spectrum of an atom or molecule depends on its energy level structure, and absorption spectra are useful for identifying of compounds.



1.4.2 Emission

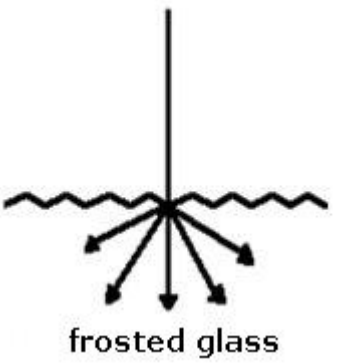
The emission spectrum of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted due to an atom's electrons making a transition from a high energy state to a lower energy state. Atoms or molecules that are excited to high energy levels can decay to lower levels by emitting radiation (emission or luminescence). For atoms excited by a high-temperature energy source this light emission is commonly called atomic or optical emission, and for atoms excited with light it is called atomic fluorescence. For molecules it is called fluorescence if the transition is between states of the same spin (singlet to singlet transition) and phosphorescence if the transition occurs between states of different spin (triplet to singlet transition).

The emission intensity of an emitting substance is linearly proportional to analyte concentration at low concentrations, and is useful for quantitating emitting species.

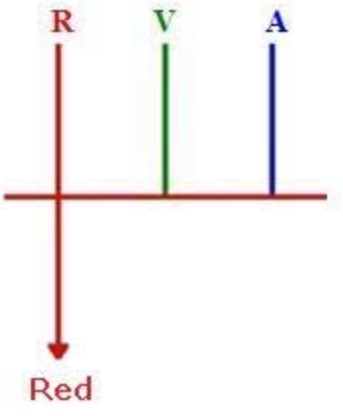
1.4.3 Transmission

Transmission happens when light goes through a surface or object. There are 3 types of transmission: direct, diffuse or selective.

1. Direct transmission: it is when light goes through an object and no change in direction or quality takes place. For example, through glass or air.
2. Diffuse transmission: it is produced when light goes through a transparent or semi-transparent object with texture. For example, frosted glass or drafting paper. Light, instead of going in one direction, is redirected to other directions. Light which is transmitted in a diffused manner tends to be softer; it will have less contrast and less intensity; it will generate clearer shades; and it will have a smoother transition between highlights and shadows than direct light.



3. Selective transmission: it is produced when light goes through a coloured object. A portion of light will be absorbed and another portion will be transmitted through this object. In the example below, white light (red, green and blue) goes through a red surface. The green and blue are absorbed and only red is transmitted. As a result, we will only see red light on the other side of this surface.



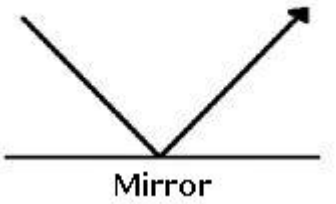
Filters or gels, which we mentioned in the lesson about colour temperature, work through selective transmission. Colour filters will only allow one colour to go through (a blue filter allows only blue light go through) and it will absorb the rest of the colours. A blue filter lets blue wave lengths through and absorbs red and green wave lengths.

1.4.4. Reflection

Reflection happens when light reaches an object and it bounces or is reflected, partially or totally, from this object. Light can be reflected directly or in a diffused manner.

1. **Direct reflection**: it is produced when light is reflected from a flat or smooth

surface such as, for example, a mirror. Light will be reflected in the same angle as it reached this surface (law of reflection).



2. Diffused reflection: it is produced when light reaches a surface or object which has texture such as, for example, a wall with texture.

A diffused reflection will produce a softer light than that produced by direct reflection. It will also generate less contrast in the scene, clearer shades and a smoother transition between highlights and shadows.

A direct reflection will produce a more intense light, with higher contrast and darker and well-defined shadows.

As we mentioned previously, white reflects (theoretically) every form of light. A coloured surface will reflect its own colour while absorbing the rest. For example, a green object will reflect green and it will absorb red and blue.

1.4.5. Scattering:

When electromagnetic radiation passes through matter, most of the radiation continues in its original direction but a small fraction is scattered in other directions. Light that is scattered at the same wavelength as the incoming light is called Rayleigh scattering. Light that is scattered in transparent solids due to vibrations (phonons) is called Brillouin scattering. Brillouin scattering is typically shifted by 0.1 to 1 cm^{-1} from the incident light. Light that is scattered due to vibrations in molecules or optical phonons in solids is called Raman scattering. Raman scattered light is shifted by as much as 4000 cm-1 from the incident light.

1.6 Electronic Selection Rules

1.6.1 Electronic transitions in atoms

Atoms are described by the primary quantum number n, angular momentum quantum number L, spin quantum number S, and total angular momentum quantum number J. Based on Russell-Saunders approximation of electron coupling, the atomic term symbol can be represented as $(2S+1)\ L_J$.

1. The total spin cannot change, $\Delta S=0$;
2. The change in total orbital angular momentum can be $\Delta L=0, \pm 1$, but $L=0 \leftrightarrow L=0$ transition is not allowed;
3. The change in the total angular momentum can be $\Delta J=0, \pm 1$, but $J=0 \leftrightarrow J=0$ transition is not allowed;
4. The initial and final wave functions must change in parity. Parity is related to the orbital angular momentum summation over all elections Σ li, which can be even or odd; only even $\leftrightarrow$ odd transitions are allowed.

1.6.2 Electronic transitions in molecules*:*

The electronic-state configurations for molecules can be described by the primary quantum number n, the angular momentum quantum number Λ, the spin quantum number S, which remains a good quantum number, the quantum number Σ (S, S-1, ..., -S), and the projection of the total angular momentum quantum number onto the molecular symmetry axis Ω, which can be derived as $\Omega=\Lambda+\Sigma$. The term symbol for the electronic states can be represented as

Group theory makes great contributions to the prediction of the electronic selection rules for many molecules. An example is used to illustrate the possibility of electronic transitions via group theory.

1. The total spin cannot change, $\Delta S=0$; the rule $\Sigma\Delta=0$ holds for multiplets;

If the spin-orbit coupling is not large, the electronic spin wavefunction can be separated from the electronic wavefunctions. Since the electron spin is a magnetic

effect, electronic dipole transitions will not alter the electron spin. As a result, the spin multiplicity should not change during the electronic dipole transition.

2. The total orbital angular momentum change should be $\Delta\Lambda=0, \pm1$;

3. Parity conditions are related to the symmetry of the molecular wavefunction reflecting against its symmetry axis. For homonuclear molecules, the g $\leftrightarrow$ u transition is allowed.

Vibrational Selection rules

1 Transitions with $\Delta v=\pm1, \pm2, \ldots$ are all allowed for anharmonic potential, but the intensity of the peaks become weaker as Δv increases.

2 v=0 to v=1 transition is normally called the fundamental vibration, while those with larger Δv are called overtones.

3 $\Delta v=0$ transition is allowed between the lower and upper electronic states with energy E1 and E2 are involved, i.e. (E1, v''=n) $\longrightarrow$ (E2, v'=n), where the double prime and single prime indicate the lower and upper quantum state.

4 The geometry of vibrational wavefunctions plays an important role in vibrational selection rules. For diatomic molecules, the vibrational wavefunction is symmetric with respect to all the electronic states. Therefore, the Franck-Condon integral is always totally symmetric for diatomic molecules. The vibrational selection rule does not exist for diatomic molecules.

For polyatomic molecules, the nonlinear molecules possess 3N-6 normal vibrational modes, while linear molecules possess 3N-5 vibrational modes.

Rotational Selection rules:

1. Transitions with $\Delta J=\pm1$ are allowed;

Photons do not have any mass, but they have angular momentum. The conservation of angular momentum is the fundamental criteria for spectroscopic transitions. As a result, the total angular momentum has to be conserved after a molecule absorbs or emits a photon. The rotational selection rule relies on the fact that photon has one unit of quantized angular momentum. During the photon emission and absorption process, the angular moment J cannot change by more than one unit.

Let's consider a single photon transition process for a diatomic molecule. The rotational selection rule requires that transitions with $\Delta J=\pm 1$ are allowed. Transitions with $\Delta J=1$ are defined as R branch transitions, while those with $\Delta J=-1$ are defined as P branch transitions. Rotational transitions are conventional labeled as P or R with the rotational quantum number J of the lower electronic state in the parentheses. For example, R(2) specifies the rotational transition from J=2 in the lower electronic state to J=3 in the upper electronic state.

2. $\Delta J=0$ transitions are allowed when two different electronic or vibrational states are involved

1.7 Born-Oppenheimer approximation

A molecule is an assembly of positively charged nuclei and negatively charged electrons that form a stable entity through the electrostatic forces which hold it all together. Since all the particles which make up the molecule are moving relative to each other, a full quantum mechanical description of the molecule is very complicated and can only be obtained approximately. Fortunately, the overall motion of the molecule can be broken down into various types of motion, namely, translational, rotational, vibrational, and electronic. To a good approximation, the so called Born-Oppenheimer approximation, each of these motions can be considered on its own (Born & Oppenheimer 1927).

Their main objective was the separation of electronic and nuclear motions in a molecule. The physical basis of this separation is quite simple. Both electrons and nuclei experience similar forces in a molecular system, since they arise from a mutual electrostatic interaction. However, the mass of the electron, is about four orders of magnitude smaller than the mass of the nucleus. Consequently, the electrons are accelerated at a much greater rate and move much more quickly than the nuclei. Therefore, as an approximation, we can regard the dynamics of the electrons and nuclei as largely independent. When describing the electrons, the nuclei can be considered as being fixed in space. On longer timescales, the electrons can immediately follow the much slower nuclear motions. To a very good approximation, the total energy of a molecule is given as the sum of three components, corresponding to the three modes of motion mentioned above, namely

$$E = E_e + E_{vib} + E_{rot} \ , \qquad \text{Eq. (3.1}$$

Where the three terms on the right hand side represent the electronic, vibrational, and rotational energy. We disregard overall translational energy of the molecule because it leads mainly to collisions and, thus, has only an indirect influence on the internal structure of molecules. Furthermore, we have neglected in Eq. (3.1) the interaction between the three different types of motion. These interaction terms have to be considered in a consistent treatment, and we will come back to them in the course of this chapter, but it is more illustrative to neglect them as a first approximation. In molecular spectroscopy, Eq. (3.1) is often expressed in units of the wave number $\tilde{\upsilon} = \nu/c$, using the notation

$$T = T_e + G + F \ , \qquad (3.2)$$

with

$$T_e = E_e/(hc) \ ,$$
$$G = E_{vib}/(hc) \ ,$$
$$F = E_{rot}/(hc) \ . \qquad (3.3)$$

The energy difference between two states can then be denoted by

$$\tilde{\nu} = \Delta T_e + \Delta G + \Delta F \ , \qquad (3.4)$$

where the units of $\tilde{\upsilon}$ are cm^{-1}

Since electrons move more rapidly than the nuclei, and the vibrations of nuclei are more rapid than the rotation of molecules, the following relation holds:

$$E_e \gg E_{vib} \gg E_{rot} \qquad (3.5)$$

We have already argued that the electronic energy is largest. The relative energies of vibrations and rotations follow from simple order of magnitude estimates. The valence electrons spread over the whole molecule (of size a $\approx$ 1 Å) and thus have typical

energies

$$E_e \sim \frac{\hbar^2}{m_e a^2} \sim 1-10 \text{ eV} \quad (3.6)$$

In this estimate we have used the Rydberg energy but with a instead of the Bohr radius. The energy scale of vibrations about the equilibrium separation req of two nuclei in a molecule is defined by $\hbar\omega$. To find $\hbar\omega$ we consider the potential energy of the vibrational modes given by Mnω2(r – req) 2 , cf. Eqs. (3.33) and (3.34). We have req ~ a. For vibrations with (r – req) ~ a the electron configuration would be modified strongly and "costs" roughly one electronic energy Ee. From Mnω 2 (r – req)2 ~ 2 2 e $\hbar$ m a we find

$$E_{vib} \sim \hbar\omega \sim \sqrt{\frac{m_e}{M_n}} \cdot \frac{\hbar^2}{m_e a^2} \sim 0.1 \text{ eV} \quad (3.7)$$

Rotational energies are estimated by J 2 /I (cf. Eq. (3.13)) where J is the angular momentum and I is the moment of inertia. With J 2 ~ 2 2 $\hbar \sim \hbar$ j j ( ) +1 and I ~ Mna 2 we get

$$E_{rot} \approx \frac{J^2}{I} \sim \frac{m_e}{M_n} \cdot \frac{\hbar^2}{m_e a^2} \sim 1 \text{ meV} \quad (3.8)$$

The corresponding length scales are λe ~ 100–1000 nm (i.e. in the order of visible wavelengths), λvib ~ 10 μm (i.e. in the infrared region), and λ rot ~ 1 mm. Therefore, spectral lines of molecules are observed in the visible (actually near UV to about 1 μm) in the case of electronic transitions, in the infrared for vibrational transitions, and in the sub-mm to about 1 mm region (microwaves) for rotational transitions.

Rotational energy level

Molecular rotations require little energy to excite them. Pure rotation spectra occur in the microwave region of the spectrum (~1 - 200 cm^{-1}). It is important to note that a

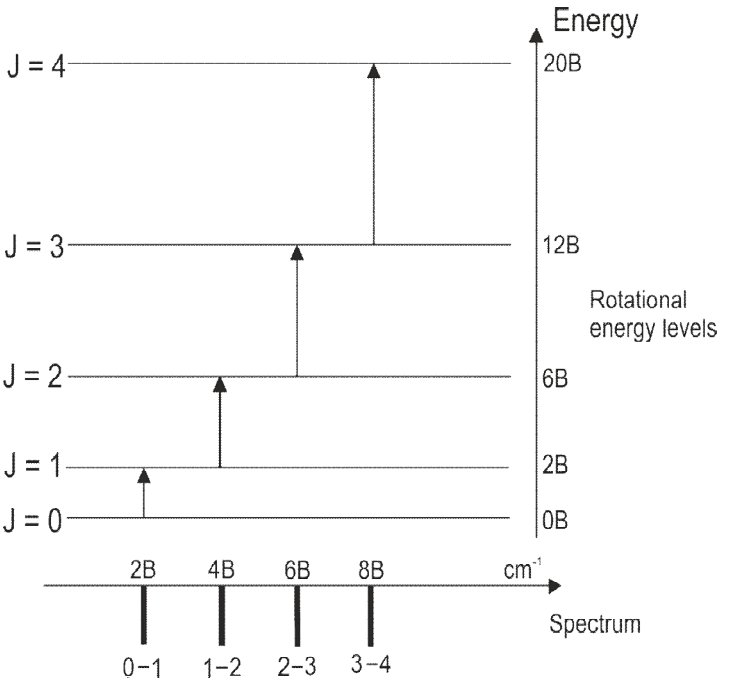
molecule cannot rotate about some arbitrary axis - the principle of conservation of angular momentum dictates that only a few rotations are possible. In general, rotation must be about the centre of mass of a molecule, and the axis must allow for conservation of angular momentum. In simple cases, this can often be recognised intuitively through symmetry - such as with the water molecule.
A pure rotation spectrum can only arise when the molecule possesses a permanent electric dipole moment. Like with vibrational spectroscopy, the physical effect that couples to photons is a changing dipole moment. Since molecular bond lengths remain constant in pure rotation, the magnitude of a molecule's dipole cannot change. However, since electric dipole is a vector quantity (it has both size and direction) rotation can cause a permanent dipole to change direction, and hence we observe its spectra. Since homonuclear molecules such as dinitrogen N_2 have no dipole moment they have no rotation spectrum. Highly symmetric polyatomic molecules, such as carbon dioxide, also have no net dipole moment - the dipoles along the C-O bonds are always equal and opposite and cancel each other out. It is important to recognise also that if a molecule has a permanent dipole, but this dipole lies along the main rotation axis, then the molecule will not have a rotational spectrum - such as for a water molecule.

In pure rotational spectroscopy for a simple diatomic molecule, the energy levels - as displayed below - are given by $E_J = BJ\ (J+1)$, where J is the *rotational quantum number*, B is the rotational constant for the particular molecule given by $B = \frac{h^2}{8\pi^2 I}$ with the unit of Joules, where I is the moment of inertia, given by $I = \mu r^2$ - where r is the bond length of this particular diatomic molecule and μ is the reduced mass, given by $\mu = m_1 m_2 / m_1 + m_2$.

Most energy level transitions in spectroscopy come with selection rules. These rules restrict certain transitions from occuring - though often they can be broken. In pure rotational spectroscopy, the selection rule is $\Delta J = \pm 1$.

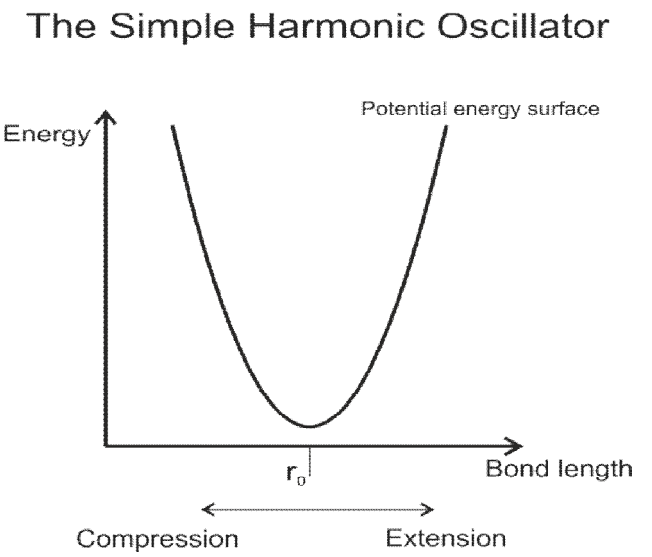
A vibrational spectrum would have the following appearence. Each line corresponds to a transition between energy levels, as shown. Notice that there are no lines for, for example, J = 0 to J = 2 etc. This is because the pure rotation spectrum obeys the

selection rule $\Delta J = \pm 1$. The energy gap between each level increases by 2B as the energy levels we consider increase by J = 1. This leads to the line spacing of 2B in the spectrum. Each transition has an energy value of 2B more than the previous transition.



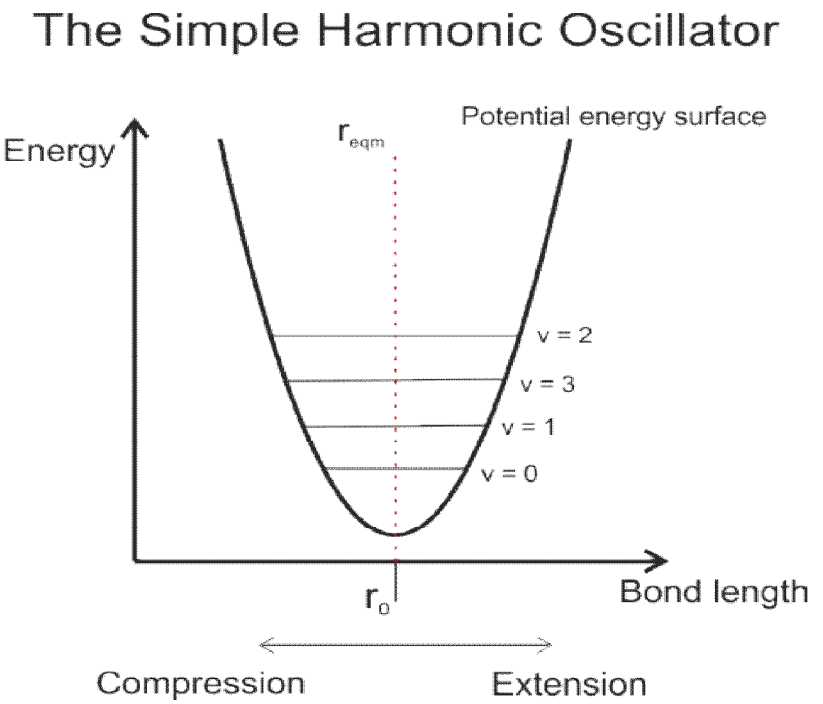
Vibrational Spectroscopy:

Vibrational spectroscopy can be thought of by starting with a simple harmonic oscillator (SHO) model. In this model, we consider two atoms joined by a bond to be equivalent to two masses joined by a spring. The spring can be compressed, forcing the spheres close to each other - stretched, moving them apart - or allowed to freely come to rest in the spheres' equilibrium positions. This can be shown in a potential energy curve:

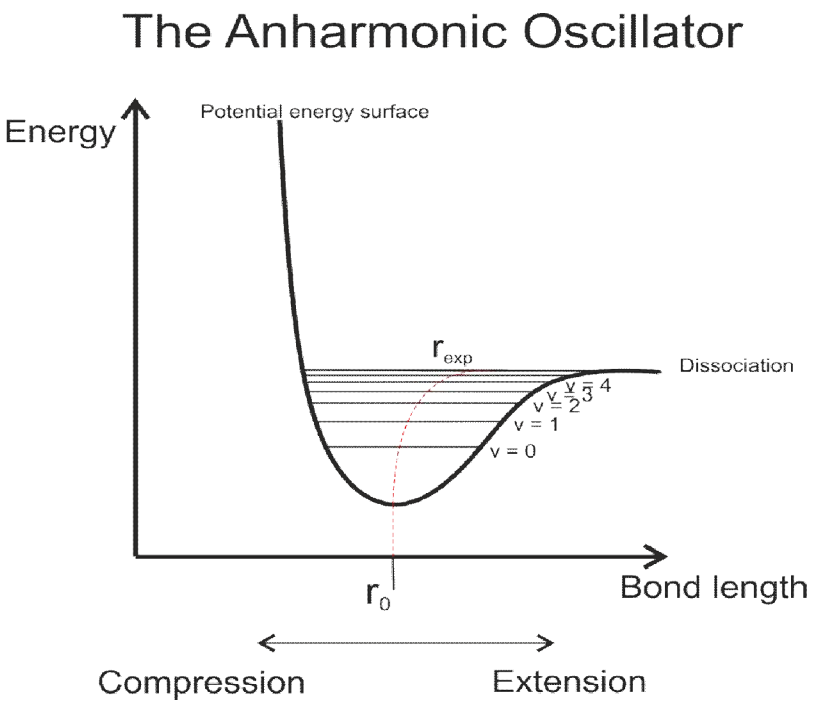


However, not all energies are possible. The possible vibrational states are given by the vibration quantum number, v, and vibrational selection rule $\Delta v = \pm 1$.

The energy of each level, E_ϑ, is given by $E_\vartheta = \left(_\vartheta + \frac{1}{2} \right)^h$ (the second ν is the Greek character nu, the fundamental frequency). The fundamental frequency is given by the equation $\nu = (1/2\pi)\times(k/\mu)1/2$, where μ is the reduced mass of the molecule, and k is the bond force constant. Notice that this k is similar to the spring force constant from Hooke's Law F = -kx. This leads to a potential energy surface that looks like this:



As you can see, the energy levels are equally spaced, and the equilibrium bond length is constant for all energy levels. However, this model is imperfect - it does not account for the posibility of bond dissociation (under this model, the bond would never break, no matter the magnitude of the vibrational energy). It also does not account for extra repulsive effects at very small bond lengths caused by the electroweak force. This is the force which prevents atoms for being forced together as the distance between them gets very small (the reason nuclear fusion only occurs at very high temperatures, for example). A model which takes into account these factors, and which more accurately models a vibration diatomic molecule, is the Anharmonic Oscillator (AHO), and the corresponding potential energy surface called the **Morse potential**. The potential energy curve now looks like this:



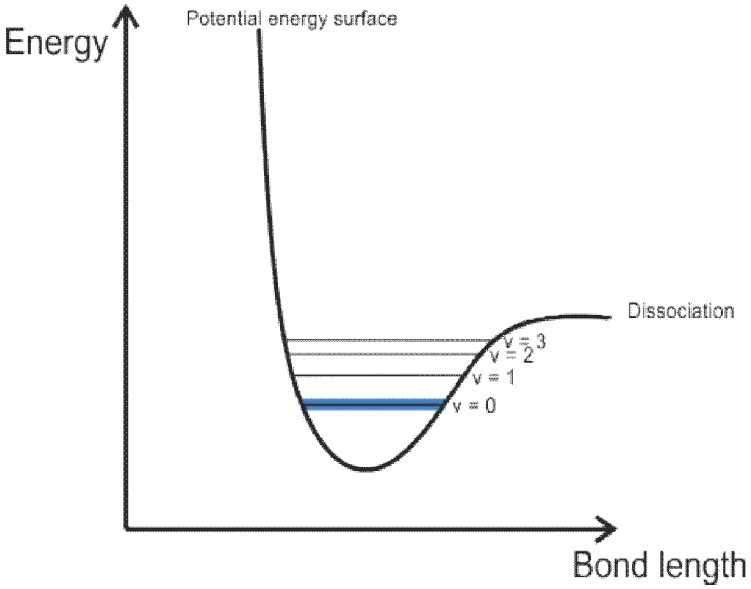
Notice how the expectation (or average) bond length, rexp is no longer the same for all energy levels. One effect of the anharmonicity is this deformation as the energy of the vibrations increases. Another is that now, the vibrational energy levels are no longer equally spaced, but instead get closer together as the vibrational quantum number increases. This model also illustrates that there aren't an infinite number of vibrational energy levels - above some energy, the bond breaks and the molecule dissociates.

Vibrational energies occur roughly in the 100 - 4000 cm-1 (about 1 - 50 kJ mol-1), or **infra-red (IR) region** of the electromagnetic spectrum. The fundamental principle for obtaining a vibrational spectra is that the electric dipole moment of the molecule must change during the vibration. If there is no change in dipole moment, then this particular vibration will not give rise to any absorption in the IR region. An example of this can be seen below for the symmetric stretch (Σg+) mode of carbon dioxide. Because both C=O bond lengths change exactly in phase, there is never a net dipole moment on the molecule. A homonuclear diatomic molecule such as dioxygen O_2 has zero dipole moment, so it has no IR spectrum.

The number of modes (types) of vibration can be predicted for a molecule, containing N atoms, using the following general expressions.

Linear molecules	Non-linear molecules
3N - 5	3N - 6

Energy level diagram



1.9 Electronic transitions:

The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;

1. Transitions involving σ, π, and n electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving d and f electrons (not covered in this Unit)

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to

each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level.

Absorbing species containing □, □, and n electrons:

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy. The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band.

Possible *electronic* transitions of □, □, and *n* electrons are;

$\sigma \rightarrow \sigma^*$ Transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required 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. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

$n \rightarrow \sigma^*$ Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \pi^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of *n* or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons. Molar absorbtivities from $n \rightarrow \pi^*$ transitions are relatively low, and range from 10 to100 L mol^{-1} cm^{-1} . $\pi \rightarrow \pi^*$ transitions normally give molar absorbtivities between 1000 and 10,000 L mol^{-1} cm^{-1} .

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n \rightarrow \pi^*$ transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the *n* orbital. Often (but *not* always), the reverse (i.e. *red shift*) is seen for $\pi \rightarrow \pi^*$ transitions. This is caused by attractive polarisation forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences $n \rightarrow \pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

2.0 Summery

Electromagnetic radiation, particle-wave dualism, atomic structure that light consists of electromagnetic waves was long time known. But around 1900 new observations about light and matter brought new explanations and new insights. These new theories where necessary, because without them experiments could not be explained. General believe before 1900: physics is basically known, only some details are still needed. But then came new experiments which nobody could explain. Electromagnetic waves or water waves: A particular property oscillates in space and time and the oscillation moves. When two waves occupy the same space, then constructive and destructive interference can happen, depending on what are the phases where the waves meet. The oscillating properties in electromagnetic waves are the electric field (E) and the magnetic field (H) which are perpendicular to each other and also perpendicular to the direction of motion and they oscillate.

Unit –2 : Raman Spectroscopy

Structure of Unit:

2.1 Objective

A Raman signature provides positive material identification of unknown specimens to a degree that is unmatched by other spectroscopy's. Raman spectroscopy presents demanding requirements for the detection and resolution of narrow-bands of light with very low intensity and minimal frequency shift relative to the source. We are committed to supporting this science with optical coatings of the highest phase thickness and resulting superior performance.

2.2 Introduction

When radiation passes through a medium, the species present scatter a fraction of the beam in every direction. In 1928, the Indian physicist, C. V. Raman discovered that the visible wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam and furthermore the shifts in wavelength depend upon the chemical structure of the molecules responsible for the scattering. He was awarded the 1931 Nobel Prize in physics for this discovery.

Raman spectroscopy provides valuable structural information about materials. When laser light is incident upon a sample, a small percentage of the scattered light may be shifted in frequency. The frequency shift of the Raman scattered light is directly related to the structural properties of the material. A Raman spectrum provides a "fingerprint" that is unique to the material. Raman spectroscopy is employed in many applications including mineralogy, pharmacology, corrosion studies, analysis of semiconductors and catalysts, in situ measurements on biological systems, and even single molecule detection. Applications will continue to increase rapidly along with further improvements in the technology

In comparison to other vibrational spectroscopy methods, such as FT-IR and NMR, Raman has several major advantages. These advantages stem from the fact that the Raman effect manifests itself in the light scattered off of a sample as opposed to the light absorbed by a sample. As a result, Raman spectroscopy requires little to no sample preparation and is insensitive to aqueous absorption bands. This property of Raman facilitates the measurement of solids, liquids, and gases not only directly, but also through transparent containers such as glass, quartz, and plastic.

The energy of the scattered radiation is less than the incident radiation for the Stokes line and the energy of the scattered radiation is more than the incident radiation for the anti-Stokes line. The energy increase or decrease from the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule and therefore the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule.

2.3 Theory of Raman Scattering

When considering Raman scattering, we can think about the physics in one of two ways: the classical wave interpretation or the quantum particle interpretation. In the classical wave interpretation, light is considered as electromagnetic radiation, which contains an oscillating electric field that interacts with a molecule through its polarizability. Polarizability is determined by the electron cloud's ability to interact with an electric field. For example, soft molecules such as benzene tend to be strong Raman scatterers while harder molecules like water tend to be fairly weak Raman scatterers.

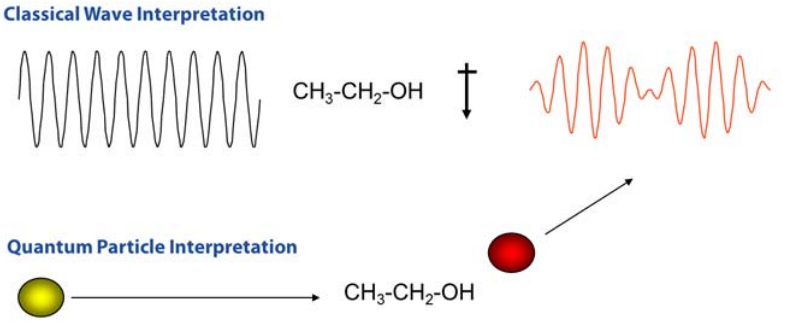


Fig. 1 Comparison of Raman Scattering Interpretations

When considering the quantum particle interpretation, light is thought of as a photon which strikes the molecule and then inelasticaly scatters. In this interpretation the number of scattered photons is proportional to the size of the bond. For example, molecules with large Pi bonds such as benzene tend to scatter lots of photons, while water with small single bonds tends to be a very weak Raman scatterer. Figure 2 shows a visual comparison of the two methods.

When deriving the Raman effect, it is generally easiest to start with the classical interpretation by considering a simple diatomic molecule as a mass on a spring (as shown in figure R-3) where *m* represents the atomic mass, *x* represents the displacement, and *K* represents the bond strength.

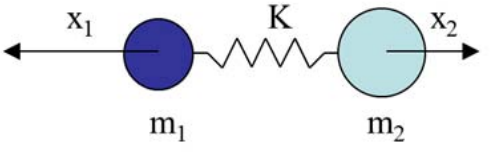


Fig.2 Diatomic Molecule as a Mass on a Spring

When using this approximation, the displacement of the molecule can be expressed by using Hooke's law as,

$$\frac{m_1 m_2}{m_1+m_2}\left(\frac{d^2x_1}{dt^2}+\frac{d^2x_2}{dt^2}\right) = -K(x_1+x_2)\,.$$

Equation 1

By replacing the reduced mass $\left(\frac{m_1 m_2}{m_1+m_2}\right)$ with μ and the total displacement (x_1+x_2) with q, the equation can be simplified to,

$$\mu\frac{d^2q}{dt^2} = -Kq,$$

Equation 2

By solving this equation for q we get,

$$q = q_o\cos(2\pi\nu_m t),$$

Equation 3

where ν_m is the molecular vibration and is defined as,

$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}\,.$$

Equation 4

From equations 3 and 4, it is apparent that the molecule vibrates in a cosine pattern with a frequency proportional to the bond strength and inversely proportional to the reduced mass. From this we can see that each molecule will have its own unique vibrational signatures which are determined not only by the atoms in the molecule, but also the characteristics of the individual bonds. Through the Raman effect, these vibrational frequencies can be measured due to the fact that the polorizability of a molecule, α, is a function of displacement, q. When incident light interacts with a molecule, it induces a dipole moment, P, equal to that of the product of the polorizability of the molecule and the electric field of the incident light source. This can be expressed as,

$$P = \alpha E_o \cos(2\pi \nu_o t),$$

Equation 5

where E_o is the intensity and ν_o is the frequency of the electric field. Using the small amplitude approximation, the polorizability can be described as a linear function of displacement,

$$\alpha = \alpha_o + q\left(\frac{\partial \alpha}{\partial t}\right)_{q=0} + \cdots,$$

Equation 6

which when combined with equations 3 and 5 results in,

$$P = \alpha_o E_o \cos(2\pi \nu_o t) + q_o \cos(2\pi \nu_m t)\, E_o \cos(2\pi \nu_o t)\left(\frac{\partial \alpha}{\partial t}\right)_{q=0}.$$

Equation 7

In Equation 7 we see that there are two resultant effects from the interaction of the molecule and the incident light. The first term is called Rayleigh scattering, which is the dominate effect and results in no change in the frequency of the incident light. The second term is the Raman scattered component and when expanded to,

$$q_o E_o \left(\frac{\partial \alpha}{\partial t}\right)_{q=0} [\cos(2\pi\{\nu_o - \nu_m\}t) + \cos(2\pi\{\nu_o + \nu_m\}t)],$$

Equation 8

can be shown to shift the frequency of the incident light by plus or minus the frequency of the molecular vibration. The increase in frequency is known as an Anti-Stokes shift and the decrease in frequency is known as a Stokes shift. By measuring the change in frequency from the incident light (typically only the Stokes shift is used for this measurement) the Raman effect now gives spectroscopists a means of directly measuring the vibrational frequency of a molecular bond.

Now that we have derived the Raman effect using the classical wave interpretation, we can now use the quantum particle interpretation to better visualize the process and determine additional information. As discussed earlier in the quantum interpretation, the Raman effect is described as inelastic scattering of a photon off of an molecular

bond. From the Jablonski diagram shown in fig. 4, we can see that this results from the incident photon exciting the molecule into a virtual energy state.

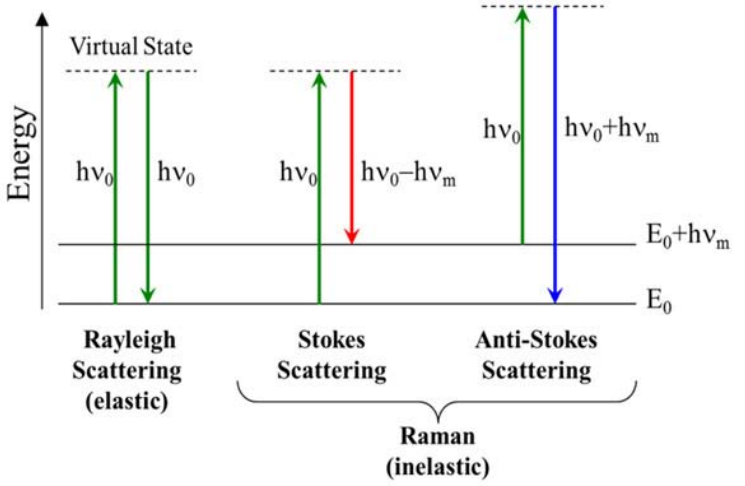


Fig. 4 Jablonski Diagram Representing
Quantum Energy Transitions for Rayleigh and Raman Scattering

When this occurs, there are three different potential outcomes. First, the molecule can relax back down to the ground state and emit a photon of equal energy to that of the incident photon; this is an elastic process and is again referred to as Rayleigh scattering. Second, the molecule can relax to a real phonon state and emit a photon with less energy than the incident photon; this is called Stokes shifted Raman scattering. The third potential outcome is that the molecule is already in an excited phonon state, is excited to a higher virtual state, and then relaxes back down to the ground state emitting a photon with more energy than the incident photon; this is called Anti-Stokes Raman scattering. Due to the fact that most molecules will be found in the ground state at room temperature, there is a much lower probability that a photon will be Anti-Stokes scattered. As a result, most Raman measurements are performed considering only the Stokes shifted light.

By further investigating the quantum interpretation of the Raman effect, it can be shown that the power of the scattered light, P_s, is equal to the product of the intensity of the incident photons, I_o, and a value known as the Raman cross-section, σ_R. It can be shown that,

$$\sigma_R \propto \frac{1}{\lambda^4},$$

Equation 9

where λ equals the wavelength of the incident photon. Therefore,

$$P_s \propto \frac{I_o}{\lambda^4}.$$

Equation 10

From equation 10 it is clear that there is a linear relationship between the power of the scattered light and the intensity of the incident light as well as a relationship between the power of the scattered light and the inverse of the wavelength to the fourth power. Therefore, it would appear that it is always desirable to use a short excitation wavelength and a high power excitation source based on these relationships. However, as we will see in the next section, this is not always the case.

1.4 Pure Rotational Raman Spectra

For linear Molecules :-

The rotational energy levels of linear molecules

$\varepsilon_J = BJ (J + 1) – 2DJ (J + 1)^2$ (J = 0 , 1 , 2 ….)

but in Raman Spectroscopy , the precision of the measurements does not warrant the retention of D term .

Thus we take the simpler expression :-

$\varepsilon_J = BJ (J + 1)$ cm^{-1} (J = 0 , 1 , 2 ….)

Transitions between these energy levels follow

Δ J = 0 , or ± 2 only .

(micro wave Δ J = ± 1) (ΔJ=0 Rayligh

ΔJ= ± 2 Raman)

Rotation about the bond axis produce no change in polarizability , we concern our selves only with end – over – end rotation .

Δ J = (J) upper state – (J) lower state

Δ J = -2 (O branch) is ignored , because for pure rotational change , the upper state quantum number must be greater than that in lower ,

Δ J = 0 is trivial since it represent no change in the molecular energy (Rayleigh)

Δ J = + 2 $\longrightarrow$ S- branch

$$\Delta\varepsilon = \varepsilon_{(J+2)} - \varepsilon_J = B(4J + 6)$$

Since Δ J = + 2 we may label these lines (S) branch lines , and

$\Delta\varepsilon_s$ = B(4J + 6) cm-1

(J = 0 , 1 , 2 ….)

Thus if the molecule gains rotational energy from the photon during collision we have a series of S branch lines to the low wave number side of the exciting line (Stokes') , while if the molecule loses energy to the photon the S branch line appear on the high wave number side (anti – Stokes'). The wave numbers of the corresponding spectral lines are given by :-

$\bar{U}s = \bar{U}ex \pm \Delta\varepsilon s$

$= \bar{U}ex \pm B\ (4J + 6)$ ……(1)

Where:

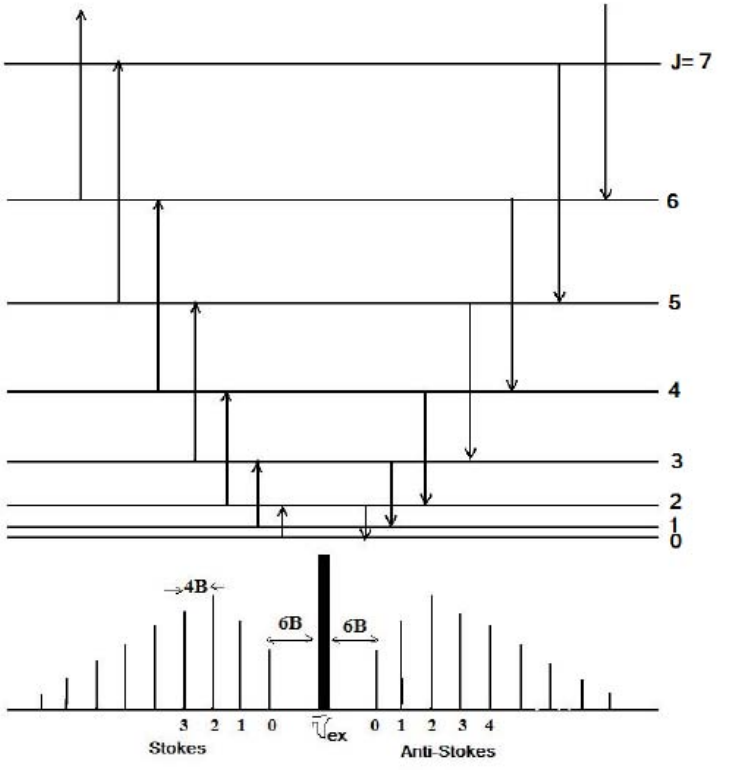
(+) Anti – Stokes'

(-) Stokes'

$\bar{U}$ex : wave number of the exciting radiation .

When J = 0 is inserted to eq. (1) , the separation of the first line from the exciting line is 6B cm-1 while the separation b successive lines is 4B. (fig)

.



For diatomic and light tri atomic molecules the rotational Raman spectroscopy will normally be resolved and obtain B , and hence the moment of inertia , bond length can be found . In Homo – nuclear diatomic molecules (H_2 , O_2 , …) it give no I.R or microwave spectra since they possess no dipole moment , but they do give rotational Raman spectra , thus Raman technique give structural data un obtainable from the techniques discussed before .

Raman spectroscopy is complementary to microwave and I.R studies. Note:- If the molecule has a center of symm. (H_2 , O_2 , CO_2) then the effects of nuclear spin will be observed in the Raman as in I.R . Thus for O_2 and CO_2 (sine the spin of oxygen is zero) every alternate rotational level is absent, for ex. In O2 ,energy level with (even) J values is missing

J = 0 , 2 , 4 …. Is missing from the spec . But in H_2 and other molecules composed of nuclei with non – zero spin, the spec. line show them.

Linear molecules with more than three heavy atoms have large moment of inertia and their rotational Raman spec. is not resolved.

1.5 Vibrational Raman Spectra

Raman activity of vibrations:

If a molecule has little or no symmetry, all its vibrational modes will be Raman active.

But when the molecule has considerable symmetry, it is nor easy to say it is Raman active or not, without detailed consideration, whether or not polarizability changes during the vibration.

For H_2O, symmetric stretching, the molecule as a whole increase and decrease in size. When a bond is stretched, the electrons forming it are less held by the nuclei and so the polarizability ellipsoid is decrease in size while the bonds stretch, and increase while they compress.

In a symmetric stretching, the direction of the major axis changes markedly. Thus all three vibrations involve obvious changes in at least one aspect of the polarizability ellipsoid and all are Raman active.

Rule of Mutual Exclusion

If a molecule has a center of symmetry, then Raman active vibrations are IR inactive, and IR active are Raman inactive.

If there is no center of symmetry, then some (not all) vibrations may be both Raman and IR active.

The converse of of this rule is also true, example:- the observance of Raman and IR spectra showing no common lines implies that the molecule has a center of symmetry.

Vibrational Raman Spectra

For every vibrational mode we can write an expression of :-

$$\varepsilon_{vib} = \varepsilon_{v+1} - \varepsilon_v = \left(v + \frac{1}{2}\right) \varpi_e - (v + \frac{1}{2})^2 \varpi_e \chi_e$$

$$v = 0, 1, 2, 3, 4 \ldots.$$

Such expression is general whatever the shape of the molecule or the nature of the vibration.

The general selection rule:-

$\Delta\upsilon = 0, \pm1, \pm2$

Which is the same for Raman as for IR.

The probability of $\Delta\upsilon = \pm2, \pm3$ …… decrease rapidly.

For Raman active modes we can apply the

$\Delta\upsilon = 0, \pm1, \pm2,$ ……

To the energy level expression:

$$\varepsilon_{vib} = \varepsilon_{v+1} - \varepsilon_v = \left(v + \frac{1}{2}\right)\varpi_e - (v + \frac{1}{2})^2 \varpi_e \chi_e$$

And obtain the transition energies:-

$$\Delta\varepsilon_{fundamental} = \varpi_e(1 - 2\chi_e)$$

$$\Delta\varepsilon_{overton} = 2\varpi_e(1 - 3\chi_e)$$

$$\Delta\varepsilon_{hotband} = \varpi_e(1 - 4\chi_e)$$

Since Raman scattered light is of low intensity, we can ignore all weaker effect such as overtones and hot bands, and restrict our discussion to the fundamentals.

$$\acute{\upsilon}_{fund} = \acute{\upsilon}_{ex} \mp \Delta\varepsilon_{fundamental}$$

(-) Stokes' lines (the molecule has gained energy at the expense of the radiation). (+) Anti-Stokes' lines, which are too weak (Anti-Stokes;) to be observed, since as we saw before, very few of the molecules exist in the v=1 state at normal temperatures. Vibrational Raman spectra of a molecule is, then, basically simple. It will show a series of reasonably intense lines to the low frequency side of the exciting line with a

much weaker, mirror image series on the high frequency side. The separation of each line from the centre of the exciting line gives the

Raman active fundamental vibration frequencies of the molecule.

1.6 Selection Rules

1. Vibrational energy levels

   $\Delta v = \pm 1$

2. Polarisability must change during particular vibration

3. Rotational energy levels

   $\Delta J = \pm 2$

4. Non-isotropic polarisability (ie molecule must not be spherically symmetric like CH4, SF6, etc.)

The Mutual Exclusion Rule

One crucial result which arises from this analysis is that irrespective of other symmetry considerations, for a centrosymmetric molecule, only vibrations which are g in character can be Raman active and only vibrations which are u in character can be infrared active. This is because irrespective of the exact irreducible representation, the g and u labels can be multiplied out and the final product must contain the totally symmetric representation and hence g. The rules are g x g = g, u x u = g and g x u = u. Since the Raman operators are g in character and the ground state is g, the excited state must be g if the vibration is to be allowed. In contrast, the infrared operator is u in character and so the excited state must be u if the vibration is to be allowed. Thus, in a molecule with a centre of symmetry, vibrations which are Raman active will not be infrared active, and vibrations which are infrared active will not be Raman active. Note that, it is the symmetric vibrations (g) which are Raman active, and the asymmetric vibrations (u) which are infrared active. This analysis leads to a rule known as the mutual exclusion rule, which states that any vibration in a molecule containing a centre of symmetry can be either Raman or infrared active, but not both. In molecules without a centre of symmetry, there is no such specific rule. Nonetheless,

in general, symmetric vibrations are more intense in Raman scattering and asymmetric vibrations in infrared scattering.

1.7 Instrumentation

Raman scattering is an extremely weak process. Only about 10^{-7} of the incident photons are scattered as compared to 10^{-4} in Rayleigh scattering. [Despite this weakness, Raman discovered the scattering using sunlight as the source and his eyes as the detector!] To get quantitative results in this experiment we will have to use some rather sophisticated light detection apparatus. Figure 2 gives a block diagram of the equipment. We will now discuss the components in detail:

1. **YAG laser:** The light source is a pulsed laser, whose operation is discussed in Appendix A. The intensity of Raman scattering increases as the fourth power of the frequency. To get a large signal, we want to use as high a frequency light source as possible. The YAG laser puts out ~ 5 ns wide pulses with an ultraviolet wavelength of 355 nm at a pulse rate of 10 per second. The pulse energy is 4.5 mJ, which translates into a peak power of 0.9 MW. The laser pulse contains some residual 1064 nm infrared light as well. Both of these wavelengths are invisible to the human eye. Although this might seem to be a rather small amount of energy, it can damage the eyes and is especially dangerous since the beam is invisible. Be sure to wear goggles whenever the laser is operating.
2. **Sample Cell:** One of the strengths of Raman scattering as an analytical tool is that no special sample preparation is required. The liquid (or solid dissolved in a solvent) is placed in a 1 cm thick quartz sample cell. The only requirement for the sample is that is be transparent to the incident beam and not fluoresce. Because of the danger to your eyes from stray laser light, the path from the laser output to the sample cell is enclosed and the sample cell is covered with a light shield. **Never attempt to operate the laser without having the sample shield in place.**

Fig.2 Block Diagram of the Raman spectrometer

3. **Photogate Trigger:** Since the signal is weak and the laser is pulsed, we can use pulsed electronics to detect the signal. The laser has a 5 ns jitter (variation in the starting time of the pulses) after the flashlamp fires. In order to eliminate the effects of this jitter on the detection process, a phototransistor is placed in the beam path after it passes through the sample cell. When a pulse strikes the phototransistor, it generates a voltage pulse (trigger) that is used to synchronize the detection electronics with the laser.
4. **Monochrometer:** The scattered light from the sample cell is a mixture of all the Raman lines, plus the intense Rayleigh scattered light. In order to measure the spectrum, the light is resolved into its components with a grating monochrometer, Fig. 3. The diffraction grating is mounted on a motor driven gear mechanism so that the wavelength reaching the exit slit varies linearly with time. The grating has a spectral range of 3---850 nm. It is calibrated to ± 1 nm and has a linear dispersion of 4 nm/mm (i.e. if the exit slit is 1 mm wide, it will pass a 4 nm wide band of light). The entrance and exit slits are ~ 0.1 mm wide, and thus the bandpass is 0.4 nm.

Figure 3. The Grating Monochrometer

The widths of the entrance and exit slits to the monochrometer are fixed (~ 0.1 mm) but the height (8 mm max) can be varied using the "fish-tail" slides located at the each end of the spectrometer. Pushing them all the way in gives maximum height and transmitted light, but reduces the resolution. There is a trade-off between resolution and signal-to-noise and the length of time it takes to perform the experiment (see below).

5. **Photomultiplier (PM):** The light from the monochrometer is detected with a Hamamatsu phototube, which has a quantum efficiency in excess of 5% over the range 150 to 700 nm (i.e. it detects more than 5% of the photons striking it). The PM is highly sensitive and must be protected from ambient light at all times when the accelerating voltage (800 to 1000 V) is applied to the tube. The tube is equipped with a shutter to be closed whenever the high voltage is on if there is a possibility of ambient light reaching the tube. Be sure that the high voltage is turned off or the shutter is closed whenever you remove the sample shield to change samples. To avoid damaging the boxcar with a voltage pulse from the PM, always turn the high voltage power supply down to zero before turning it off or on.
6. **Boxcar Integrator:** The output of the PM consists of 5 ns wide, negative pulses, occurring at a rate of 10 pps (pulses per second) and partially obscured by considerable noise generated in the phototube. To obtain a signal with adequate signal-to-noise ratio, we will use two techniques:

   The first is signal averaging (or integrating); the PM signal will be integrated over P pulses. Since the desired Raman signal from the PM will always be negative, the

integrated signal after P pulses will be P times larger than that of a single pulse. The phototube noise on the other hand will fluctuate randomly with both positive and negative polarity. Thus the integrated noise will partially cancel out. Calculation shows that if P pulses are integrated the signal-to-noise will improve by $\sqrt{P}$. For this experiment you will integrate over 10 to 30 pulses for a S/N gain of 3 to 5.5.

A much more significant improvement in the S/N will be achieved by using a boxcar integrator, an integrating circuit that is gated (turned on) only during the time period when a gate pulse is present. The Raman signal is present for only a small fraction of the time (.000005% of the time for a 5 ns pulse repeated at a 10 pps rate). During the time between pulses there is no useful signal from the PM; if we integrate during this time, we only add noise. Thus by using a boxcar integrator gated to coincide with the PM signal we can integrate only during the short time when the desired signal is present and ignore all the intervening noise.

Timing: The measurement process is initiated by the photogate trigger pulse traveling from the phototransistor to the boxcar. There are a number of sources of delay in the system: the PM cannot respond instantly to the laser pulse, the phototransistor and other electronic circuits do not respond instantly, and there is a propagation delay of about 5 ns/m in the coax cable connecting the PM to the input amplifier. We also intentionally delay the amplified signal by about 30 ns so that when we observe the signal on the oscilloscope, it does not fall at the edge of the screen. We compensate for these delays using an adjustable delay in the boxcar between the time the boxcar receives the trigger pulse and when it generates the gate pulse that initiates the integration. Adjustment of the timing is simple; the gate signal and the delayed PM signal are observed on the oscilloscope and the boxcar delay is adjusted so that the gate pulse coincides with the PM pulse. The width of the gate can also be adjusted to improve the S/N. It should be set narrow enough that it only covers the time when the pulse from the photomultiplier is present but not so narrow that it excludes too much signal. The S/N is sufficiently large that neither the gate pulse delay setting nor the gate-width is critical.

7. **The Chart Recorder**: The boxcar output is recorded with a chart recorder. Since the paper moves past the pen at a constant rate, and the wavelength is also swept at

a constant rate, the x-axis is proportional to the wavelength. In order to calibrate this axis you must make marks on the paper corresponding to the wavelength readings on the monochrometer. For this purpose the push button on the back of the recorder momentarily shorts the input and makes a vertical mark on the paper. After using the recorder be sure to turn off the chart paper drive and **put the cap back on the pen to prevent it from drying out.**

1.8 Applications of Raman Spectroscopy

Raman spectroscopy is commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecule can be identified. For instance, the vibrational frequencies of SiO, Si_2O_2, and Si_3O_3 were identified and assigned on the basis of normal coordinate analyses using infrared and Raman spectra. The fingerprint region of organic molecules is in the (wavenumber) range 500–2000 cm^{-1}. Another way that the technique is used is to study changes in chemical bonding, as when a substrate is added to an enzyme.

Raman Spectra of Inorganic Species

The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed. In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700 cm^{-1}, a region of the infrared that is experimentally difficult to study. These vibrations are frequently Raman active, however, and peaks with $\Delta\nu$ values in this range are readily observed. Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds.

Raman Spectra of Organic Species

Raman spectra are similar to infrared spectra in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds. Raman spectra yield more information about certain types of organic compounds than do their infrared counterparts.

Biological Applications of Raman Spectroscopy

Raman spectroscopy has been applied widely for the study of biological systems. The advantages of his technique include the small sample requirement, the minimal sensitivity toward interference by water, the spectral detail, and the conformational and environmental sensitivity.

Quantitative applications

Raman spectra tend to be less cluttered with peaks than infrared spectra. As a consequence, peak overlap in mixtures is less likely, and quantitative measurements are simpler. In addition, Raman sampling devices are not subject to attack by moisture, and small amounts of water in a sample do not interfere. Despite these advantages, Raman spectroscopy has not yet been exploited widely for quantitative analysis. This lack of use has been due largely to the rather high cost of Raman spectrometers relative to that of absorption instrumentation.

As has been described, Raman spectroscopy can be used to obtain information about the vibrational spectrum of a material. This can lead to a better understanding of the chemical composition of the sample, as in many organic compounds, where different chemical bonds have very characteristic vibrational frequencies. It may also be possible to deduce the structure of a material; for example, in molecular systems, the juxtaposition of different chemical species leads to small modifications of the usual vibrational frequencies, so that longer-scale structure may be investigated. In crystalline solids, the selection rules for scattering from the lattice vibrations (phonons) indicate the symmetry of the crystal unit cell and can thus reveal (for example) phase changes. Finally, via resonance Raman spectra, one can sometimes correlate a particular vibrational mode with a particular electronic transition energy and thus learn more about the electronic structure of the material.

1.9 Examples of experimental techniques.

Only a brief discussion of techniques is possible here as the field has become immense; one useful book containing a great deal of practical information is that by Gardiner and Graves, where the traditional experimental set-up for Raman spectroscopy is discussed along with many new developments.

1. Spontaneous emission from the laser

One comment on the use of lasers in Raman spectroscopy is that although lasers are often regarded as ideal monochromatic light sources, this is far from the case in practice. In the case of tunable lasers, there is always broad-band spontaneous emission over the whole tuning range of the gain medium, whilst in the case of ion lasers, there are many atomic transitions which give rise to sharp spectral lines; both of these can easily be comparable in intensity to the required signals. There are two common solutions; the most effective is to use a small monochromator, which acts as a filter for the laser beam before it reaches the sample. About 50% of the laser power is generally lost in this process. Another solution is to pass the beam through an aperture. Since the spontaneous emission is radiated isotropically, much of it can be blocked before it is focused onto the sample along with the laser beam.

2. Choice of laser wavelength

The massive enhancement of Raman scattering when the excitation is resonant with some electronic transition of the material has already been mentioned. To exploit this effect, one may require a range of laser lines or even a tunable laser. However, other factors influence the choice of excitation wavelength. Many materials show strong photoluminescence (fluorescence) when the excitation lies close in energy to an absorption band. This may mean that it is advantageous to avoid resonance conditions. One instrument which is popular for avoiding fluorescence problems is the Fourier Transform spectrometer, which uses very low energy excitation (wavelength 1064 nm), usually insufficient to stimulate fluorescence.

3. Spectrometers

Many developments have been made recently in the area of spectrometers. This is in part due to the advent of charge-coupled devices (CCDs) and other forms of array detector, which have different requirements to single-channel detectors such as photomultipliers. Essentially, a single spectrometer can have a high enough resolution for Raman spectroscopy but generally will not have good enough stray light rejection. The use of a double spectrometer improves the stray light rejection at the expense of efficiency. In both these instruments, the exit slit is necessary to obtain the best stray light rejection, so that they are not ideal for use with array detectors.

The triple instrument is specifically designed for array detectors. The light is passed through a wide central slit between the first and second stages and the gratings are set so that the entire spectral range of interest passes through this slit, but most of the Rayleigh-scattered light is blocked. The first and second stages are arranged so the dispersions of the two gratings are opposed; thus, the light entering the final stage is not dispersed. The final stage disperses this light once more, with as high a resolution as is required and now no longer requires an exit slit, so that an array detector can be fitted. Two other recent developments are worth mentioning; the first involves the use of echelle gratings and the second, holographic filters. Echelle gratings are a special type of grating which have high dispersions but which suffer from the problem that the different diffraction orders overlap significantly. This problem is overcome if an array detector is used with a second, low-resolution grating oriented at right-angles to the echelle grating, so that the different orders are displaced from one another. The echelle grating disperses the light vertically and the cross-disperser disperses the different orders horizontally. With this system, the entire frequency range of vibrational modes can be covered at high resolution in one acquisition; a complete spectrum of cyclohexane, for example, could be acquired in just 1 second.

4. Raman imaging

One exciting recent development in Raman spectroscopy is the use of CCDs to form images of samples using the light emitted in a specific Raman band, so that regions composed of different materials can be distinguished. The key to this technique is the use of holographic filters to provide adequate stray laser light rejection. These filters operate at specific wavelengths and have very narrow band passes of down to 100 cm-1; their advantage over diffraction gratings is that two-dimensional spatial information is preserved. A particularly successful instrument uses a combination of holographic filters and a Fabry-Perot etalon to achieve a spectral resolution of about 20 cm-1 in a true two-dimensional imaging mode. The instrument can also be used with a single diffraction grating to provide conventional spectra at higher resolution. The instrument is combined with a microscope, as is discussed below. One potential disadvantage of this instrument is the difficulty of using tunable lasers as excitation sources.

5. Raman microscopy

Raman spectroscopy can be combined with optical microscopy to investigate microscopic samples present as, for example, inclusions within other materials. This technique has found many industrial applications, for instance, in the diagnosis of problems in the production of plastics, where catalyst particles embedded in the polymer can be identified.

A microscope may be used in conjunction with a Raman spectrometer in two basic ways. Firstly, one may select a region of a sample by inspecting its white-light image; the Raman spectrum of that region may then be recorded. Alternatively, one may record a two-dimensional "map" of the intensity of some Raman band of the material as a function of position contains a very useful introductory chapter on this subject. The laser beam is generally introduced into the microscope via a side-arm with a spatial filter to improve the beam profile; a beam splitter then reflects some of the laser beam down to the sample through the objective lens. The scattered light is collected through the same objective lens and some of it passes through the beam splitter. A movable prism or mirror can be inserted into the microscope column to reflect the beam out to a spectrometer; the prism can also be withdrawn so that the light passes up to a video camera in order to allow one to identify the desired region of the sample. Spatial resolutions of around 10^{-6} m can be achieved, depending on the particular optical system used. Note that by use of a confocal system with appropriate spatial filtering, it is possible to obtain a very restricted depth of field, so that spectra may even be obtained from different depths in transparent samples.

6. Optical fibres

A common difficulty in industrial applications of Raman spectroscopy is that it may not be convenient to examine samples in the laboratory, either because frequent sampling is required or because the material of interest must be examined under extreme conditions of temperature, pressure, or chemical environment. Optical fibres provide a means of delivering the laser light to the sample and of collecting the scattered light. A single fibre may be used to transmit the excitation light, whereas the scattered light is collected by several fibres formed into a "bundle". A lens is used to image the light emitted from the bundle into a conventional Raman spectrometer; often, the bundle is shaped into a line of fibres which match the size of the spectrometer slit. A disadvantage is that the glass of the fibre carrying the laser light

will itself give rise to some Raman scattering. Background subtraction procedures can solve this, but another approach uses a bandpass filter before the sample to block the Raman-scattered light from the input fibre, whilst a holographic filter after the sample prevents excitation light from entering the collection fibre.

7. Surface-enhanced Raman scattering

Finally, surface-enhanced Raman scattering (SERS) deserves a mention here. The effect was a subject of much research activity when it was first discovered; a good review is given in [6] and there are several textbooks on the subject. Essentially, a large enhancement of Raman-scattering cross-sections is sometimes observed for samples supported on roughened or corrugated metallic surfaces (frequently silver is used). The explanation lies in the increased electric field of the excitation light near the surface; a full discussion cannot be given here. However, the effect is becoming a standard technique for increasing sensitivity, especially where only small quantities of samples are available. A comparison can be made between the spectra of approximately a monolayer of pyridine on an "activated" silver surface and a thick layer of pyridine on an inactive surface; it is then seen that the signals arising from the monolayer and different to, and more intense than, the signals from the thick layer. Similar intensities are obtained from very different quantities of material. The interaction with the surface can also modify the form of the spectrum. The nature of the spectrum may also be influenced by the electrical potential of the silver surface; the interaction between adsorbate and metal surface is a complex one so that this is not necessarily a simple technique to apply. Recently, SERS has been combined with microscopy to use extremely fine silver wires as probes which can selectively enhance signals from the very small region of the sample surrounding the tip of the wire; this has found application in biological systems.

Unit-3: ^{13}C-NMR spectroscopy

Structure of Unit:

3.0 Objectives

At the end of the unit learner will be able to

- ^{13}C has spin states similar to H.
- Natural occurrence is 1.1% making ^{13}C-^{13}C spin spin splitting very rare.
- H atoms can spin-spin split a ^{13}C peak. ($^{13}CH_4$ would yield a quintet). This would yield complicated spectra.
- H splitting eliminated by irradiating with an additional frequency chosen to rapidly flip (decouple) the H's averaging their magnetic field to zero.

- A decoupled spectrum consists of a single peak for each kind of carbon present.
- The magnitude of the peak is not important.

3.1 Introduction

The ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules - does not have a nuclear magnetic moment, and thus is NMR-inactive. Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons. Most of what we have learned about ^{1}H-NMR spectroscopy also applies to ^{13}C-NMR, although there are several important differences. Proton NMR and C-13 NMR are compared with respect to isotopic percent, sensitivity of the instrument, the time required to run the spectra, extent of expected chemical shifts, the radio frequency required, and the relationship among peak areas. The manner in which it is necessary to boost the C-13 signal because the signal is so much weaker than that expected for the proton signal is addressed. The huge chemical shifts experienced with C-13, when compared to the very small chemical shifts from proton NMR, are explained. The signal being driven downfield to a greater extent in C-13 than in proton NMR because of proximity to the deshielding group is also discussed.

Because the gyromagnetic ratio for C-13 is small, only about a quarter of that of the proton, it is noted that C-13 NMR only requires about one quarter the frequency needed for proton spectroscopy within an instrument of the same magnetic strength. At this point the student begins to realize and appreciate the significant differences between the two forms of NMR.

The number of signals reflects the number of different carbon atoms producing the signals, so the student must learn to determine identity and non-identity of carbon atoms. Since Fourier transform, the method used most often, does not use a technique that relates the area under the curve and the frequency of a specific carbon's occurrence, the student must look for different information from the height of the peak or area under the curve.

Chemical shift patterns are diagrammed so students can determine where a particular carbon would be expected to produce a signal. The impact of proximity to electronegative groups is noted.

Splitting of signals for C-13 NMR differs markedly from splitting of signals in proton NMR. C-13 spectra are usually recorded using proton spin decoupling, a method that produces a C-13 spectrum with a series of singlets, one for each different carbon environment. The student is introduced both to the proton spin decoupling and the method of off-resonance decoupling which gives information about the number of protons (hydrogens) bonded directly to the carbon in question.

C-13 NMR is often used in conjunction with other spectroscopic techniques to take advantage of the strengths of each, as in the case of C-13 and proton NMR. However, that combination is not addressed in this unit.

3.2 The basics of ^{13}C-NMR spectroscopy

The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton, meaning that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals. This, combined with the low natural abundance of ^{13}C, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels. Unlike $1H^1$-NMR signals, the area under a ^{13}C-NMR signal cannot be used to determine the number of carbons to which it corresponds. This is because the signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene (CH_2) peaks. Peak integration is generally not useful in ^{13}C-NMR spectroscopy, except when investigating molecules that have been enriched with ^{13}C isotope.

Instrumentation:

An NMR instrument consists of a Magnet (permanent magnet/elctromagnet or iron magnet/superconducting magnet). The sample is inserted into the centre of the magnetic field. The sample is surrounded by RF coils as mentioned earlier. Signals are detected by either the same coil or another coil depending upon the manufacturer's

design. The main spectrometer consists of the RF generator, magnetic field monitor, RF signal receiving and detecting system recording device, necessary power supplies etc. Optionally there can be computer connected (interfaced) to the spectrometer to collect (acquire) the spectral data and store/process etc.

There are two classes of NMR spectrometers, viz., CW (continuous wave) and pulsed Fourier Transform (FT) spectrometers. The CW technique is old and is almost obsolete whereas almost all present manufacturers produce only FT NMR spectrometers, which are much more versatile. Though both type of spectrometers contain the magnet and the sample probe, the design of the RF transmitter and the detection circuitry are different. In FT NMR the sample in a resonant coil is subjected to an intense and short RF pulse. Since the short pulse contains a broad band of frequencies (Fourier components of the RF pulse) this system is subjected to a broad band excitation, and irrespective of the differences in the chemical shift spread all nuclei of given kind are simultaneously excited and gives a time-response which is acquired by a fast digital computer to give the so-called Free Induction Decay (FID).

The FID upon a mathematical Fourier transform produce a frequency spectrum which will be identical to the spectrum obtained by the conventional CW sweep of the frequency. The advantage is that several thousand responses from a sample can be coherently added increasing the signal to noise ratio enormously. This makes it possible to address by MR any Magnetic nucleus in the Periodic Table irrespective of the magnetic moment and natural abundance. Further pulsed FT techniques when be used to measure dynamic process in the system such as relaxation times and also leads to a newer class of multidimensional correlation spectroscopy that has led to important advances in the application of NMR to the elucidation of biomolecular structure. The details of such techniques are beyond the scope of this article, and the reader may refer to books cited at the end of this write-up.

Advantages, applications and limitations of NMR technique:

The proton and C^{13} NMR spectral data are quite useful and well adapted for the structural elucidation of most of the organic compounds. As mentioned earlier, a fairly good idea of the structure of the compound can be arrived at using the NMR spectrum. This is quite useful when identification of a new compound in R&D, natural products

separated from plants etc., and in Quality Control in Industries where purity of a product is to be monitored.

However this is not an ultimate technique. One should be aware of the limitations before resorting to NMR:

1. First, it should be noted than inherently NMR is a very insensitive technique. This problem is still more acute when one wishes to do C^{13} or N^{15} NMR of ordinary organic compounds.
2. Another point the user must keep in mind is that the test sample should be pure, non-paramagnetic and should not be a mixture of many compounds. If the sample is impure or a mixture, understandably, the spectrum also will show signals from all the individual components present, adding more confusion and problems in analyzing the results. Except in cases where the test sample contains known impurities or known unwanted compounds for which the spectral signals are known, the assignment becomes formidable. The presence of paramagnetic impurities causes spectral pattern to become broad, feature-less and uninformative.
3. Most of the routine NMR spectral measurements are done in dissolved/liquid state. So it becomes mandatory to make sample in solution form. The solvent itself has to be free from the nuclei one is interested in the sample. For example, for taking proton NMR spectrum of a compound, the sample should be freely soluble in Carbon tetrachloride (CCl_4) or Carbon disulfide (CS_2), which do not contain any 'H' (proton). In case the sample is soluble only in say, Chloroform($CHCl_3$) or any other solvent which contains protons, then one has to use these solvents in the -deuterated form, i.e., all the 'H' atoms are replaced by deuterium in the solvent, so that the solvent itself will not give any signal and mask the sample signal.

It is worth mentioning that solvent concentration generally will be much more than 99.9% in the solution. Needless to say that these deuterated solvents are very expensive and one can not afford to stock all these solvents in bulk quantities. For ^{13}C measurements this problem will not be serious, though, there also it is advisable to use

deuterated solvents. For other nuclei like N^{15}, P^{31}, Si^{29} etc., one can afford to use ordinary solvents, in as much as they do not contain the nuclei of measurement.

In the recent years, techniques to do NMR measurements of samples in the solid state have been developed. However, this does not have such wide adaptability as a routine analytical tool, since, the resolution of the spectra are inherently very poor thus putting constraints in the information availability. These include multiple pulse line narrowing sequences and cross polarization with 'magic angle' spinning techniques. Please see appropriate references cited at the end.

The resonance frequencies of ^{13}C nuclei are lower than those of protons in the same applied field - in a 7.05 Tesla instrument; protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in $1H^{1}$-NMR, the standard used in ^{13}C-NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in ^{13}C-NMR it is the signal from the four equivalent carbons in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for C^{13} compared to 12 ppm for protons (see Table 1 for a list of typical ^{13}C-NMR chemical shifts). This is also fortunate, because it means that the signal from each carbon in a compound can almost always be seen as a distinct peak, without the overlapping that often plagues ^{1}H-NMR spectra. The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C-NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen.

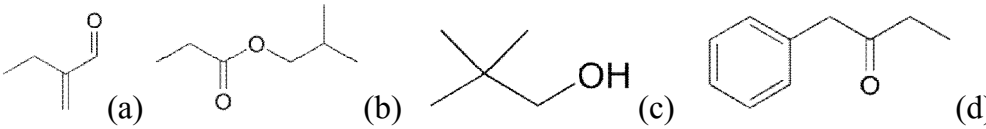
Exercise: How many sets of non-equivalent carbons are there in?

a. Toluene

b. 2-pentanone

c. Para-xylene

d. Triclosan



Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two 13C atoms near each other in the same molecule, and thus we do not see spin-spin coupling between neighboring carbons in a ^{13}C-NMR spectrum. There is, however, heteronuclear coupling between ^{13}C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. For clarity, chemists generally use a technique called broadband decoupling, which essentially 'turns off' C-H coupling, resulting in a spectrum in which all carbon signals are singlets. Below is the proton-decoupled C^{13} - NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons.

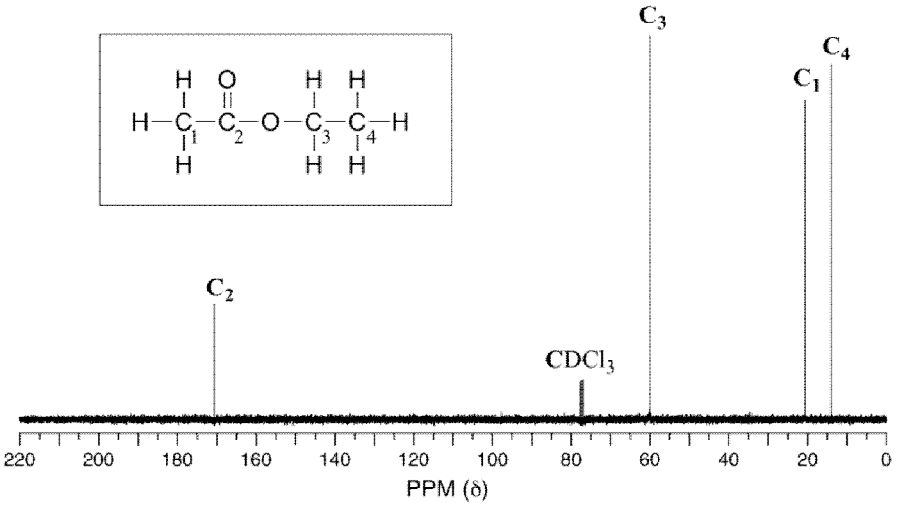


Figure-1 ^{13}C NMR spectra of ethyl acetated

While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, another modern NMR technique called DEPT (Distortionless Enhancement by Polarization Transfer) allows us to determine how many hydrogens are bound to each carbon. For example, a DEPT experiment tells us that the signal at 171 ppm in the ethyl acetate spectrum is a quaternary carbon (no hydrogens bound, in this case a carbonyl carbon), that the 61 ppm signal is from a methylene (CH_2) carbon, and that the 21 ppm and 14 ppm signals are both methyl (CH_3) carbons. The details of the DEPT experiment are beyond the

scope of this text, but DEPT information will often be provided along with ^{13}C spectral data in examples and problems.

Below are two more examples of ^{13}C NMR spectra of simple organic molecules, along with DEPT information.

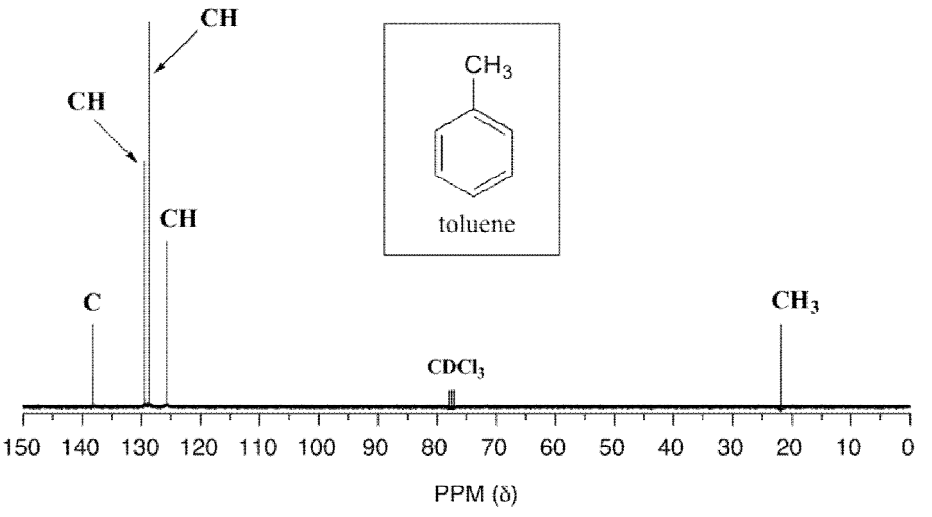
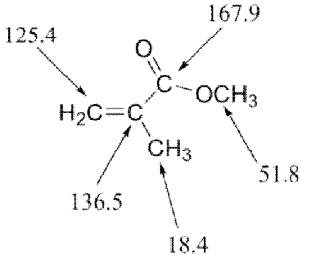


Figure-2 ^{13}C NMR spectra of toluene

Exercise: Give peak assignments for the ^{13}C-NMR spectrum of methyl methacrylate, shown above.



One of the greatest advantages of ^{13}C-NMR compared to ^{1}H-NMR is the breadth of the spectrum - recall that carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, ^{13}C signals rarely overlap, and we can almost always distinguish separate peaks for each carbon, even in a relatively large compound containing carbons in very similar environments. In the proton spectrum of 1-heptanol, for example, only the signals for the alcohol proton

(Ha) and the two protons on the adjacent carbon (Hb) are easily analyzed. The other proton signals overlap, making analysis difficult.

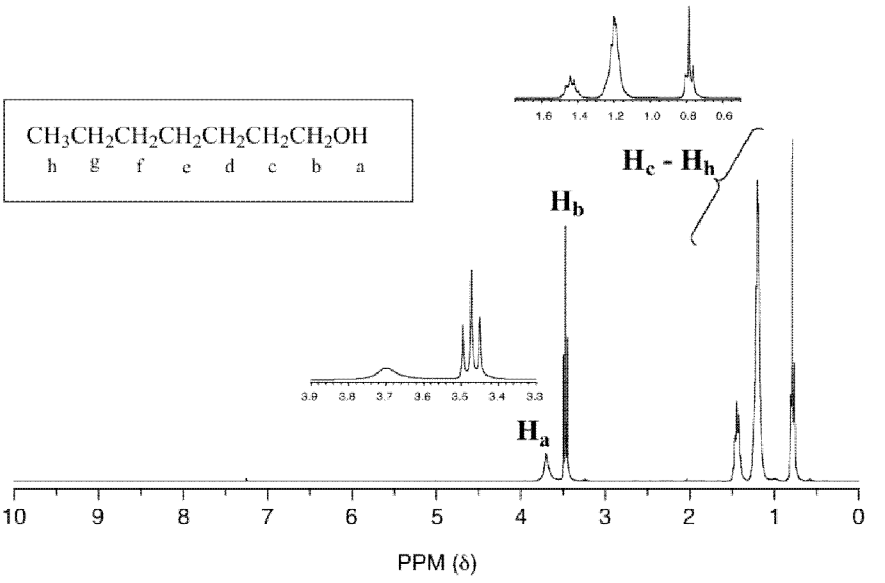


Figure-3a: ^{1}H NMR spectra of Heptan-1-ol.

In the ^{13}C spectrum of the same molecule, however, we can easily distinguish each carbon signal, and we know from this data that our sample has seven non-equivalent carbons. (Notice also that, as we would expect, the chemical shifts of the carbons get progressively smaller as they get farther away from the deshielding oxygen.)

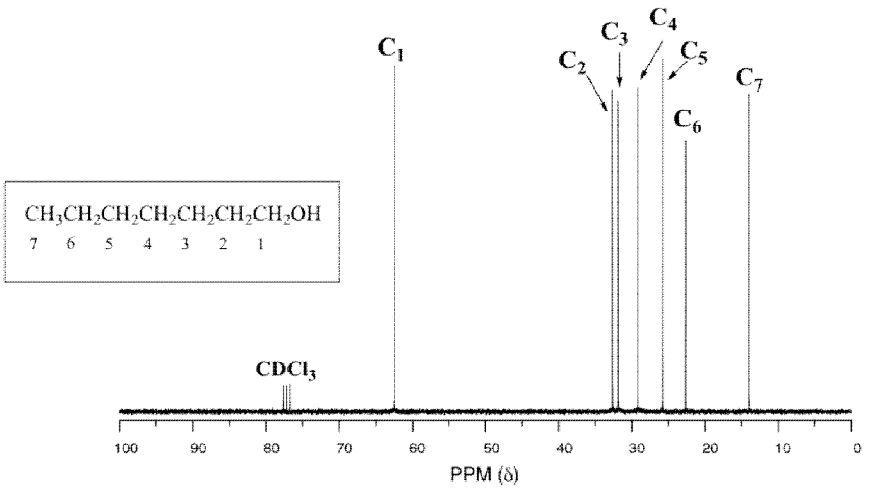
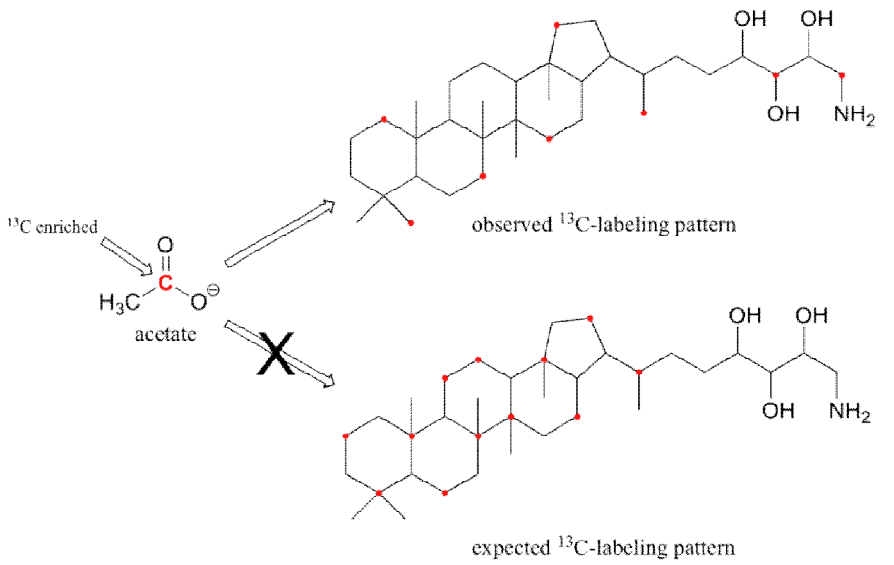


Figure-3b: ^{13}C NMR spectra of Heptan-1-ol

3.3 ^{13}C-NMR in isotopic labelling studies

Although only about 1 out of 100 carbon atoms in a naturally occurring organic molecule is the ^{13}C isotope, chemists are often able to synthesize molecules that are artificially enriched in ^{13}C at specific carbon positions, sometimes to the point where the ^{13}C isotope is incorporated at a given position in over half of the molecules in the sample. This can be very useful, especially in biochemical studies, because it allows us to 'label' one or more carbons in a small precursor molecule and then trace the presence of the ^{13}C label through a metabolic pathway all the way to a larger biomolecule product. For example, scientists were able to grow bacteria in a medium in which the only source of carbon was acetate enriched in ^{13}C at the C1 (carbonyl) position. When they isolated a large molecule called amino-bacterio-hopanetriol (very similar in structure to cholesterol) from these bacteria and looked at its ^{13}C-NMR spectrum, they observed that the ^{13}C label from acetate had been incorporated at eight specific positions. They knew this because the ^{13}C-NMR signals for these carbons were much stronger compared to the same signals in a control (unlabeled) molecule.



This result was very surprising - the scientists had expected a completely different pattern of ^{13}C incorporation based on what they believed to be the metabolic pathway involved. This unexpected result led eventually to the discovery that bacteria synthesize these types of molecules in a very different way than yeasts, plants, and animals (*Eur. J. Biochem*. **1988**, *175*, 405). The newly discovered bacterial metabolic pathway is currently a key target for the development of new antibiotic and antimalaria drugs.

3.4 ^{13}C Chemical Shifts:

Just as chemical shifts in ^{1}H NMR are measured relative to the protons of tetramethylsilane, chemical shifts in ^{13}C NMR are measured relative to the carbons of tetramethylsilane. Table- 1 lists typical chemical-shift ranges for some representative types of carbon atoms. In general, the factors that most affect ^{13}C chemical shifts are

1. The electronegativity of the groups attached to carbon

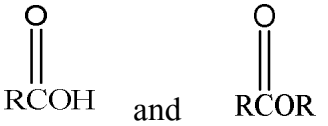
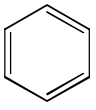
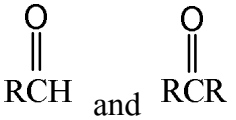
2. The hybridization of carbon

Electronegativity Effects. Electronegative substituents affect C^{13} chemical shifts in the same way as they affect 1H chemical shifts, by withdrawing electrons. For 1H NMR, recall that because carbon is more electronegative than hydrogen, the protons in

methane (CH4) are more shielded than primary hydrogens (RCH_3), primary hydrogens are more shielded than secondary (R_2CH_2), and secondary more shielded than tertiary (R_3CH). The same holds true for carbons in ^{13}C NMR, but the effects can be 10–20 times greater.

TABLE 13.3 TABLE 1: Chemical Shifts of Representative Carbons

Type of carbon	**Chemical shift (δ) ppm***	**Type of carbon**	**Chemical shift (δ) ppm***
Hydrocarbons		Functionally substituted carbons	
RCH_3	0–35	RCH_2Br	20–40
R_2CH_2	15–40	RCH_2Cl	25–50
R_3CH	25–50	RCH_2NH_2	35–50
R_4C	30–40	RCH_2OH and RCH_2OR	50–65

RC ≡CR	65–90	RC ≡ N	110–125
R_2C =CR_2	100–150		160–185
	110–175		190–220

*Approximate values relative to tetramethylsilane.

	$(CH_3)_4C$	$(CH_3)_3CH$	$CH_3CH_2CH_3$	CH_3CH_3	CH_4
Classificatio:	Quaternary	Tertiary	Secondary	Primary	
Chemical shift (δ), ppm:					
H		1.7	1.3	0.9	0.2
C	28	25	16	8	-2

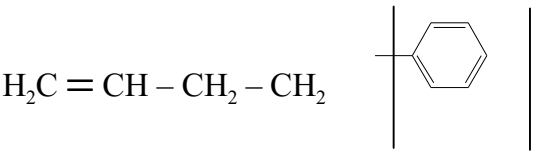
Figure-3a and b compared the appearance of the ^{1}H and ^{13}C NMR spectra of haptan-1-ol and drew attention to the fact each carbon gave a separate peak, well separated from the others. Let's now take a closer look at the ^{13}C NMR spectrum of haptan-1-ol with respect to assigning these peaks to individual carbons.

Likewise, for functionally substituted methyl groups:

	CH_3F	CH_3OH	CH_3NH_2	CH_4
Chemical shift (δ), ppm:				
H	4.3	3.4	2.5	O.2
C	75	50	27	-2

The most obvious feature of these ^{13}C chemical shifts is that the closer the carbon is to the electronegative chlorine, the more deshielded it is. Peak assignments will not always be this easy, but the correspondence with electronegativity is so pronounced that spectrum simulators are available that allow reliable prediction of ^{13}C chemical shifts from structural formulas. These simulators are based on arithmetic formulas that combine experimentally derived chemical shift increments for the various structural units within a molecule.

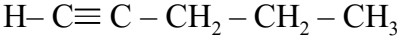
Hybridization Effects. Here again, the effects are similar to those seen in ^{1}H NMR. As illustrated by 4-phenyl-1-butene, sp^3-hybridized carbons are more shielded than sp^2-hybridized ones.



^{13}C chemical shift (δ), ppm:	114	138	36	36	126	142

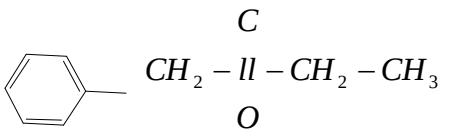
Of the sp^2-hybridized carbons, C-1 is the most shielded because it is bonded to only one other carbon. The least shielded carbon is the ring carbon to which the side chain is attached. It is the only sp^2-hybridized carbon connected to three others.

Acetylenes are anomalous in ^{13}C, as in ^{1}H NMR. Sp-Hybridized carbons are less shielded than sp^3-hybridized ones, but more shielded than sp^2-hybridized ones.



^{13}C chemical shift (δ), ppm: 68 84 22 20 13

Electronegativity and hybridization effects combine to make the carbon of a carbonyl group especially deshielded. Normally, the carbon of C=O is the least shielded one in a ^{13}C NMR spectrum.



^{13}C chemical shift (δ), ppm: 127 134 41 171 61 14

3.5 ^{13}C NMR and Peak Intensities

Two features that are fundamental to ^{1}H NMR spectroscopy—integrated areas and splitting patterns—are not very important in ^{13}C NMR. Although it is a simple matter to integrate ^{13}C signals, it is rarely done because the observed ratios can be more misleading than helpful. The pulsed FT technique that is standard for ^{13}C NMR has the side effect of distorting the signal intensities, especially for carbons that lack attached hydrogens. Examine Figure-4, which shows the ^{13}C NMR spectrum of 3-methylphenol (m-cresol). Notice that, contrary to what we might expect for a compound with seven peaks for seven different carbons, the intensities of these peaks are not nearly the same. The two least intense signals, those at 140 and 157, correspond to carbons that lack attached hydrogens.

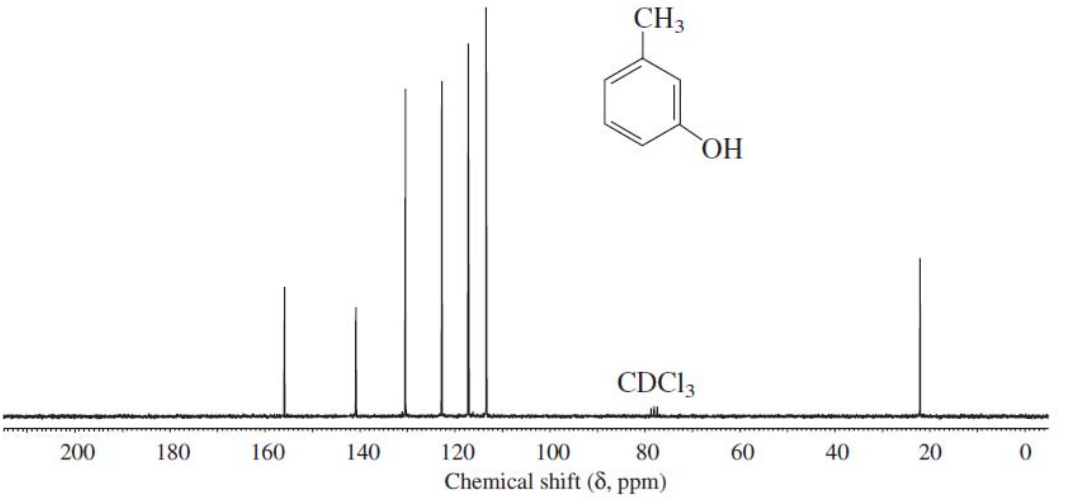


Figure-4: The ^{13}C NMR spectrum of m-cresol. Each of the seven carbons of m-cresol gives a separate peak.

3.6 ^{13}C - ^{1}H Coupling:

The lack of splitting due to ^{13}C-^{13}C coupling is easy to understand. ^{13}C NMR spectra are measured on samples that contain ^{13}C at the "natural abundance" level. Only 1% of all the carbons in the sample are ^{13}C, and the probability that any molecule contains more than one C^{13} atom is quite small.

Splitting due to ^{13}C - ^{1}H coupling is absent for a different reason, one that has to do with the way the spectrum is run. Because a ^{13}C signal can be split not only by the protons to which it is directly attached, but also by protons separated from it by two, three, or even more bonds, the number of splitting might be so large as to make the spectrum too complicated to interpret. Thus, the spectrum is measured under conditions, called broadband decoupling, that suppress such splitting. In addition to pulsing the sample by a radiofrequency tuned for ^{13}C, the sample is continuously irradiated by a second RF transmitter that covers the entire frequency range for all the ^{1}H nuclei. The effect of this second RF is to decouple the ^{1}H spins from the ^{13}C spins, which causes all the ^{13}C signals to collapse to singlets.

What we gain from broadband decoupling in terms of a simple-looking spectrum comes at the expense of some useful information. For example, being able to see

splitting corresponding to one-bond ^{13}C-^{1}H coupling would immediately tell us the number of hydrogens directly attached to each carbon. The signal for a carbon with no attached hydrogens (a quaternary carbon) would be a singlet, the hydrogen of a CH group would split the carbon signal into a doublet, and the signals for the carbons of a CH_2 and a CH_3 group would appear as a triplet and a quartet, respectively. Although it is possible, with a technique called off-resonance decoupling, to observe such one-bond couplings, identifying a signal as belonging to a quaternary carbon or to the carbon of a CH, CH_2, or CH_3 group is normally done by a method called DEPT, which is described in the next section.

3.7 Using DEPT to Count Hydrogens Attached to ^{13}C

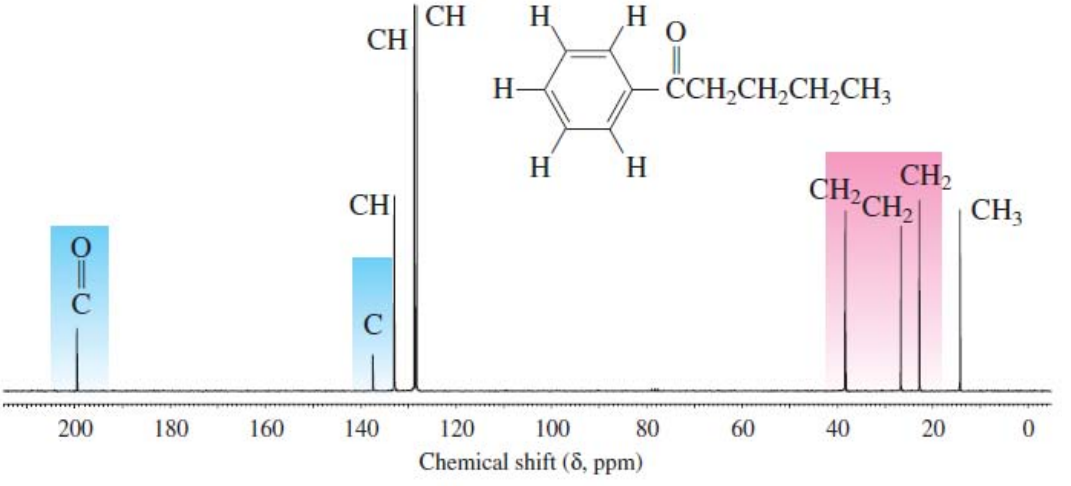
In general, a simple pulse FT-NMR experiment involves the following stages:

1 Equilibration of the nuclei between the lower and higher spin states under the influence of a magnetic field

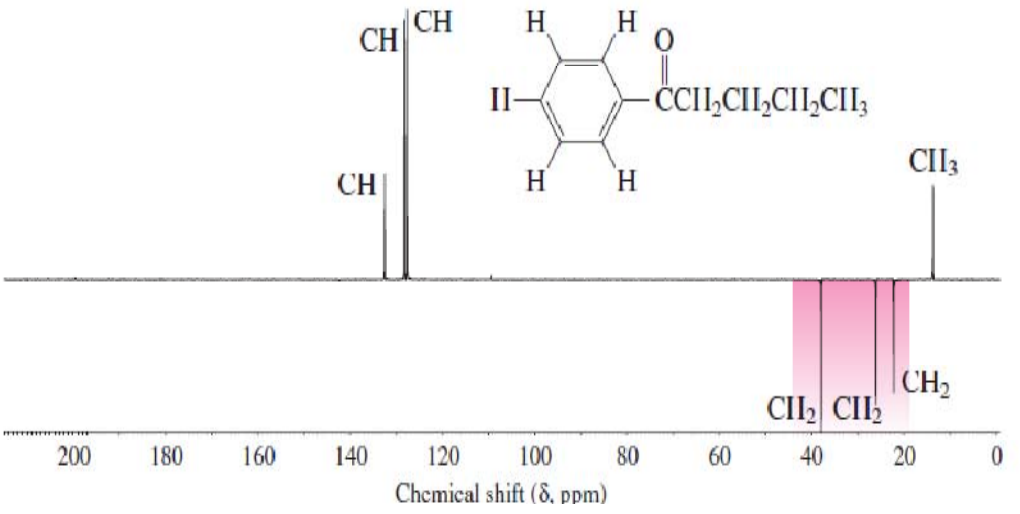
2 Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state

3 Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored

4 Mathematical manipulation (Fourier transform) of the data to plot a spectrum



(a)



(b)

Figure-5: ^{13}C NMR spectra of 1-phenyl-1-pentanone. (a) Normal spectrum. (b) DEPT spectrum recorded using a pulse sequence in which CH_3 and CH carbons appear as positive peaks, CH_2 carbons as negative peaks, and carbons without any attached hydrogens are nulled.

The pulse sequence (stages 2–3) can be repeated hundreds of times to enhance the signal-to- noise ratio. The duration of time for stage 2 is on the order of milliseconds, and that for stage 3 is about 1 second. Major advances in NMR have been made by using a second RF transmitter to irradiate the sample at some point during the sequence. There are several such techniques, of which we'll describe just one, called distortionless enhancement of polarization transfer, abbreviated as DEPT.

In the DEPT routine, a second transmitter excites $1H^1$, which affects the appearance of the 13C spectrum. A typical DEPT experiment is illustrated for the case of 1-phenyl-1-pentanone in Figure 13.26. In addition to the normal spectrum shown in Figure 13.26a, four more spectra are run using prescribed pulse sequences. In one (Figure 13.26b), the signals for carbons of CH_3 and CH groups appear normally, whereas those for CH_2 groups are inverted and those for C without any attached hydrogens are nulled. In the others (not shown) different pulse sequences produce combinations of normal, nulled, and inverted peaks that allow assignments to be made to the various types of carbons with confidence.

3.8 NOE in Carbon-13 NMR Spectroscopy

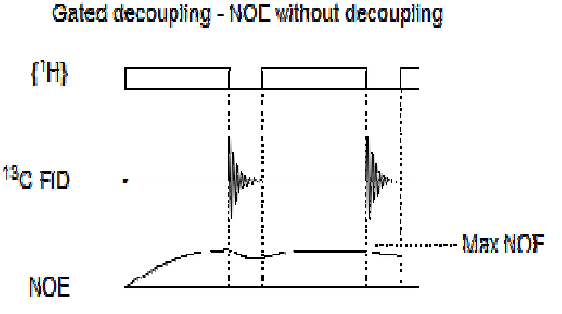
NOE is an interaction between a target nucleus and it's radiatively-saturated

neighbours. Spin is transferred from the target nucleus to its saturated neighbours, increasing the population of low-spin target nuclei. This increases the signal of the target nucleus. As a result, during a standard H-decoupled

experiment, 13C atoms attached to hydrogens show enhanced signals compared to quaternary C^{13} atoms.

Coupled C^{13} NMR Spectra with NOE

The measurement of undecoupled C^{13} NMR spectra is usually very time consuming since many of the carbon signals are split into complex multiplets, and there is no NOE enhancement of signal intensities. However, a nearly maximum NOE enhancement can be achieved by the use of gated decoupling, in which the decoupler is kept on during a delay period when the NOE enhancement builds up, but turned off during acquisition of the FID, so that fully coupled spectra are obtained. This works because the decoupling effect turns on and off nearly instantaneously (microseconds), whereas the NOE enhancement builds up and decays on the time scale of T1 (seconds).



3.8 Summery

The general phenomenon of nuclear magnetic resonance is introduced using both a classical and a quantum mechanical perspective. This provides the basis for understanding measurable and informative NMR parameters: chemical shift, spin-spin splitting, linewidths, relaxation, the nuclear Overhauser effect and chemical exchange. The emphasis here is on molecules in solution but much of the fundamentals pertain to molecules in the gas or solid phase as well.

Unit - 4 : X-ray diffraction technique

Structure of Unit:

4.0 Objective

X-ray diffraction technique is widely used for material analysis, which enables crystalline phase identification, which is important for characterization of crystalline materials such as metals, ceramics, cement and other materials.

4.1 Introduction

It is now over a centary since the phenomenon of x-radiation was discovered by Wilhelm Conrad Roengten. It was soon realized that x-rays have wavelengths in the angstrom range, are sufficiently energetic to penetrate solids, and are well poised to probe their internal structure. Based on these findings quite a few useful tools and techniques for materials analysis and evaluation have been developed and perfected for application. Among them, there are two major systems that are well known and

widely practised, one based on x-ray fluorescence for elemental analysis and another based on x-ray diffraction (XRD) for structural and phase composition studies.

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law

$$n\lambda = 2d \sin \theta$$

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this. X-ray diffraction technique is widely used for material analysis, which enables crystalline phase identification, which is important for characterization of crystalline materials such as metals, ceramics, cement and other materials.

In X-ray powder diffractometry, X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament within the tube, the higher the current the greater the number of electrons emitted from the filament.

A high voltage, typically 15-60 kilovolts, is applied within the tube. This high voltage

accelerates the electrons, which then hit a target, commonly made of copper. When these electrons hit the target, X-rays are produced. These X-rays are collimated and directed onto the sample. When an X-ray beam hits a sample and is diffracted, we can measure the distances between the planes of the atoms by applying Bragg's Law.

Peak positions in X-ray powder diffractogram occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this pattern called 'fingerprint' of the material.

To identify a substance, the powder diffraction pattern is recorded with the help of a diffractometer and a list of d-values and the relative intensities of the diffraction lines is prepared. These data are compared with the standard line patterns available for various compounds in the International Center Diffraction Data (ICDD) or formerly known as (JCPDS) Joint Committee on Powder Diffraction Standards. This organization maintains the data base of inorganic and organic spectra. This file is annually updated by the International Centre for Diffraction Data (ICDD). It contains line patterns of more than 60,000 different crystallographic phases. In practice, for any unknown sample, the appearance of three most intense characteristic lines from the standard PDF line pattern is a sufficiently convincing evidence of the existence of a crystalline phase in either a homogeneous substance or even in a multi component mixture.

Basic principle

X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament within the tube, the higher the current the greater the number of electrons emitted from the filament.

A high voltage, typically 15-60 kilovolts, is applied within the tube. This high voltage accelerates the electrons, which then hit a target, commonly made of copper. When these electrons hit the target, X-rays are produced. These X-rays are collimated and directed onto the sample. When an X-ray beam hits a sample and is diffracted, we can measure the distances between the planes of the atoms by applying Bragg's Law. Bragg's Law is denoted by

$$n\lambda = 2d \sin \theta$$

Where,

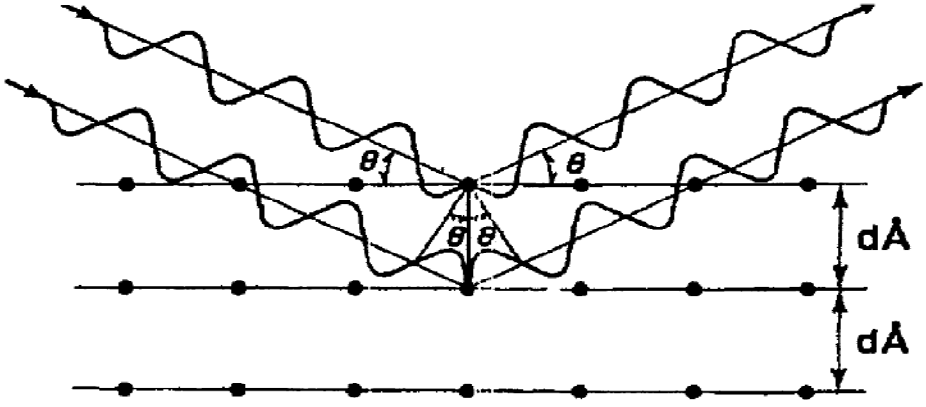
n =Integer called the order of reflection,

λ = Wavelength of x-rays,

d = Characteristic spacing between the crystal planes of a given specimen and

θ = Angle between the incident beam and the normal to the reflecting lattice plane.

If an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new Bragg law equation. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg law or equation. Because each crystalline material has a characteristic atomic structure, it will diffract X-rays in a unique characteristic pattern.



Peak positions in X-ray powder diffractogram occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this pattern called 'fingerprint' of the material.

Bragg's Law

W. L. Bragg presented a simple explanation of the diffracted beams from a crystal. Suppose that the incident waves are reflected specularly from parallel planes of atoms

in the crystal, with each plane reflecting only a very small fraction of the radiation, as with a very lightly silvered mirror. The diffracted beams are found only when the reflections from parallel planes of atoms interfere constructively, as in Fig. 4.2. We consider elastic scattering, so that the wavelength of the photon or neutron is not changed on reflection. The angle of incidence of the two parallel rays is θ. You can prove that the small angle in the little triangle is equal to θ by showing that the two right triangles, ABC and ACD, are similar. The interplanar spacing, d, sets the difference in path length for the ray scattered from the top plane and the ray scattered from the bottom plane. Figure-1 shows that this difference in path lengths is 2d sin θ. Constructive wave interference (and hence strong diffraction) occurs when the difference in path length for the top and bottom rays is equal to one wavelength, λ:

$n\lambda = 2d \sin\theta$……..*(1)*

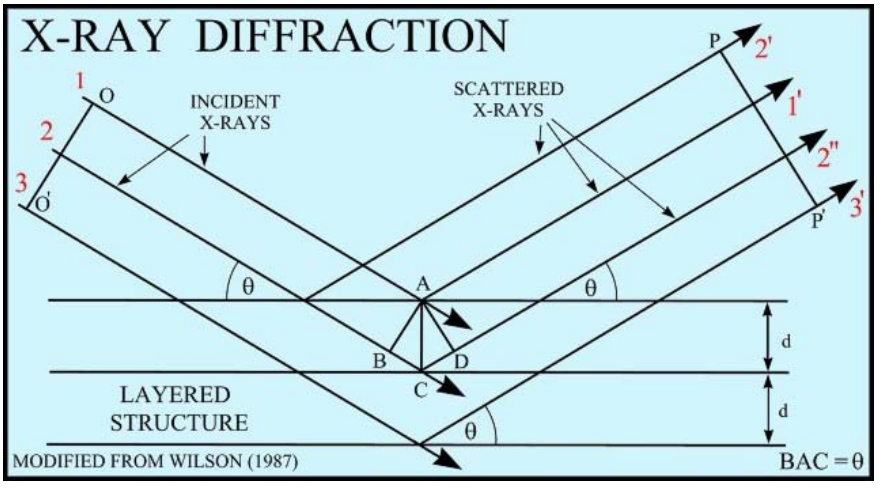
Where,

n =Integer called the order of reflection,

λ = Wavelength of x-rays,

d = Characteristic spacing between the crystal planes of a given specimen and

θ = Angle between the incident beam and the normal to the reflecting lattice plane.



The right hand side is sometimes multiplied by an integer, n, since this condition also provides constructive interference. Our convention, however, sets n = 1. When there is a path length difference of nλ between adjacent planes, we change d (even though this new d may not correspond to a real interatomic distance). For example, when our diffracting planes are (100) cube faces, and

$2\lambda = 2d100 \sin\theta$ ……..(2)

then we speak of a (200) diffraction from planes separated by d200 = (d100)/2. A diffraction pattern from a material typically contains many distinct peaks, each corresponding to a different interplanar spacing, d. For cubic crystals with lattice parameter α0, the interplanar spacings, dhkl , of planes labeled by Miller indices (hkl) are:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad \text{……..(3)}$$

We find that the (hkl) diffraction peak occurs at the measured angle 2θhkl :

$$2\theta_{hkl} = 2\arcsin\left(\frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2a_0}\right) \quad \text{……(4)}$$

There are often many individual crystals of random orientation in the sample, so all possible Bragg diffractions can be observed in the "powder pattern." There is a convention for labeling, or "indexing," the different Bragg peaks in a powder diffraction pattern using the numbers (hkl). An example of an indexed diffraction pattern is shown in Fig. 1.2. The intensities of the different diffraction peaks vary widely, and are zero for some combinations of h, k, and l. For this example of polycrystalline silicon, notice the absence of all combinations of h, k, and l that are mixtures of even and odd integers, and the absence of all even integer combinations whose sum is not divisible by 4.

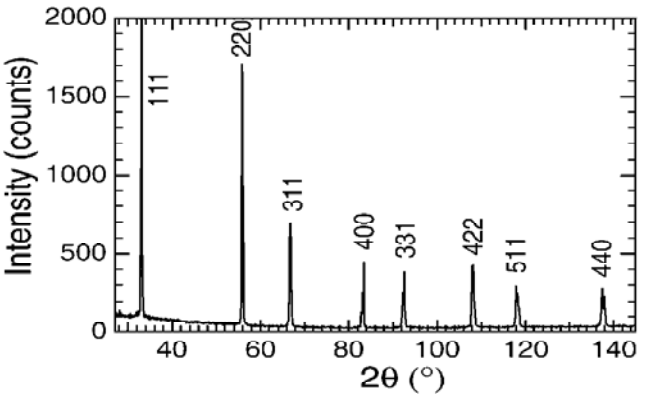


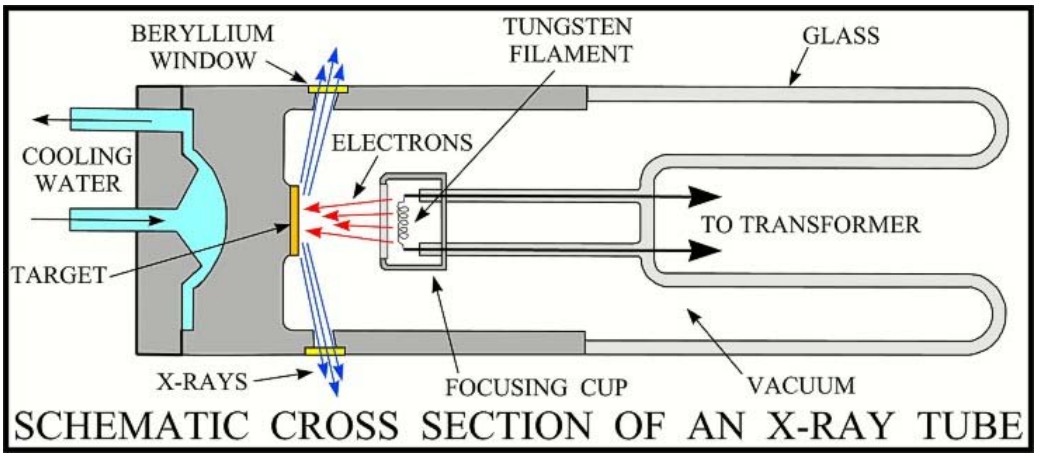
Fig. 1.2 Indexed powder diffraction pattern from polycrystalline silicon, obtained with Co Kα radiation.

One important use of x-ray powder diffractometry is for identifying unknown crystals in a sample. The idea is to match the positions and the intensities of the peaks in the observed diffraction pattern to a known pattern of peaks from a standard sample or from a calculation. There should be a one-to-one correspondence between the observed peaks and the indexed peaks in the candidate diffraction pattern. For a simple diffraction pattern as in Fig. 4.2, This tentative indexing still needs to be checked. To do so, the θ -angles of the diffraction peaks are obtained, and used with (1) to obtain the interplanar spacing for each diffraction peak. For cubic crystals it is then possible to use (3) to convert each interplanar spacing into a lattice parameter, $a0$. (Non-cubic crystals usually require an iterative refinement of lattice parameters and angles.) The indexing is consistent if all peaks provide the same lattice parameter(s).

4.2 Instrumentation for X-ray Powder Diffraction

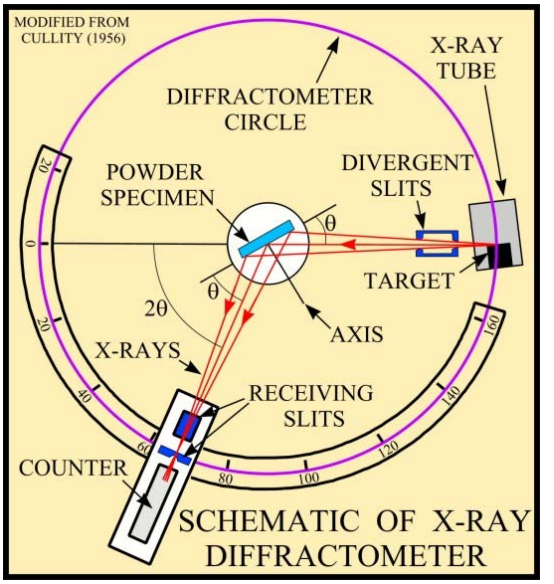
X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength. They are Schematic cross section of an x-ray tube. X-rays are produced when electrically charged particles of sufficient energy are deaccelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions. Tubes with copper targets, which produce their strongest characteristic radiation at a wavelength of about 1.5 angstroms, are commonly used for geological applications.

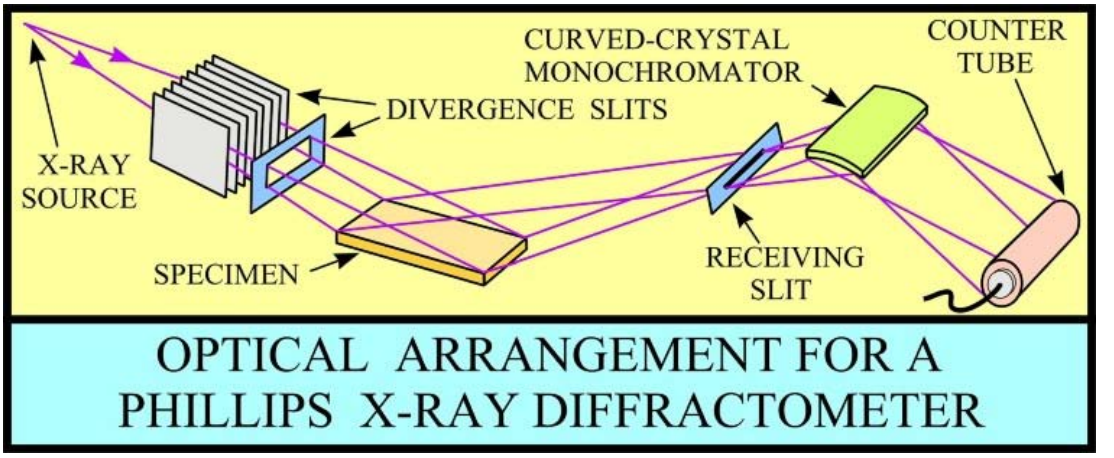
X-ray diffractometer consists: an X-ray tube, sample chamber, goniometer, and X-ray detector.



SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are then produced. It consists of an X-ray tube capable of producing a beam of monochromatic X-rays due to the decay of K to Ar involves the capture of an electron by the nucleus and the consequent emission of an X-ray photon that can be rotated to angles from 0^{o} to 90^{o}. A powdered sample is placed on a sample stage and can be irradiated by the X-ray tube. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube. The X-ray tube and the detector is called a goniometer. The goniometer keeps track of the angle θ, and when the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and intense peak occurs.





In a diffraction experiment, the incident waves must have wavelengths comparable to the spacings between atoms. Three types of waves have proved useful for these experiments. X-ray diffraction (XRD), conceived by von Laue and the Braggs, was the first. The oscillating electric field of an incident x-ray moves the atomic electrons and their accelerations generate an outgoing wave. In electron diffraction, originating with Davisson and Germer, the charge of the incident electron interacts with the positively-charged core of the atom, generating an outgoing electron wavefunction. In neutron diffraction, pioneered by Shull, the incident neutron wavefunction interacts with nuclei

or unpaired electron spins. These three diffraction processes involve very different physical mechanisms, so they often provide complementary

Information about atomic arrangements in materials.

4.2.2. Types of samples and sample preparation

Ideal diffraction experiments should provide clean low-background patterns with high resolution. A range of special experimental techniques exists to achieve this and each requires different methods of sample preparation. This is the non-trivial part of the process, because most polycrystalline substances may be altered during preparations. Texture (the preferred orientation of crystallites), amorphisation, defects, and even phase transformations may be introduced during the sample preparation. Nevertheless, methods exist to minimise the influence on the actual sample preparation. For characterisation of pharmaceuticals, the following types of samples may, by way of example, be prepared and submitted for analysis:

- Solid dosage form - tablets of different shapes, possibly with a protective layer.
- Powder pressed to the flat surface for surface analysis. Drawbacks include possible strong texture effects, possible influence from the milling process, and exposure of the sample to the atmosphere
- Powder or slurry in thin capillary for volume analysis. The sample is protected, texture is nearly absent, and quantity below 1mg is sufficient. The milling of aggregates may be required. Samples may be sealed at the customer site.
- Powder deposited as thin layer on a surface (can also be achieved through drying). Exhibits reduced texture and a small quantity is sufficient but the sample is unprotected
- Powder deposited as a loose layer of low density (20%-40% from bulk) . Exhibits reduced texture, but sample is unprotected
- Solid form split in a controlled manner to access the interior - very low sample influence. Drawbacks - possible texture, sample is unprotected

Applications of X-Ray Diffraction

4.3 Applications to Metallurgy and Metallography

1. The Composition and Structure of Alloys.

(a) Identification of alloy components and compounds.

This is a special case of the general problem of chemical analysis by x-ray diffraction, and is used routinely in many laboratories as a check on the results of other methods of examination.

(b) Differentiation between compound formation and solid solution.

This is also a special case of chemical analysis in which a compound formed between two or more elements will give rise to a new x-ray pattern which is different from that of any of the constituents, while the solid solution will in general give the pattern of one of the elements, but with a shift in line positions which depends upon the relative amounts of the other elements present in the solution,

(c) Routine determination of percentage composition of solid solution phases, on the basis of measurement of line shift with varying amounts of solute present.

(d) Determination of the mechanism of alloy formation.

This involves study of reflection and back reflection patterns of a series of alloys with various thermal treatments, and the correlation of the conclusions with chemical and microscopic data.

(e) Determination of miscibility limits and solid-phase boundaries of many-component alloy systems, by correlating lattice parameters with increasing percentage of alloying constituents.

(f) Working out and checking the details of the solidus phases of the equilibrium diagrams of binary and many-component alloy systems. X-ray diffraction analysis is the most convenient and dependable of the accepted modern methods for this purpose.

(g) The most rational classification of alloy types and systems has been made on the basis of x-ray crystal analysis.

(h) Study of the "order-disorder" phenomena in alloy systems.

2. The Effects of Rolling and Working on Metals and Alloys.

(a) Determination of structural changes accompanying successive reductions of sheet and wire, as a comparison of methods of reduction .by different techniques.

(b) Study of the effect of initial grain size, carbon content, initial strip thickness, and of rolling variables on the final structure of rolled strip steel in determining the proper scientific methods of working and forming.

(c) Determination of the effects of twisting and bending strip and wire.

(d) Measurement of the extent of deformation and distortion by rolling, drawing, shaping, etc., as a routine check on the efficacy of the manufacturing process.

(e) Determination of slip planes, "fiber" structure, etc., of rolled sheet and drawn wires.

(f) Differentiation between surface and interior structures,or study of "zonal" structural characteristics.

(g) Determination of the most desirable structure of a sheet or wire to be subjected to a forming operation, and a rational method of classifying metals as to workability. This method is used in many laboratories to "grade" every production lot. In this way the sheet mill can guarantee delivery of metal best suited to the manufacturer's shaping processes,

(h) Furnishes an explanation of structural failures in spinning, cupping, and stamping operations. "Trouble shooting" in regard to these operations is one of the best paying uses of x-ray crystal analysis in the metallographic laboratory.

(i) Measurement of the depth of cold work caused by machining, drilling, punching, grinding, etc.

(j) Study of the mechanism of "fatigue" and other types-of metal failures, and in many cases a determination of the cause for premature or unexpected failures.

3. The Effects of Annealing and Other Thermal Treatments on Metals.

(a) Establishment and routine maintenance of scientifically correct annealing techniques, and in many eases also for heat treating techniques.

(b) Study of recrystallization mechanism, and exact determination of recrystallization temperature.

(c) Study of precipitation and age hardening phenomena.

(d) Study of the relation of carbon content to annealing, and the relations between amount of reduction, time and temperature of anneal, and the final structure.

(e) Determination of quench and temper structures of spring steels, and a continuous check on hardening and tempering operations.

(f) Study of growth of texture in castings.

(g) Measurement of strain relief upon annealing.

(h) Determination of surface effects, such as decarburization, oxidation, excessive crystal growth, etc., as differentiated from interior structure.

4. Miscellaneous Applications to Metals.

(a) Determination of true "crystal size" as distinguished from microscopic 'grain size". This is a common and much used procedure in many factories.

(b) Determination of the structure of welds and the presence of strain or distortion in the neighborhood of the weld.

(c) Determination of the reason for and indication of the cure for "embrittlement" of malleable iron.

(d) Measurement of crystal size, crystal orientation, and absence of distortion (or degree of crystal perfection) in relation to electrical and magnetic properties of transformer steels.

(e) Determination of the effects of thermal treatments on the "spoilage" and recovery of permanent magnet alloys.

(f) Determination of uniformity, depth, and mechanism of surface hardening.

(g) Measurement of crystal size, preferred orientation, and thickness of electrodeposited films, a routine check on the plating process.

(h) Determination of the chemical composition of protective films, and study of mirrors and sputtered films.

(i) Study of the effects of included and absorbed or adsorbed gases on the structure of metals.

(j) Determination of optimum crystal size and best structure for electrical contact points, and a continuous check on these during manufacture.

(k) Study of the effects of crystal size and crystal orientation on electrical properties.

(1) Aid in the study of corrosion and corrosion or thermal "fatigue" and chemical embrittlement, and determination of the chemical composition of boiler scales.

(m) Furnishes a scientific approach to the preparation of new alloys, and a prediction of the properties of new or untried alloys.

(n) Study of the transition zone between base and covering of plated or enameled metals.

(o) Rational determination of the effects of minute impurities upon the structure of metals.

(p) Identification of inclusions in metals. This is a special case of chemical analysis by x-ray diffraction.

(q) An absolute and non-destructive measure of residual elastic surface stresses in metals. This is used quite extensively in several countries in the study of steel structures such as bridges and building frameworks.

(r) Determination of particle size in the colloidal region.

4.4 Applications in Chemistry

1. General and Physical Chemistry

(a) Determination of ultimate crystal structure, including lattice types, unit cell dimensions, atomic positions, ionic groupings,and crystallographic systems of substances.

(b) Furnishes a unique and unquestionable characterization of individual chemical compounds. This is the basis of the wide-spread use of x-ray

diffraction for chemical analysis. The analysis is, of course, made in terms of chemical compounds rather than in terms ofelements and ionic groupings.

(c) Differentiation between a mixture, solid solution or complex compound formation.

(d) Supplies a quantitative estimate of the relative amounts of the various compounds in a mixture. The estimate can be refined by the proper use of a recording microphotometer.

(e) Furnishes a certain test for the crystallinity or non-crystallinity of a material, either in the solid state or in solution.

(f) Determination of crystal sizes in the microscopic and sub-microscopic (colloidal) ranges.

(g) Study of allotropic modifications and transitions of an element or compound, and the effects of impurities on these.

(h) Determination of the ideal or theoretical density of a substance, giving a basis for the estimation of porosity.

(i) Differentiation between true and false hydrates.

(j) Discovery of unsuspected chemical reactions.

(k) Recognition of colloidally dispersed phases, and differentiation between true solutions and suspensions.

(1) Determination of crystal size and structure of colloidal sol and gels.

(m) Identification of adsorbed films and chemical changes involved in adsorption.

(n) Determination of optimum crystal sizes and orientations for maximum catalytic activity, and study of the mechanism of catalysis and "poisoning" of catalysts. This is used not only to find the best processes for preparing a catalyst but also as a routine test of production.

(o) Determination of molecular sizes in liquid solutions, and molecular weights of liquids.

(p) Determination of the mechanism and course of dry reactions and allotropic transformations in the solid state, even at extremely high or extremely low temperatures.

2. Organic Chemistry

The list given above for General and Physical Chemistry, and in addition furnishes:

(a) A sure test for the identity or non-identity of synthetic and naturally occurring materials.

(b) Estimation of molecular weights of hydrocarbons, etc.

(c) Measurement of atomic sizes, interatomic distance and diameters of molecules.

(d) A method of following chemical reactions, as for example addition to or oxidation of a multiple bond.

(e) Estimation of the purity of soaps, acids, etc.

(f) Estimation of the positions of side chains and functional groups.

(g) Measurement of the thickness of oriented films.

(h) Determination of molecular orientation in fibers, and molecular structure of naturally occurring fibers and membranes.

(i) A method of following polymerization and condensation reactions, and decomposition in breaking up long chain compounds.

(j) Study of lubrication and lubricants, including a routine method of quantitatively comparing efficiencies of lubricants.

(k) Study of changes taking place in the ripening of cheese, and during other processing of dairy products.

(1) A rational classification of synthetic and natural plastics, and a qualitative scheme for identification of these.

3. Analytical Chemistry.

In addition to the applications listed above, x-ray diffraction provides for:

(a) Identification of the chemical composition of precipitates.

(b) Tests for purity and identification of impurities in precipitates.

(c) Measurement of particle (crystal) sizes of precipitates in relation to treatment and reagent concentrations.

(d) Determination of the state of perfection of the crystal lattice in precipitates, particularly in regard to aging effects, etc.

4.5 Applications in the Process Industries

Since the process industries are engaged in chemical manufacture, the general applications listed under "chemistry" could be repeated here. To avoid duplication, however, only those applications of x-ray crystal analysis to some particular problems will be given.

1, Paints and Pigments.

(a) Structure and crystal sizes as functions of color, spreading, wetting and obscuring power, stability, gloss, and method of preparation.

(b) Study of the drying and setting of oils, the mechanisms of the reactions involved, etc., and their relationships to the structure and composition of pigments.

(c) Tests for solution of driers, and study of the mechanisms of their action.

(d) Routine analysis for purity of pigments. This is an important production test, particularly for those pigments which can exist in more than one crystal form, as for example titanium dioxide.

2, Ceramics and Glass.

(a) Routine qualitative and quantitative analysis of materials and clay mixtures, in terms of compounds present.

(b) Determination of the structural and chemical changes occurring during sintering, fusing, and other thermal treatments and the mechanisms of these reactions.

(c) Furnishes the best and fastest method for determining and checking the solidus phases of many component systems, and for determining miscibility limits.

(d) Gives a definite test for incipient devitrification of glass.

(e) Identification of substances imparting color or opacity to glasses or enamels.

(f) Determination of crystal size with relation to color of pigment.

(g) Study of transition zones between base metal and vitreous enamel.

(h) Measurement of chemical reaction rates in melt or during sintering.

3. Cement and Plaster.

(a) Study of reaction rates and mechanisms taking place during manufacture and use of cement.

(b) Routine chemical analysis of raw materials and clinker.

(c) Differentiation between particle size of aggregates and true crystal size.

(d) Method of determining and checking complex phase diagrams with certainty.

(e) Investigation of setting accelerators and their effects on the final structure of concrete.

(f) Control analysis of lime for crystal size, etc., to ensure proper plastic properties of plaster.

(g) Study of structure of limestone and its kiln behaviour in relation to the properties of the final product.

(h) Study of the dehydration of gypsum and the structural changes involved in the use and reuse of plaster of Paris molds.

4. Storage Batteries.

(a) Study of physical and chemical structure of plates as related to performance.

(b) Study of chemical reactions occurring during charge and discharge.

(c) Study of the influence of the structure of grid and composition and aging of the paste upon the physical properties of the plates, and control analysis for the manufacturing process.

(d) Identification of deposits and sediments on plates, separators, and in cell.

5. Rubber and Allied Products.

(a) Study of chemical reactions taking place during vulcanization and other processing.

(b) Determination of crystallinity, state of dispersions, crystal sizes of fillers, etc., and their relation to the physical characteristics of the finished products.

(c) Study of the basic structure of rubber and rubber-like materials. X-ray diffraction furnishes the only sure test of the fundamental relationships between natural and synthetic rubber.

(d) Study of fabrics and other binding materials used in the manufacture of rubber products, and routine grading of fibers as explained below.

6. Textiles and Fibers.

(a) Determination of the degree of fibering . A quantitative relationship between the degree of fibering and tensile strength of cotton fibers has been developed and is being used as a

routine method of grading cotton.

(b) Furnishes a scientific method of classifying cotton, silk, wool, and other natural and synthetic fibers.

(c) Determination of the rate, mechanism, and completeness of mercerization, nitration, and other chemical reactions, and use in control analysis.

(d) Determination of the mechanism of fire-proofing fibers, and of exact amount of reagent required.

(e) Identification of adsorbed films and the chemical changes involved in adsorption, particularly as applied to dyeing of fibers.

(f) Great improvements in quality, tensile strength, and non-wrinkling properties of rayon and other synthetic fibers has been made through x-ray studies. The development of artificial wool from skim milk, peanuts, beans, etc., can be traced directly to x-ray diffraction studies of the structures of the various proteins. The development of "nylon", the new synthetic silk, has depended to a great degree on x-ray studies of its fiber characteristics by x-ray diffraction.

(g) X-ray diffraction studies on collagen fibers (side walls of animal intestines, tendons, etc.) have resulted in enormous improvement in the quality and wearing properties of tennis racket strings, and in the strength and controlled digestibility of surgical ligatures and sutures.

4.6 **Applications in Mineralogy**

1. General Mineralogy.

(a) Complete and unambiguous mineralogical analysis of ores, clays, and other mineral mixtures.

(b) Analysis of industrial dusts, and correlation with the occurrence of industrial diseases.

(c) Classification and evaluation of certain commercial ores.

(d) Identification and classification of the clay minerals and complexes making up the so-called soil-colloid.

(e) A scientific method of studying the changes produced in natural minerals by weathering, accelerated weathering tests, and other chemical and physical degradations.

(f) Specifications for asbestos, mica, and other natural insulating materials for special purposes.

(g) Classification of coal, charcoal, etc.

2. Precious Stones and Gems.

(a) Identification, classification, and differentiation of genuine, both natural and synthetic, and imitation gems by a non-destructive test.

(b) Differentiation between natural and synthetic gems, nondestructively.

(c) Differentiation between natural and cultured pearls, non-destructively. This is a routine procedure with some of the leading jewelry manufacturers throughout the world.

(d) Determination of the proper orientation for a "jeweled" bearing (in watches, electric meters, etc.) to give maximum service and wearing qualities.

(e) Selection and classification of "black" diamonds for drills and dies, determination of causes for undue wear, and proper crystallographic orientations for optimum service.

(f) Determination of the proper direction of cutting quartz crystals for crystal oscillators in radio broadcasting and telephone equipment.

4.7 Applications in Physiology, Pathology, And Biology

1. The applications under this heading are quite recent developments and are not yet generally used. Listing of some, however, will serve to show the general trend and possibilities of x-ray diffraction research in these complex and difficult, but extremely important fields,

   (a) Differentiation between some normal and pathological tissues.

   (b) Study of the effects of diseases on the structures of tissues, as on bone structure changes in rickets, cancer of the bone, and other bone diseases.

   (c) Study of structure of living tissue, as nerve and muscle, in relation to body functions.

   (d) Identification and classification of mineral deposits in organs, such as calcifications, gall stones, siliceous deposits, etc. Much interest is evident at present in the study of the action of free quartz on lung tissue in silicosis, and of other industrial diseases and their occurrence, and many papers have been published in medical journals on x-ray diffractipn studies of silicotic lung tissue.

   (e) Structure and classification of tooth enamel, dentyne, etc., and structures of the teeth in relation to diet.

2. **Papers of interest to pharmacists have appeared recently on the following subjects:**

   (a) Identification of minerals in rhubarb.

   (b) Differentiation between natural and synthetic camphor.

   (c) Study of the reactions between menthol and the mercuric oxides.

4.8 Radiography

As stated at the outset, most of us are familiar with some form of radiography, at least medical radiography. Less familiar are the multitude of industrial applications. Objects for investigation by this non-destructive testing method may range in size from huge fromes or entire bridges to microtomic sections or flowers. Voltages vary from several million to a few thousand. The bulk of industrial radiographic inspections employ voltages between 30 kv and 440 kv. The x-ray laboratory has facilities for radiography from the very lowest voltages up to 150 k-v. This voltage range is suitable for most of the applications listed below, including microradiography. The maximum thickness that can be successfully radiographed with this equipment is about 25 gm/cm. This is equivalent to about inches of steel, or 31 inches of aluminum. The following listing is intended to be indicative only, and not by any means complete.

Typical radiographic investigations

1. Castings and forgings may be investigated for

   (a) inclusions

   (b) porosity

   (c) cracks

2. Welds may be investigated for

   (a) fusion and penetration

   (b) inclusions, porosity, and cracks

   (c) undercutting (burn-through)

   (d) crater cracks (skrinkage cracks)

3. Concealed assemblies may be investigated for

   (a) orientation and position of parts differing in density from the surrounding medium (e.g., metal in plastic, rubber, plaster, etc.)

   (b) location of channeling in objects such as engine blocks, water-cooled dies, walls, concrete construction, etc.

   (c) inspection of packages, overstuffed furniture, persons, auto tires, etc. for concealed contraband.

   (d) assembly line inspection for proper filling of containers.

4. Microradiography

This is a relatively new radiographic technique which is capable of yielding three dimensional information about samples less than 1/100 inch thick. Radiographs of very small specimens are taken with grainless film. The film is then enlarged to a usable size, thus giving an effective magnification similar to optical micrography. The technique has been of particular use in metallurgy.

5. Diffusion studies

This type of study is usually made by adding heavy atoms to the liquid whose diffusion rate is to be studied. Some examples of such studies are

(a) diffusion of preservative liquids into hams and other food stuffs.

(b) in biology and medicine, location of organs or regions where certain solutions tend to concentrate.

(c) diffusion along the veins of a great variety of veined materials, including leaves and flowers.

6. Low-voltage radiography is used for such things as

(a) radiography of paintings and documents to establish authenticity or reveal alterations.

(b) investigation of paper products. This technique shows the grain of the paper.

(c) investigation of glued joints for adhesion.

Unit - 5 : Solvent Extraction techniques

Structure of Unit:

5.0 Objectives

At the end of the unit learner will be able to

- What is solvent extraction
- Liquid-liquid extraction and formation of metal complexes
- Methods of extraction

- Techniques in extraction

5.1 Introduction and Principles of solvent extraction

Solvent extraction is also known as Liquid-liquid extraction. Liquid -liquid extraction consists in transferring one or more solute(s) contained in a feed solution to another immiscible liquid (solvent). The solvent that is enriched in solute(s) is called extract. The feed solution that is depleted in solute(s) is called raffinate.

Liquid–liquid extraction also known as partitioning and solvent extraction, is a method to separate compounds based on their relative solubility in two different immiscible liquids, usually used water and an organic solvent. It is an extraction of a substance from one liquid into another liquid phase. Liquid–liquid extraction is a basic technique, where it is performed using a separatory funnel. This type of process is commonly performed after a chemical reaction as part of the work-up.

The term solvent extraction can also refer to the separation of a substance from mixture by preferentially dissolving that substance in a suitable solvent. In that case, a soluble compound is separated from insoluble compound or a complex matrix. The term partitioning is commonly used to refer to underlying chemical and physical processes involved in liquid–liquid extraction but may be fully synonymous.

Solvent extraction is used in nuclear ore processing, reprocessing, the processing of perfumes, the production of fine organic compounds, the production of vegetable oils and biodiesel, and other industries.

Liquid–liquid extraction is possible in non-aqueous systems. In a system consisting of a molten metal in contact with molten salts and metals can be extracted from one phase to the other. This is related to a mercury electrode where a metal can be reduced and metal will often then dissolve in the mercury to form an amalgam that modifies its electrochemistry greatly. For example, the sodium cations to be reduced at a mercury cathode to form sodium amalgam, while at an inert electrode the sodium cations are not reduced. Instead, water is reduced to hydrogen. A detergent or fine solid can be used to stabilize an emulsion, or third phase.

Distribution ratio

In solvent extraction, distribution ratio is often as a measure of how well-extracted a species. The distribution ratio (D) is equal to the concentration of a solute in the organic phase divided by its concentration in the aqueous phase. Depending on the system, distribution ratio can be a function of the concentration of chemical species in the system, temperature, and a large number of other parameters.

The distribution ratio is also referred to as the partition coefficient, which is often expressed as the logarithm. Note that a distribution ratio for neptunium and uranium between two inorganic solids (perovskite and zirconolite) has been reported. In solvent extraction, two immiscible liquids are shaken together. The more polar solutes dissolve in the more polar solvent, and the less polar solutes in the less polar solvent. In this experiment, the nonpolar halogens preferentially dissolve in the nonpolar mineral oil.

Extraction of few common metals mentioned below-

The extraction methods for a range of metals include-

Cobalt (Co)– The extraction of cobalt from hydrochloric acid using alamine 336 in meta-xylene. Cobalt can be extracted also using Cyanex 272 {bis-(2,4,4-trimethylpentyl) phosphinic acid}.

Copper (Cu)– Copper can be extracted using hydroxyoximes as extractants, a recent paper describes an extractant that has a good selectivity for copper over nickel and cobalt.

Neodymium (Nd) – This rare earth is extracted by di(2-ethyl-hexyl)phosphoric acid into hexane by an ion exchange mechanism.

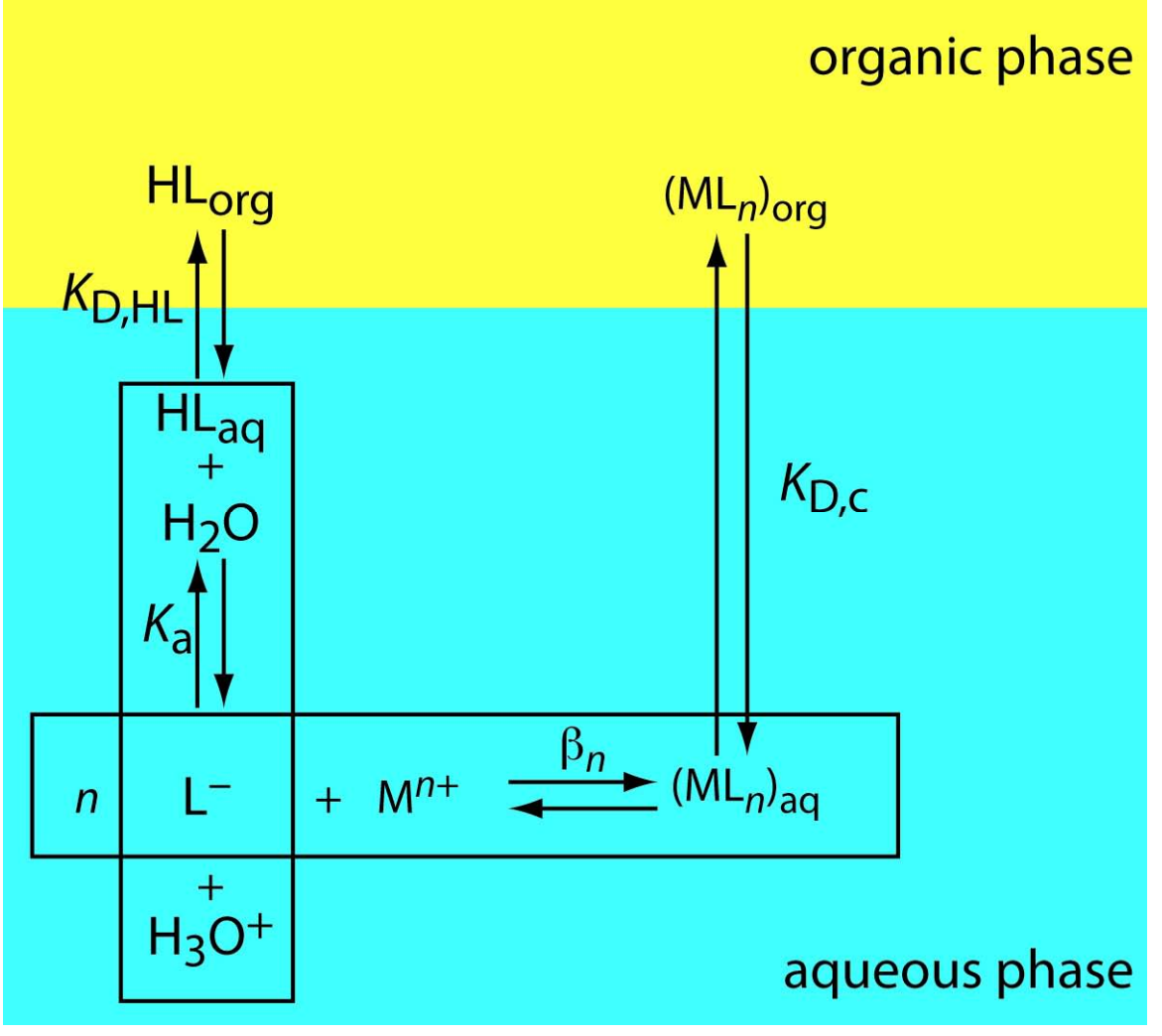
Nickel (Ni)– Nickel can be extracted using di(2-ethyl-hexyl)phosphoric acid and tributyl phosphate in a hydrocarbon diluent (Shellsol).

Palladium (Pd) and platinum (Pt) – Dialkyl sulfides, tributyl phosphate and alkyl amines have been used for extracting these metals.

5.2 Liquid-liquid extraction and formation of metal complexes

One important application of liquid–liquid extractions is the selective extraction of metal ions using ligand. Although, many ligands are not very soluble in water or

undergo hydrolysis or oxidation in aqueous solutions. For these reasons the ligand is added to the organic solvent instead of the aqueous solution. the relevant equilibria (and equilibrium constants) for the extraction of Mn+ by the ligand HL, including the ligand extraction into the aqueous phase ($K_{D,HL}$), the formation of the metal–ligand complex (βn), the ligand's acid dissociation reaction K_a, and the complex's extraction into the organic phase ($K_{D,c}$).

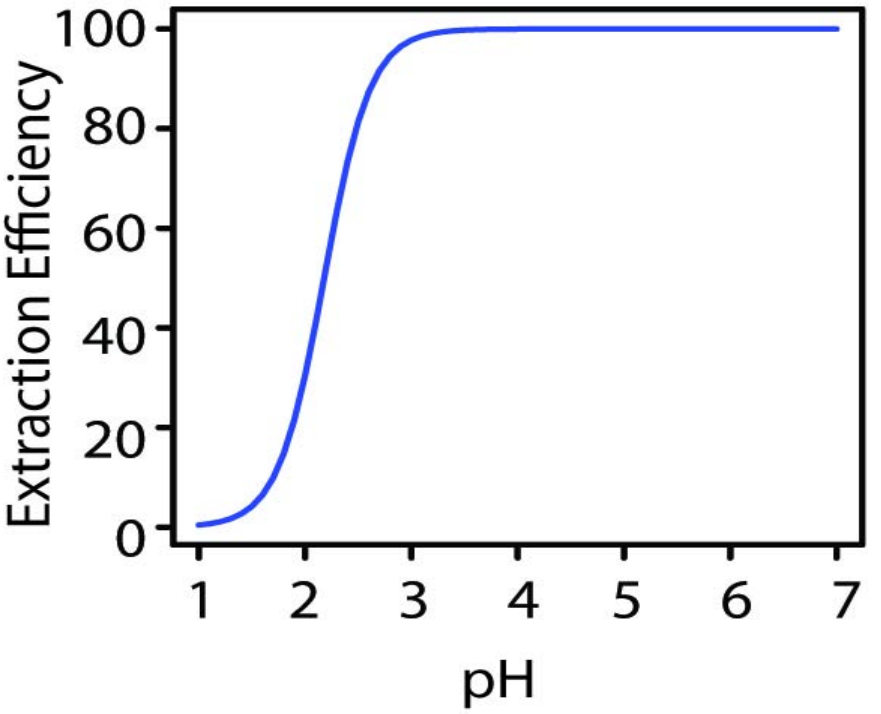


The liquid–liquid extraction of a metal ion, Mn+, by the ligand L–. The ligand initially is present in the organic phase as HL. Four equilibrium reactions are needed to explain the extraction efficiency.

The ligand's concentration is much greater than the metal ion's concentration, then the distribution ratio is

$$D = \frac{\beta_n K_{\mathrm{D,c}} (K_\mathrm{a})^n (C_\mathrm{HL})^n}{(K_{\mathrm{D,HL}})^n [\mathrm{H_3O^+}]^n + \beta_n (K_\mathrm{a})^n (C_\mathrm{HL})^n}$$

where C_{HL} is the ligand's initial concentration in the organic phase. the extraction efficiency for metal ions shows a marked pH dependency.



One advantage of using a ligand to extract a metal ion is the high degree of selectivity that it brings to a liquid–liquid extraction. Divalent metal ion's extraction efficiency increases from approximately 0% to 100% over a range of 2 pH units. Due to a ligand's ability to form a metal–ligand complex varies substantially from metal ion to metal ion, significant selectivity is possible by carefully controlling pH. The minimum pH for extracting is 99% of a metal ion from an aqueous solution using an equal volume of 4 mM concentration dithizone in CCl_4.

Types of inorganic extractable complexes

Most salts are strong electrolytes whose solubility in water can be attributed to the high dielectric constant of water which greatly reduced the work of dissociation and

solvating tendency of water since hydrated ions experience less inter ionic attraction and resemble more closely the medium in which they are dispersed. In fact, for a metal to form an extractable complex, it is necessary to remove of the water molecules associated with the metal ion. Complexing of metal ions leading to the formation of uncharged species falls into two main categories, one involving coordination and the other ion association.

Coordination complexes

A coordination complex, is formed by coordinate bonds in which a previously unshared pair of electrons on donor atom or ion is now shared with an acceptor atom or ion. Three types of coordination complexes are -

Monodentate or Simple complexes

In monodentate or simple complexes, central metal ion acting as acceptor having a coordination number "n", accepts 'n' pairs of electrons from 'n' individual donor groups, e.g.

$$Ge^{4+} + 4:Cl \rightarrow GeCl_4$$

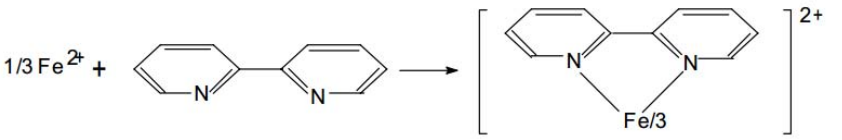
$$Fe^{3+} + 4:Cl \rightarrow FeCl_4^-$$

$$Cu^{2+} + 4:NH_3 \rightarrow Cu(NH_3)_4^{2+}$$

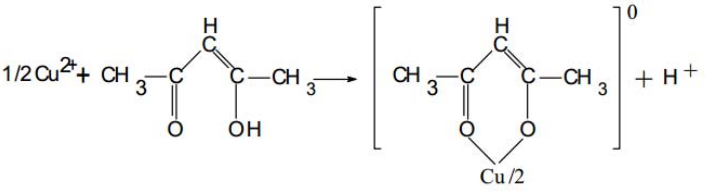
From the above examples, only the first one gives the neutral, extractable complex.

Polydentate Chelate or complexes

Polydentate or Chelate complexes with the central metal atom or ion having coordination number n, combines with not more than n/2 molecules of a specie having at least two donor atoms per molecule, these being so located as to permit the formation of a relatively strain free ring, e.g.



dipyridyl cationic



acetylacetone uncharged

Chelates have relatively large stability, so their formation greatly lowers the concentration of hydrated metal ion. Those chelating agents such as cupferron, dithizone, acetylacetone, and 8-quinolinol form uncharged, essentially covalent compounds, which are readily soluble in organic solvents. Chelating agents such as ethylene diamine tetra acid (EDTA) or dipyridyl which form charged chelates are useful as metal masking agents.

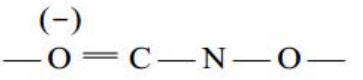
Metal Extraction Systems

Chelate Systems

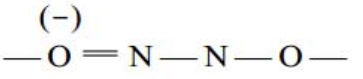
A. 4-Membered ring systems	***Reactive Grouping***
1. Dialkyl dithiocarbamates	$-\overset{(-)}{N}-C-S-$
2. Xanthates	$-\overset{(-)}{S}=C-S-$

B. *5-Membered ring systems*

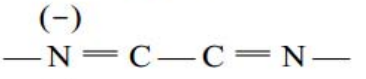
1. Benzoylphenylhydroxylamine



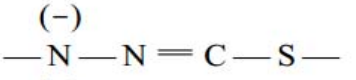
2. Cupferron



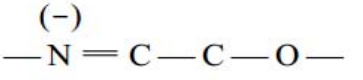
3. *a*-Dioximes



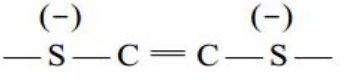
4. Dithizone



5. 8-Quinolinols

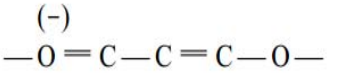


6. Toluene-3:4-dithiol



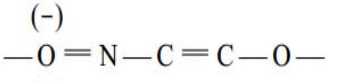
C. 6-*Membered ring systems*

1. β-Diketones and Hydroxycarbonyls

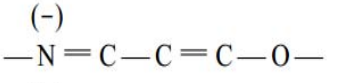


   a) Acetylacetone
   b) Thenoyltrifluoracetone
   c) Morin
   d) Quinalizarine

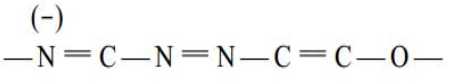
2. Nitrosonaphthols



3. Salicylaldoxime



1. Pyridyl-azo-naphthol (PAN)



Distribution Ratio (D)

The typical example of liquid-liquid extraction described here, the product was a fairly large organic molecule which you would predict to be not very soluble in water. Although, if the product were a lower molecular weight or "small" molecule, you should predict that it might be at least partially water-soluble. Therefore, it might not completely "move" into the organic layer, but also partially dissolve in the aqueous layer. Water-soluble organic materials, such as sugar or acetic acid, most of the solute will reside in the water phase. A quantitative measure of the how an organic

compound will distribute between aqueous and organic phases is called the partition or distribution coefficient. It is the ratio, K, of the solubility of solute dissolved in the organic layer to the solubility of material in the aqueous layer. (Note that K is independent of the actual amounts of the two solvents mixed.)

K= distribution coefficient

$$K = \frac{\text{solubility of organic (g/100 mL)}}{\text{solubility of water (g/100 mL)}}$$

The constant K, is essentially the ratio of the concentrations of the solute in the two different solvents once the system reaches equilibrium. At equilibrium the molecules naturally distribute themselves in the solvent. Inorganic and water soluble materials will stay in the water layer and more organic molecules will remain in the organic layer. By using the correct solvent, a molecule can be specifically selected and extracted from another solvent. The distribution coefficient is a ratio, unless K is very large, not all of a solute will reside in the organic layer in a single extraction. Usually the two, three, or four extractions of the aqueous layer with an organic solvent are carried out in sequence in order to remove as much of the desired product from the aqueous layer as possible. The effectiveness of multiple small volume extractions versus one large volume extraction can be demonstrated by a simple calculation. Example, one extraction can recover 90% of the compound. A second extraction with the same solvent may be able to pull out 90% of the remaining material. Effectively 99% of the compound was recovered with two extractions. One large extraction would have only obtained the initial 90%. Many smaller extractions are efficient than one large extraction. This phenomenon can be proved mathematically, but in short follows the equation-

$$\text{fraction extracted into B} = \left(\frac{1}{1 + \frac{V_B}{V_A n\, K}} \right)^n$$

The distribution of a solute between two immiscible solvents can be described by the distribution ratio “D”

$$D = \frac{[A]_1}{[A]_2}$$

Where, [A] represents the stoichiometric concentration of a substance A and the subscripts 1 and 2 refer to the two phases. Since in most cases, two-phase system is of analytical interest, an organic solvent and aqueous are involved.

A distribution coefficient plays a large role in the efficacy of a drug. In order for a drug to be absorbed into a brain cell, it must pass through what is called the blood-brain barrier, into the brain cell. The drug must have enough water solubility to dissolve in the blood. However, to pass through the cell wall which consists largely of water insoluble fatty lipids with solubility properties similar to an organic solvent, the drug must have a reasonable organic solvent solubility too. The cell membranes use the same fundamental solubility principles as the extraction process. The cell membrane consists of an ionic head and a very hydrophobic or nonpolar center.

The ionic head of the lipid orients itself in aqueous environments creating a very nonpolar interior. Ions such as K^+ and Ca^+ cannot traverse the interior of cell readily because the interior is very nonpolar and will not support these ions. Extraction uses this same partitioning effect to isolate organic compounds. Example, in the extraction process organic compounds will choose where to dwell according to the distribution coefficient. The synthetic drug design must take into account the importance of having a distribution coefficient that will allow transport in both aqueous blood and through organic membranes.

5.4 Quantitative treatment of extractable equilibria

Calculating Volumes and Extractions

Percent Extraction (E)

The more commonly used term for expressing the extraction efficiency by analytical chemist is the percent extraction “E”, which is related to “D” as

$$\% \text{ Extraction(E)} = \frac{100[\text{A}]_{\text{Org}} \text{V}_{\text{Org}}}{[\text{A}]_{\text{Org}} \text{V}_{\text{Org}} + [\text{A}]_{\text{Aq}} \text{V}_{\text{Aq}}} = \frac{100D}{D + V_{Aq}/V_{Org}}$$

Where, V represent solvent volume and the other quantities remain as previously defined.

The percent extraction may be seen to vary with the volume ratio of the two phases as well as with D. It may also be seen from equation that at extreme values of "D" and "E" becomes less sensitive to changes in "D". For example, at a phase volume ratio of unity, for any value of D below 0.001, the solute may be considered quantitatively retained in the aqueous phase whereas for D values from 500 to 1000, the value of "E" changes only from 99.5 to 99.9%.

Separation Factor (γ)

The solvent extraction is used for the separation of different elements and species from each other, it becomes necessary to introduce a term to describe the effectiveness of separation of two solutes. The separation factor γ is related to the individual distribution ratios as follows:

$$\gamma = \frac{[A]_{Org}/[B]_{Org}}{[A]_{Aq}/[B]_{Aq}} = \frac{[A]_{Org}/[A]_{Aq}}{[B]_{Org}/[B]_{Aq}} = \frac{D_A}{D_B}$$

Where, A and B represent the respective solutes.

In those systems, where one of the distribution ratios is small and the other relatively large, complete separations can be quickly and easily achieved. If the separation factor is large but the smaller distribution ratio is sufficiently large then less separation of both components occurs. It is then necessary to apply various techniques to suppress the extraction of the undesired components.

Distribution Law

In the simplest extraction cases, the distribution ratio is constant in accordance with the classical Nernst distribution law, which is a solute will distribute itself between two essentially immiscible solvents so that at equilibrium the ratio of the

concentrations of the solute in the two phases at a particular temperature will be constant, provided the solute is not involved in chemical interactions in either phase. For such a solute, then

$$K_d = \frac{[A]_{Org}}{[A]_{Aq}} = D$$

Where "K_d" is termed as the distribution coefficient.

Deviations from the distribution law arise from two sources: (i) neglect of activity corrections and (ii) participations of the distributing solute in chemical interactions in either or both of the two solvent phases. Although the distribution law, variation in K_d due to variation in activity coefficients is likely to be under one order of magnitude for most extraction systems of interest to analysts. The more important are the changes in extraction characteristics of solute because of chemical changes, which occur. Such changes do not represent failure of the law. Rather, they add complexity to the distribution expressions, which can be properly accounted for by using appropriate equilibrium expressions.

Distribution of acetic acid between benzene and water may serve as an illustration of the effects of chemical interactions of the solute. The distribution of acetic acid itself may be described as follows-

$$(CH_3COOH)_{Aq} \Leftrightarrow (CH_3COOH)_{Org}$$

$$K_D = \frac{[CH_3COOH]_{Org}}{[CH_3COOH]_{Aq}}$$

However, acetic acid dissociates in aqueous phase

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

$$K_A = \frac{[H^+][CH_3COO]^-}{[CH_3COOH]_W}$$

and forms a dimmer in benzene

$$2CH_3COOH \leftrightarrow (CH_3COOH)_2$$

$$K_P = \frac{[(CH_3COOH)_2]_O}{[CH_3COOH]_O^2}$$

The overall distribution of acetic acid is described by "*D*", which is

$$D = \frac{[CH_3COOH]_O}{[CH_3COOH]_W} = \frac{[CH_3COOH]_O + [(CH_3COOH)_2]^2{}_O}{[CH_3COOH]_W + [CH_3COO^-]}$$

from above equations we obtained

$$D = \frac{K_D[1 + 2K_P[CH_3COOH]_O]}{1 + K_A/[H^+]}$$

This shows how the distribution of acetic acid varies as a function of pH and acetic acid concentration.

5.5 Methods of extraction

The three essential aspects are involved in the extraction of acetic acid-

- Chemical interaction in the aqueous phase
- Distribution of extractable species
- Chemical interactions in the organic phase

These three aspects are shared by almost all extraction systems and serve as the basis of a useful organizational pattern

Chemical interactions in the aqueous phase

The major point of differentiation between extraction of inorganic and organic materials is the extent to which the formation of an uncharged extractable species depends on chemical interactions in the aqueous phase. Most organic compounds are

already extractable and uncharged. Such aqueous phase reactions if do occur might well transform these to charged non-extractable species, e.g

$$RCOOH + H_2O \leftrightarrow RCOO^- + H_3O^+$$

$$RNH_2 + H_2O \leftrightarrow R\overset{+}{N}H_3 + OH^-$$

In the contrast, most of the inorganic compounds are dissociated, so that in order to extract a species of interest into organic solvent, reactions in the aqueous phase leading to the formation of an uncharged, extractable complex must be utilized. Example, in order to extract Aluminum-III from an aqueous solution of aluminum nitrate, one must bring about the reaction of the Aluminum-III cation with a reagent such as 8-quinolinol to form aluminum-8-quinolinate, which may be extracted into a variety of organic solvents such as benzene or chloroform.

The formation of an uncharged complex is very important in the extraction of metals and other inorganic species that makes it convenient to classify such extractions according to the nature of the complexes.

Distribution of extractable species

The ratio of solubilities of a solute in each of two solvents may not be critically equated to the distribution coefficient of the solute between the two solvents the underlying factors affecting relative solubility and distribution are undoubtedly similar. Therefore, useful to discuss solubility characteristics of various types of substances and to note structural effects in both solvent and solute on the solubility. In solutions where specific chemical forces are not active, the classical principle of "like dissolves like" is of great help in predicting solubility. This principle may be expressed in terms as Hildebrand's theory of regular solutions from which, the solubility is seen to increase as values of the solubility parameter "δ" of solute and solvent approach each other. The solubility parameter, defined as square root of the heat of vaporization per milliliter, is a measure of cohesive energy density. The comparison of solubility parameters should be of maximum assistance of dealing with those organic extraction systems in which specific associative or chemical forces are inoperative. Burrell has successfully used solubility parameters to rationalize the

solubility behavior of various polymers.

In the systems, where hydrogen bonding may be present, particularly those involving an aqueous phase, the solubility parameter is inadequate in predicting solubility. This concept is, strictly speaking, applicable only in regular solutions. Collander has been able to observe regularities in distribution characteristics in systems involving the hydrogen bonding. On the basis of the determination of K_d values for two hundreds of the organic compounds in the ethyl ether-water system, it is noted that low K_d values were obtained for compounds having groups capable of hydrogen bonding, such as alcohol, amines, carboxylic acids, and acid amides.

Increasing molecular weight of the organic portion of the molecule would increase the K_d value about two to four times for each additional methylene group in homologous series. The effect to the oxygen in the molecule seemed to be about the same for ketones, aldehydes, alcohols, and carboxylic acids. Increase in K_d resulting the replacing carboxylic or alcoholic hydrogen with methyl group seemed to be little more than would be expected upon the increase in molecular weight. Increase the K_d were observed with the introduction of a halogen atom.

Solubility of the metal salts in aqueous media can be explained on the basis of two special properties of water. First, its high dielectric constant permits dissociation of ionic species relatively easily. Even the more important, the high basic character of water results in the solvation of cations and anions, which gives these ions a solvent sheath serving to reduce electrostatic interaction and to make the ions more "solvent-like". The role of complex forming extraction agent is largely to replace the coordinated water from around the metal ion to give a species that is more likely to be soluble in organic solvents. The solubility characteristics of metal chelates in the organic solvents in the general terms are not at all unlike those of conventional organic compounds. For the example, hydrocarbon substituents will increase the solubility of chelates in the organic solvents. Although neodymium chelate of cupferron-(I) is not soluble in chloroform where as the corresponding neocupferron (II) is soluble in chloroform

Among the ion association complexes, oxonium type is noteworthy, since in most cases solvent participates directly in complex formation. The ability of oxonium solvent to replace water from the coordination sphere of the metal would depend upon

basicity of solvent, which in turn would reflect the electron density and steric availability of electron pair in the oxygen of the solvent molecule. Many ion association extractions are aided by the use of salting-out agents, electrolytes used in high concentrations to;

(i) Produce a mass action effect by adding a common ion,

(ii) Reduce water activity greatly,

(iii) Lower the dielectric constant so as to favor ion-pair formation.

The use of salting-out agents in organic extractions is also well known.

Chemical interactions in organic phase

The chemical interactions of the extracted species in the organic phase would naturally lower its concentration in this phase and hence, improve extractability. In the case of a carboxylic acid extraction, organic solvents is one in which the acid dimerizes, this would result in a higher the D value than if the reaction does not occur. Ion association complexes, being dipoles, tend to form higher aggregates in the organic solvents at higher concentrations. Where there is a polymerization reaction of any type, the value of the D will be found to vary with the concentration of the extracted material.

5.6 Techniques in extraction

1. Batchwise single stage extractions

This is commonly used on small scale in chemical labs. It is normal to use a separating funnel. For instance, a chemist were to extract anisole from a mixture of the water and 5% acetic acid using the ether, then the anisole will enter the organic phase. The two phases would then be separated.

The acetic acid can then be removed from the organic phase by shaking the organic extract with sodium bicarbonate.

2. Multistage countercurrent continuous processes

The multistage countercurrent continuous processes are commonly used in industry for the processing of metals such as the lanthanides; because the separation factors between lanthanides are so small many extraction stages are needed. In multistage processes, the aqueous raffinate from one extraction unit is fed to the next unit as the

aqueous feed, while organic phase is moved in the opposite direction. Hence, even if the separation between two metals in each stage is small, the overall system can have a higher decontamination factor.

The multistage countercurrent arrays have been used for the separation of lanthanides. For the design of a good process, the distribution ratio should be not too high (>100) or too low (<0.1) in the extraction portion of process. It is often the case that the process will have a section for scrubbing unwanted metals from organic phase, and finally a stripping section to obtain the metal back from organic phase.

(i) Mixer-settlers

The battery of mixer-settlers counter currently interconnected. Each mixer-settler unit provides a single stage of the extraction. A mixer settler consists of a first stage that mixes the phases together followed by a quiescent settling stage that allows phases to separate by gravity.

In the multistage countercurrent process, multiple mixer settlers are installed with mixing and settling chambers located at alternating ends for each stage (since outlet of the settling sections feed the inlets of the adjacent stage's mixing sections). Mixer-settlers are used when a process requires longer residence times and when the solutions are easily separated by the gravity. They require a large facility footprint, but do not require much headspace, and need limited remote maintenance capability for the occasional replacement of the mixing motors.

(ii) Centrifugal extractors

The centrifugal extractors mix and separate in one unit. Two liquids will be intensively mixed between the spinning rotor and stationary housing at speeds up to 6000 RPM. This develops great surfaces for an ideal mass transfer from aqueous phase into the organic phase. At 200 – 2000 g both phases will be separated again. The centrifugal extractors minimize the solvent in the process, optimize the product load in the solvent and extract aqueous phase completely. The counter current and cross current extractions are easily established.

3. Extraction without chemical change

Some of the solutes such as noble gases can be extracted from one phase to another without the need for a chemical reaction. This is the simplest type of solvent

extraction. When a solvent is extracted, two immiscible liquids are shaken together. The more polar solutes dissolve preferentially in the more polar solvent, and less polar solutes in less polar solvent. Some solutes that do not at first sight appear to undergo a reaction during the extraction process do not have distribution ratio that is independent of the concentration. A classic example is the extraction of carboxylic acids (HA) into the non-polar media such as benzene. Here, it is often the case that the carboxylic acid will form a dimer in organic layer so the distribution ratio will change as a function of acid concentration.

4. Ion pair extraction

It is the possible by careful choice of counterion to extract a metal. For instance, if the nitrate concentration is high, it is possible to extract the americium as an the anionic nitrate complex if the mixture contains a lipophilic quaternary ammonium salt.

An example that is more likely to be encountered by 'average' chemist is the use of a phase transfer catalyst. This is a charged species that transfers another ion to organic phase. The ion reacts and then forms another ion, which is then transferred back to aqueous phase.

5. Aqueous two-phase extraction

The aqueous two-phase extraction, also known as two-phase liquid extraction, is a unique form of solvent extraction. In the aqueous two-phase extraction, compounds are still separated based on their solubility, but the two immiscible phases are both water based, an aqueous two phase system.

Aqueous two-phase extractions can have a number of the advantages over traditional solvent extraction. Solvents are often destructive to the proteins, making the traditional extraction impossible for purifying the proteins. In addition, the organic solvents can be flammable, and their use can cause both environmental and health concerns. Aqueous-two phase extractions do not require the solvents, and so avoid these concerns.

5.6 Summery

The chapter deals with the basic principle of Solvent Extraction, Liquid-liquid extraction and formation of metal complexes, Distribution of extractable species,

Quantitative treatment of extractable equilibria, Methods of extraction, Techniques in extraction and various types of equations used in solvent extraction.

5.7 Review Question

1. What is Solvent Extraction? Explain principle of chromatography.
2. Explain Liquid-liquid extraction and formation of metal complexes.
3. What is distribution of extractable species.
4. Explain Quantitative treatment of extractable equilibria.

5.8 Reference and Suggested readings

1. Modern Analytical Chemistry, by David Harvey, published by The McGraw-Hill Companies, 2000.

2. Handbook of solvent extraction, edited by Teh C. Lo, Malcolm H.I. Baird, Carl Hanson, Published 1983 by Wiley in New York .

Unit - 6 : Chromatography

Structure of Unit:

6.0 Objectives

At the end of the unit learner will be able to

- Familiar with chromatography.
- Learn the separation techniques.
- Understand about extraction chromatography.
- Increase knowledge about solvent extraction chromatography.
- Familiar with Chromatographic Extraction Systems.

6.1 Introduction

Most materials in our surroundings are mixtures of two or more components. Mixtures are either homogeneous or heterogeneous. Homogeneous mixtures are uniform in composition, but heterogeneous mixtures are not. Air is a homogeneous mixture and oil in water is a heterogeneous mixture. Homogeneous and heterogeneous mixtures can be separated into their components by several physical methods. The choice of separation techniques is based on the type of mixture and difference in the chemical properties of the constituents of a mixture.

Types of separation techniques

Various types of separation processes are:

- Crystallization
- Filtration
- Decantation
- Sublimation
- Evaporation
- Simple distillation
- Fractional distillation
- Chromatography

- Centrifugation
- Separating funnel
- Magnetic separation
- Precipitation

Let's discuss Chromatography separation techniques

6.2 **Chromatography:**

Chromatography is a separation technique used to separate the different components in a liquid mixture. It was introduced by a Russian Scientist Michael Tswett. Chromatography involves the sample being dissolved in a particular solvent called mobile phase. The mobile phase may be a gas or liquid. The mobile phase is then passed through another phase called stationary phase. The stationary phase may be a solid packed in a glass plate or a piece of chromatography paper.

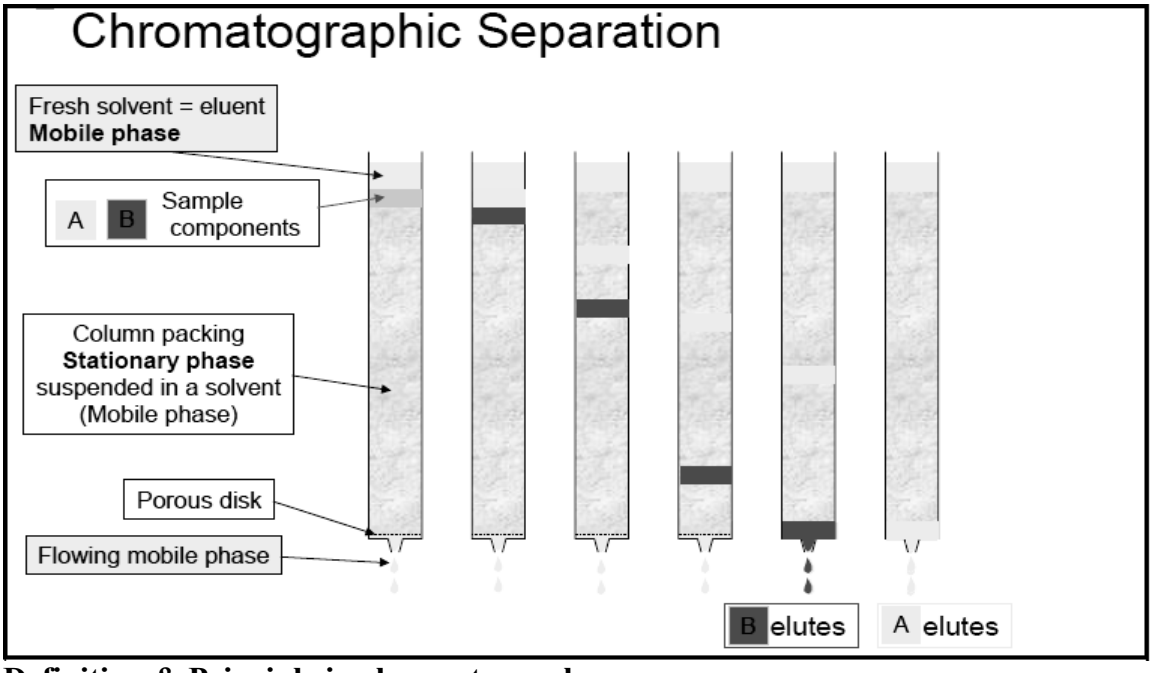
The various components of the mixture travel at different speeds, causing them to separate. There are different types of chromatographic techniques such as column chromatography, TLC, paper chromatography, and gas chromatography.

Paper chromatography is one of the important chromatographic methods. Paper chromatography uses paper as the stationary phase and a liquid solvent as the mobile phase. In paper chromatography, the sample is placed on a spot on the paper and the paper is carefully dipped into a solvent. The solvent rises up the paper due to capillary action and the components of the mixture rise up at different rates and thus are separated from one another.

Applications:

- To separate colors in a dye.
- To separate pigments from natural colors.

- To separate drugs from blood.

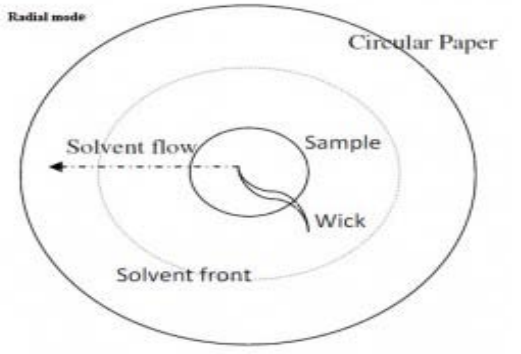


Definition & Principle in chromatography

It is defined as the process of separation of the individual components of a mixture based on their relative affinities towards stationary and mobile phases.

Principle: The samples are subjected to flow by mobile liquid onto or through the stable stationary phase. The sample components are separated into fractions based on their relative affinity towards the two phases during their travel.

The fraction with greater affinity to stationary layer travels slower and shorter distance while that with less affinity travels faster and longer.



Types of Chromatography:

Based on the technique employed in separation of components it is broadly classified as

1. **Adsorption based**: Here the stationary layer is a solid while the mobile phase is liquid. The compounds travel on the solid surface under the influence of mobile liquid. The separation depends on the extent of physical adsorption to the solid surface.
2. **Partition based**: In this mode both the stationary and mobile phase are liquids. So the compounds have affinity based on their partition coefficients into the individual liquid layer. The one with greater partition to mobile liquid has higher affinity to it so travels faster and vice versa.

   Based on the type of stationary material used for separation, it is of two types:

   a) **Normal phase:** Here the stationary material is polar in nature and hence the compounds with higher polarity elute out last while non polars come out first.

   b) **Reverse phase:** Here the stationary material is non-polar in nature and hence the compounds with lower polarity elute out last and vice-versa.

   In most HPLC analysis, the type used is reverse one as many of the biological, phytochemical compounds and drugs estimated by hplc are polar in nature.

Major components of Chromatographic separation:

Mobile phase flows through column, carries analyte.

Gas = Gas Chromatography (GC)

Liquid = Liquid Chromatography (LC), Thin Layer Chromatography (TLC)

Supercritical fluid = Supercritical Fluid Chromatography (SFC)

Stationary phase stays in a place, does not move.

 GC, LC placed inside of the column

 TLC – layer of a sorbent on the plate

6.3 Application of Chromatography

Chromatography is a powerful and versatile tool for separating closely related chemical species. In addition, it can be employed for the qualitative identification and quantitative determination of separated species.

Qualitative Analysis:

Chromatography is widely used for recognizing the presence or absence of components in mixtures that contain a limited number of species whose identities are known. For example, 30 or more amino acids in a protein hydrolysed can be detected with a reasonable degree of certainty by means of a chromatogram. On the other hand, because a chromatogram provides but a single piece of information about each species in a mixture (the retention time), the application of the technique to the qualitative analysis of complex samples of unknown composition is limited. This limitation has been largely overcome by linking chromatographic columns directly with ultraviolet, infrared, and mass spectrometers. The resulting *hyphenated* instruments are powerful tools for identifying the components of complex mixtures.

It is important to note that while a chromatogram may not lead to positive identification of the species in a sample, it often provides sure evidence of the absence of species. Thus, failure of a sample to produce a peak at the same retention time as a standard obtained under identical conditions is strong evidence that the compound in question is absent (or present at a concentration below the detection limit of the procedure).

Quantitative Analysis:

Chromatography owes its enonimous growth in part to its speed, simplicity, relatively low cost, and wide applicability as a tool for separations. However, it is doubtful that its use would have become so widespread had it not been for the fact that it can also provide quantitative information about separated species. Quantitative chromatography is based on a comparison of either the height or the

area of an analyte peak with that of one or more standards. If COD ditions are controlled properly, both of these parameters vary linearly with Concentration.

Analyses Based on Peak Height:

The height of a chromatographic peak is obtained by connecting the base lines on the two sides of the peak by a straight line and measuring the perpendicular distance from this line to the peak. This measurement can ordinarily be made with reasonably high precision and yields accurate results, provided variations in column conditions do not alter peak width during the period required to obtain chromatograms for sample and standards. The variables that must be controlled closely are column temperature, eluent flow rate, and rate of sample injection. In addition, care must be taken to avoid overloading the column. The effect of sample-injection rate is particularly critical for the early peaks of a chromatogram. Relative errors of 5% to 10% due to this cause are not unusual with syringe injection.

Analyses Based on Peak Area:

Peak area is independent of broadening effects caused by the variables mentioned in the previous paragraph. From this standpoint, therefore, area is a more satisfactory analytical parameter than peak height. On the other hand, peak heights are more easily measured and, for narrow peaks, more accurately determined. Most modern chromatographic instruments are equipped with electronic integrators that provide precise measurements of relative peak areas. If such equipment is not available, a manual estimate must be made. A simple method that works well for symmetric peaks of reasonable widths is to multiply peak height by the width at one-half peak height. Works well for symmetric peaks of reasonable widths is to multiply peak height by the width at one-half peak height.

Calibration with Standards:

The most straightforward method for quantitative chromatographic analyses involves the preparation of a series of standard solutions that approximate the

composition of the unknown. Chromatograms for the standards are then obtained, and peak heights or areas are plotted as a function of concentration. A plot of the data should yield a straight line passing through the origin; analyses are based on this plot. Frequent standardization is necessary for highest accuracy.

The Internal-Standard Method:

The highest precision for quantitative chromatography is obtained by using internal standards because the uncertainties introduced by sample injection, flow rate, and variations in column conditions are minimized. In this procedure, a carefully measured quantity of an internal-standard is introduced into each standard and sample, and the ratio of analyte peak area (or height) to internal-standard peak area (or height) is the analytical parameter. For this method to be successful, it is necessary that the internal-standard peak be well separated from the peaks of all other components in the sample, but it must appear close to the analyte peak. With a suitable internal standard, precisions of 0.5% to 1 % relative are reported.

6.4 Chromatographic Separation Techniques

Chromatographic separation techniques are multi-stage separation methods in which the components of a sample are distributed between 2 phases, one of which is stationary, while the other is mobile. The stationary phase may be a solid or a liquid supported on a solid or a gel. The stationary phase may be packed in a column, spread as a layer, or distributed as a film, etc. The mobile phase may be gaseous or liquid or supercritical fluid. The separation may be based on adsorption, mass distribution (partition), ion exchange, etc., or may be based on differences in the physico-chemical properties of the molecules such as size, mass, volume, etc. This chapter contains definitions and calculations of common parameters and generally applicable requirements for system suitability. Principles of separation, apparatus and methods are given in the following general methods:

— Paper chromatography

— Thin-layer chromatography

— Gas chromatography

— Liquid chromatography

— Size-exclusion chromatography

— Supercritical fluid chromatography

Chromatogram

A chromatogram is a graphical or other representation of detector response, effluent concentration or other quantity used as a measure of effluent concentration, versus time, volume or distance. Idealised chromatograms are represented as a sequence of gaussian peaks on a baseline.

Retention Data

Retention time and retention volume

Retention measurements in elution chromatography may be given as the retention time (t_R) directly defined by the position of the maximum of the peak in the chromatogram. From the retention time, the retention volume (V_R) may be calculated.

$$V_R = v \times t_R$$

t_R = retention time or distance along the baseline from the point of injection to the perpendicular dropped from the maximum of the peak corresponding to the component,

v = flow rate of the mobile phase.

Mass distribution ratio

The mass distribution ratio D_m (also known as the capacity factor *k'* or retention factor k) is defined as:

$$D_m = \frac{\text{amount of solute in stationary phase}}{\text{amount of solute in mobile phase}} = K_C \frac{V_S}{V_M}$$

K_C = equilibrium distribution coefficient (also known as distribution constant),

V_S = volume of the stationary phase,

V_M = volume of the mobile phase.

The mass distribution ratio of a component may be determined from the chromatogram using the expression:

$$D_m = \frac{t_R - t_M}{t_M}$$

t_R = retention time (or volume) or distance along the baseline from the point of injection to the perpendicular dropped from the maximum of the peak corresponding to the component,

t_M = hold-up time (or volume): time (or volume) or distance along the baseline from the point of injection to the perpendicular dropped from the maximum of the peak corresponding to an unretained component.

Distribution coefficient

The elution characteristics of a component in a particular column, in size-exclusion chromatography, may be given by the distribution coefficient K_o which is calculated from the expression:

$$K_o = \frac{t_R - t_o}{t_t - t_o}$$

t_R = retention time (or volume) or distance along the baseline from the point of injection to the perpendicular dropped from the maximum of the peak corresponding to the component,

t_o = hold-up time (or volume) : time (or volume) or distance along the baseline from the point of injection to the perpendicular dropped from the maximum of the peak corresponding to an unretained component,

t_t = retention time (or volume) or distance along the baseline from the point of injection to the perpendicular dropped from the maximum of the peak corresponding to a component which has full access to the pores of the stationary phase.

Retardation factor

The retardation factor (*RF*) (also known as retention factor *Rf*), used in planar chromatography, is the ratio of the distance from the point of application to the centre of the spot and the distance travelled by the solvent front from the point of application.

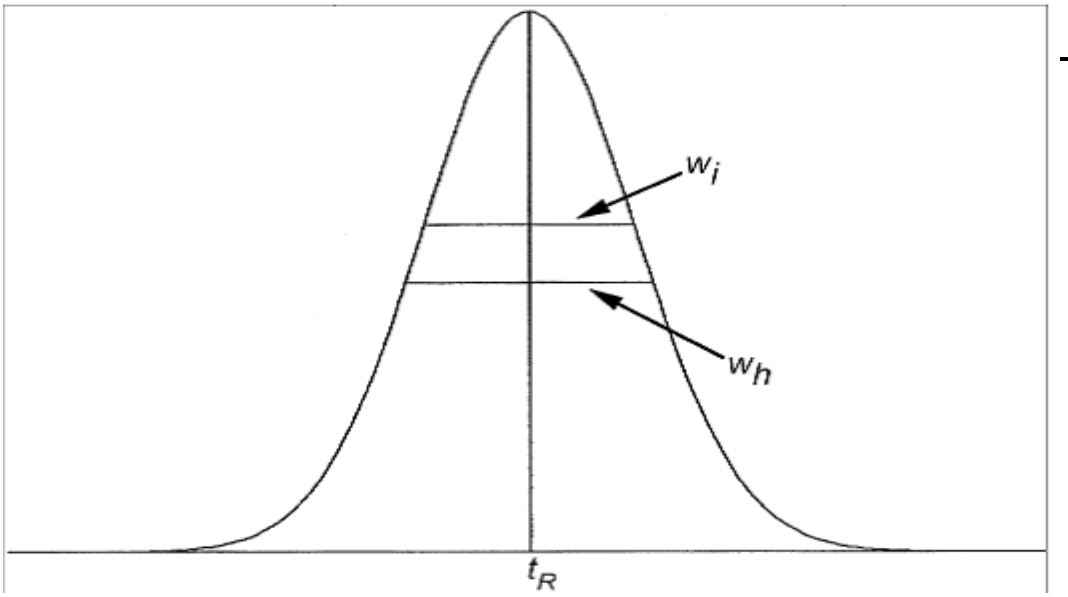
$$R_F = \frac{b}{a}$$

b = migration distance of the analyte,

a = migration distance of the solvent front.

Chromatographic Data

The peak may be defined by the *peak area (A)* or the *peak height (h)* and the *peak width at half- height* w_h or the *peak height (h)* and the *peak width between the points of inflection (wi)*. In gaussian peaks below Figure there is the relationship:



6.5 Extraction chromatogr

Extraction chromatography is a technique that combines the selectivity of solvent extraction with the ease of operation of column chromatogaphy. Extraction chromatography is ideally suited to laboratory-scale analysis of a wide range of metal ions present in environmental and bioassay samples. Eichrom Industries, Inc. manufactures and markets a number of resins specifically focused on facilitating the determination of the actinide elements and selective fission products. The selectivity of the Eichrom resins is based on exploiting the differences in the extraction of metal ion-nitrato complexes, on differences in charge density and steric effects, and on ionic recognition.

Solvent Extraction:

Although solvent extraction as a method of separation has long been known to the chemists, only in recent years it has achieved recognition among analysts as a powerful separation technique. Liquid-liquid extraction, mostly used in analysis, is a technique in which a solution is brought into contact with a second solvent, essentially immiscible with the first, in order to bring the transfer of one or more solutes into the second solvent. The separations that can be achieved by this method are simple, convenient and rapid to perform; they are clean as much as the small interfacial area certainly precludes any phenomena analogous to the undesirable co-precipitation encountered in precipitation separations.

Solvent extraction is one of the most extensively studied and most widely used techniques for the separation and pre-concentration of elements. The technique has become more useful in recent years due to the development of selective chelating agents for trace metal determination. With proper choice of extracting agents, this technique can achieve group separation or selective separation of trace elements with high efficiencies. In analytical applications solvent extraction may serve the following three purposes:

The procedure is applicable to both, trace and macro levels. A further advantage of solvent extraction method lies in the convenience of subsequent analysis of the extracted species. If the extracted species are coloured, as is the case with many chelates, spectrophotometric methods can be employed. Alternatively, the solution may be aspirated for atomic absorption or ICP-emission spectrometric analysis. If radiotracers are used, radioactive counting techniques can be employed. Before going in detailed discussion of fundamental principles of extraction, the three mostly used terms for expressing the effectiveness of extraction processes are being defined below. These terms are basic for understanding of theoretical as well as practical considerations of the subject.

Distribution Ratio (D)

The distribution of a solute between two immiscible solvents can be described by the distribution ratio "D".

$$D = [A]_1 / [A]_2$$

Where [A] represents the stoichiometric or formal concentration of a substance A and the subscripts 1 and 2 refer to the two phases. Since in most cases, two-phase system is of analytical interest, an organic solvent and aqueous are involved, *D* will be understood to be

$$D=[A]_{Org} / [A]_{Ag}$$

The subscripts org and Aq refer to the organic and aqueous phases respectively.

Percent Extraction (E)

The more commonly used term for expressing the extraction efficiency by analytical chemist is the percent extraction "*E"*, which is related to "*D" as*

$$\%\,\text{Extraction(E)} = \frac{100[\text{A}]_{\text{Org}} V_{\text{Org}}}{[\text{A}]_{\text{Org}} V_{\text{Org}} + [\text{A}]_{\text{Aq}} V_{\text{Aq}}} = \frac{100D}{D + V_{Aq}/V_{Org}}$$

Where V represent solvent volume and the other quantities remain as previously defined. The percent extraction may be seen to vary with the volume ratio of the two phases as well as with *D*.

It may also be seen from upper equation that at extreme values of "*D"*, "*E"* becomes less sensitive to changes in "*D"*. For example, at a phase volume ratio of unity, for any value of *D* below 0.001, the solute may be considered quantitatively retained in the aqueous phase whereas for D values from 500 to 1000, the value of "*E"* changes only from 99.5 to 99.9%.

Separation Factor (γ)

Since solvent extraction is used for the separation of different elements and species from each other, it becomes necessary to introduce a term to describe the effectiveness of separation of two solutes. The separation factor γ is related to the individual distribution ratios as follows:

$$\gamma = \frac{[A]_{Org}/[B]_{Org}}{[A]_{Aq}/[B]_{Aq}} = \frac{[A]_{Org}/[A]_{Aq}}{[B]_{Org}/[B]_{Aq}} = \frac{D_A}{D_B}$$

where A and B represent the respective solutes. In those systems where one of the distribution ratios is very small and the other relatively large, complete separations can be quickly and easily achieved. If the separation factor is large but the smaller distribution ratio is sufficiently large then less separation of both components occurs. It is then necessary to apply various techniques to suppress the extraction of the undesired component.

6.6 Extraction Systems

- **Types of inorganic extractable complexes-**

Most salts are strong electrolytes whose solubility in water can be attributed to the high dielectric constant of water which greatly reduced the work of dissociation and solvating tendency of water since hydrated ions experience less inter ionic attraction and resemble more closely the medium in which they are dispersed. In fact, for a metal to form an extractable complex, it is necessary to remove some or all of the water molecules associated with the metal ion. Complexing of metal ions leading to the formation of uncharged species falls into two main categories, one involving coordination and the other ion association.

- **Coordination complexes-**

A coordination complex, as the term implies, is formed by coordinate bonds in which a previously unshared pair of electrons on donor atom or ion is now shared with an acceptor atom or ion [80]. Three types of coordination complexes are of interest here:

(A) Simple or monodentate complexes

In simple or monodentate complexes, central metal ion acting as acceptor having a coordination number "n", accepts 'n' pairs of electrons from 'n' individual donor groups,

e.g.

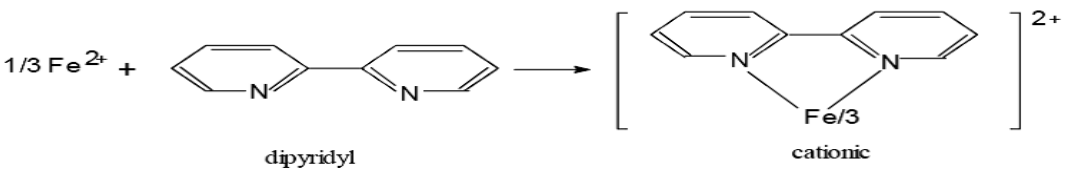
$$Ge^{4+} + 4{:}\,Cl \rightarrow GeCl_4$$

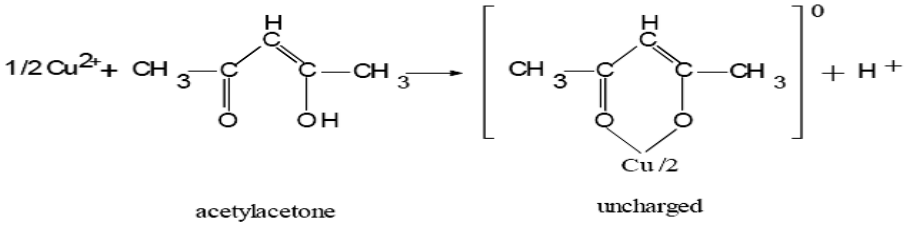
$$Fe^{+3} + 4{:}\,Cl \rightarrow FeCl_4^-$$

$$Cu^{+2} + 4{:}NH_3 \rightarrow Cu(NH_3)_4^{+2}$$

(B) Chelate or polydentate complexes:

Chelate or polydentate complexes [81] with the central metal atom or ion having coordination number n, combines with no more than n/2 molecules of a specie having at least two donor atoms per molecule; these being so located as to permit the formation of a relatively strain-free (i.e. , 5-6 membered) ring, e.g.





Chelates have relatively large stability constants, so their formation greatly lowers the concentration of hydrated metal ion. Those chelating agents such as acetyl acetone, cupferron, dithizone, and 8-quinolinol form uncharged, essentially covalent compounds, which are readily soluble in organic solvents. Chelating agents such as dipyridyl or ethylene diamine tetra acid (EDTA) which form charged chelates are useful as metal masking agents.

- **Ion association complexes**

Ion association complexes are uncharged species formed by the association of ions because of purely electrostatic attraction. The extent of such association increases sharply as the dielectric constant of the solvent decreases below 40 to 50. This condition not only exists in all of the commonly used organic solvents but also in highly concentrated aqueous solutions of strong electrolytes. Ion-pairs, which preferentially dissolve in the organic phase, are those, which resemble the solvent. Ion association complexes are capable of forming clusters larger than just pairs with increasing concentration, particularly in organic solvents. In some cases, aggregates large enough to be described as micelles are encountered.

Two categories of ion association complexes may be recognized. The first includes those ion-pair formed from a reagent having large organic ion such as tetraphenylarsonium ion, tri benzyl ammonium ion or per fluorobutyrate ion. These reagents combine with a suitable metal-containing ion to give a large

organic solvent-like ion-pair. The second type of ion-pair is essentially like that of the first with the exception that solvent molecules are directly involved in its formation. Thus in the extraction of uranyl nitrate with isobutyl alcohol, the extractable complex is probably $UO_2(BuOH)_6.(NO_3)^2$ in which the coordinated solvent molecules contribute both to the size of cation and the resemblance of the complex to the solvent [84]. Most of the solvents which participate directly in the formation of ion association complexes are containing oxygen. The term oxonium complex is used here to describe such a complex, since the solvent molecules from coordinate linkages to the metal atoms through their oxygen atoms.

Limitations of solvent extraction

- Third Phase formation.
- Need for phase-modifiers,
- Disposal of large volumes of extractants and diluents.
- Tedious multi-stage extraction procedures**.**

Advantages of Extraction Chromatography

• No third phase formation,

• No need for a modifier,

• Reusability of the synthesized resin,

• Simple and compact equipment,

• Minimal loss of organic solvent.

6.7 Summery

This Chapter increases the knowledge of chromatography, and this Chapter also explains brief about Chromatography is a powerful and versatile tool for separating closely related chemical species. In addition, it can be employed for the qualitative identification and quantitative determination of separated species.

6.8 Review Question

1. Define chromatography?
2. What is Solvent Extraction?
3. What are limitations of solvent extraction explain?
4. Define the Principle of chromatography?
5. Explain Chromatography is a powerful and versatile tool for separating closely related chemical species?

6.9 Reference and Suggested readings

1. Concise Inorganic chemistry- J.D. Lee (Blackwell Science) 2001
2. Inorganic Chemistry- F.A. Cotton (Interscience publisher) 2008

Unit - 7 : Types of chromatography and Applications

Structure of Unit:

7.0 Objective

At the end of the unit learner will be able to

- What is chromatography
- Different types of chromatography and related principles
- Liquid chromatography, types and its applications
- Solid chromatography, types and its applications

7.1 Introduction

Chromatography

Chromatography is the collective term for a set of laboratory techniques for the separation of mixtures. The mixture is dissolved in a fluid called the mobile phase, which carries it through a structure holding another material called the stationary phase. The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation.

Chromatography may be preparative or analytical. The purpose of preparative

chromatography is to separate the components of a mixture for more advanced use (and is thus a form of purification). Analytical chromatography is done normally with smaller amounts of material and is for measuring the relative proportions of analytes in a mixture.

Chromatography was first employed by Russian scientist Mikhail Tsvet in 1900. He continued to work with chromatography in the first decade of the 20th century, primarily for the separation of plant pigments such as chlorophyll, carotenes, and xanthophylls. Since these components have different colors (green, orange, and yellow, respectively) they gave the technique its name. New types of chromatography developed during the 1930s and 1940s made the technique useful for many separation processes.

7.3 Basic principles

All chromatographic methods require one static part (the stationary phase) and one moving part (the mobile phase). The techniques rely on one of the following phenomena:

- Adsorption Chromatography
- Partition Chromatography
- Ion exchange Chromatography
- Molecular exclusion Chromatography

Adsorption Chromatography

Adsorption chromatography was developed first. It has a solid stationary phase and a liquid or gaseous mobile phase. (Plant pigments were separated at the turn of the 20th century by using a calcium carbonate stationary phase and a liquid hydrocarbon mobile phase. The different solutes travelled different distances through the solid, carried along by the solvent.) Each solute has its own equilibrium between adsorption onto the surface of the solid and solubility in the solvent, the least soluble or best adsorbed ones travel more slowly. The result is a separation into bands containing different solutes. Liquid chromatography using a column containing silica gel or alumina is an example of adsorption chromatography. The solvent that is put into a column is called the eluent, and the liquid that flows out of the end of the column is

called the eluate.

Partition chromatography

In partition chromatography the stationary phase is a non-volatile liquid which is held as a thin layer (or film) on the surface of an inert solid. The mixture to be separated is carried by a gas or a liquid as the mobile phase. The solutes distribute themselves between the moving and the stationary phases, with the more soluble component in the mobile phase reaching the end of the chromatography column first. Paper chromatography is an example of partition chromatography.

Ion exchange chromatography

Ion exchange chromatography is similar to partition chromatography in that it has a coated solid as the stationary phase. The coating is referred to as a resin, and has ions (either cations or anions, depending on the resin) covalently bonded to it and ions of the opposite charge are electrostatically bound to the surface. When the mobile phase (always a liquid) is eluted through the resin the electrostatically bound ions are released as other ions are bonded preferentially. Domestic water softeners work on this principle.

Molecular exclusion chromatography

Molecular exclusion differs from other types of chromatography in that no equilibrium state is established between the solute and the stationary phase. Instead, the mixture passes as a gas or a liquid through a porous gel. The pore size is designed to allow the large solute particles to pass through uninhibited. The small particles, however, permeate the gel and are slowed down so the smaller the particles, the longer it takes for them to get through the column. Thus separation is according to particle size

Liquid Chromatography

Liquid chromatography is a technique used to separate a sample into its individual parts. This separation occurs based on the interactions of the sample with the mobile and stationary phases. Because there are many stationary/mobile phase combinations that can be employed when separating a mixture, there are several different types of chromatography that are classified based on the physical states of those phases. Liquid-solid column chromatography, the most popular chromatogrphy technique and the one discussed here, features a liquid mobile phase which slowly filters down

through the solid stationary phase, bringing the separated components with it.

History of Liquid Chromatography

The first known chromatography is traditionally attributed to Russian botanist Mikhail Tswett who used columns of calcium carbonate to separate plant compounds during his research of chlorophyll. This happened in the 20th century (1901). Furthur development of chromatography occurred when the Nobel Prize was awarded to Archer John Porter Martin and Richard Laurence Millington Synge in 1952. They were able to establish the basics of partition chromatography, and also develop Plate theory.

General Scheme

Components within a mixture are separated in a column based on each component's affinity for the mobile phase. So, if the components are of different polarities and a mobile phase of a distinct polarity is passed through the column, one component will migrate through the column faster than the other. Because molecules of the same compound will generally move in groups, the compounds are separated into distinct bands within the column. If the components being separated are colored, their corresponding bands can be seen. Otherwise as in high preformance liquid chromatography (HPLC).

Components

Chromatography is effective because different components within a mixture are attracted to the adsorbent surface of the stationary phase with varying degrees depending on each components polarity and its unique structural characteristics, and also its interaction with the mobile phase. The separation that is achieved using column chromatography is based on factors that are associated with the sample. So, a component that is more attracted to the stationary phase will migrate down the separating column at a slower rate than a component that has a higher affinity for the mobile phase. Also, the efficacy of the separation is dependent on the nature of the adsorbent solid used and the polarity of the mobile phase solvent.

Stationary Phase

The type of adsorbent material used as the stationary phase is vital for efficient separation of components in a mixture. Several different solid may be employed.

Adsorbent material can be chosen based on particle size and activity of the solid. The activity of the adsorbent is represented by its activity grade, which is a measure of an adsorbent's attraction for solutes in the sample solution. The solids with the highest activity grading are those that are completely anhydrous. Silica gel and alumina are among the most popular adsorbents used. Alumina caters well to samples that that require specific conditions to adequately separate. However, the use of non-neutral stationary phases should be done with great caution, an increase or decrease of pH in the alumina stationary phase may allow chemical reactions within the components of the mixture. Silica gel, however, is less active than alumina and can generally be used as an all-around adsorbent for most components in solution. Silica is also preferred because of its high sample capacity, making it one of the most popular adsorbent materials.

Mobile Phase

The proper mobile phase must also be chosen for the best separation of the conmponents in an unknown mixture. This eluent will be chosen based on its polarity relative to the sample and the stationary phase. With a strong polar adsorbent stationary phase like alumina, a polar solvent used as the mobile phase will be adsorbed by the stationary phase, which may displace molecules of sample in the mixture and may cause the sample components to elute very quickly. This will provide little separation of the sample, so it is best to start elution with a solvent of lower polarity to elute the components that are weakly adsorbed to the stationary phase first. The solvent may also be changed during separation in order to change the polarity and therefore elute the various components separately in a more timely manner. This method is very similar to the gradient method of separation used in High Performance Liquid Chromatography (HPLC).

7.4 Types of Chromatography

Normal Phase Chromatography

The components in a mixture will elute at different rates depending on each one's polarity relative to the next. When the column to be used for the separation is more polar than the mobile phase, the experiment is said to be a normal phase method. In normal phase chromatography, the stationary phase is polar, and so the more polar

solutes being separated will adhere more to the stationary adsorbent phase. When the solvent or gradient of solvents is passed through the column, the less polar components will be eluted faster than the more polar ones. The components can then be collected separately, assuming adequate separation was achieved, in order of increasing polarity. This method of chromatography is not unique to liquid-solid column chromatography and is often used when performing High Performance Liquid Chromatography (HPLC). Although HPLC is an example of liquid-liquid chromatography, in which both the stationary and mobile phases are liquid, normal phase elution is achieved by coating the solid adsorbent column with a polar liquid.

Reverse Phase Chromatography

In reverse phase chromatography, the polarities of the mobile and stationary phases are opposite to what they were when performing normal phase chromatography. Instead of choosing a non-polar mobile phase solvent, a polar solvent wil be chosen. Or, if the experiment requires a solvent polarity gradient, the gradient must be carried out with the most polar solvent first and the least polar solvent last (reverse order of normal phase chromatography). Common polar solvents mixtures of solvents include water, methanol, and acetonitrile. It is slightly more difficult and expensive to obtain a column where the stationary phase is non polar, as all solid adsorbents are polar by nature. The non polar stationary phase can be prepared by coating silanized silica gel with a non polar liquid. Silanizing the silica gel reduces the silica gel's ability to adsorb polar molecules. Common non polar liquid phases include silicone and various hydrocarbons. An alternative to this type of column is used in HPLC, in which a bonded liquid phase is used as the stationary phase. The less polar liquid is chemically bonded to the polar silica gel in the column. So using reverse phase, the most polar compounds in the sample solution will be eluted first, with the components following having decreasing polarities.

Flash Chromatography

Because the elution rate of the mobile phase in regular column chromatography as described above is controlled primarily by gravity, chromatographic runs can potentially take a very long time to complete. Flash chromatography is a modified method of column chromatography in which the mobile phase moves faster through the column with the help of either pressurized air or a vacuum. A vacuum line is

attached to the bottom of the separating column, this pulls the mobile phase solvent, and the components in the mobile phase, through the column at a faster rate than gravity does. A figure of this set-up can be seen in the links section. Flash chromatography is powered by compressed air or air pumps works by pushing the mobile phase through the column and achieves faster flow rates of the mobile phase just as vacuum facilitated flash chromatography does. For this method, a pressurized air line is attached to the top of the separating column. It is for this reason that flash chromatography is also referred to as medium pressure chromatography. An inert gas is used as to not interact with the mobile or stationary phase or the component mixture. Nitrogen gas is commonly used for this method of chromatography. Many instruments are available to perform flash chromatography as efficiently as possible: expensive columns, pumps, and flow controllers. This maintains a constant and precise air pressure or vacuum to the column in order to obtain steady flow rate of the mobile phase and favorable separation of the samples in solution.

7.5 Other Varieties of Liquid Chromatography

Partition Chromatography

In this method, both the stationary phase and the mobile phase are liquid. The stationary phase liquid would be an immiscible liquid with the mobile phase.

Liquid-Solid Chromatography

This method is similar to partition chromatography only that the stationary phase has been replaced with a bonded rigid silica or silica based component onto the inside of the column. Sometimes the stationary phase may be alumina. The analytes that are in the mobile phase that have an affinity for the stationary phase will be adsorbed onto it and those that do not will pass through having shorter retention times. Both normal and reverse phases of this method are applicable.

7.6 Ion Exchange or Ion Chromatography

This is a type of chromatography that is applied to separate and determine ions on columns that have a low ion exchange capacity. This is based on the equilibria of ion exchange between the ions in solution and the counter ions to pair with the oppositely charged ions that are fixed to the stationary phase. This sttionary phase would either

have positive of negative functional groups affixed to it, usually sulfonate ($-SO_3^-$) or a quaternary amine ($-N(CH_3)_3^+$), being a cation and anion exchanger respectively.

Size Exclusion Chromatography

Size exclusion chromatography separates molecules by their size. This is done by having the stationary phase be packed with small particles of silica or polymer to form uniform pores. The smaller molecules will get trapped in the silica particles and will elute from the column at a rate that is greater than that of larger molecules. Thus, the retention time depends on the size of the molecules. Larger molecules will be swept away in the mobile phase, therefore having a smaller retention time. Also notice that in this type of chromatography there isn't any interaction, being physical or chemical, between the analyte and the stationary phase.

Affinity Chromatography

This type of chromatography involves binding a reagent to the analyte molecules in a sample. After the binding, only the molecules that have this ligand are retained in the column, the unbound analyte is passed through in the mobile phase. The stationary phase is usually agrose or a porous glass bead that is able to immobilize the bonded molecule. It is possible to change the elution conditions by manipulating the pH or the ionic strength of the binding ligand. This method is often used in biochemistry in the purification of proteins. The ligand tag is bonded and after separation the tag is then removed and the and the pure protein is obtained.

Chiral Chromatography

Chiral chromatography enables the use of liquid chromatography to separate a racemic mixture into its enantiomeric parts. A chiral additive can be added to the mobile phase, or a stationary phase that has chiral properties can be used. A chiral stationary phase is the most popular option. The stationary phase has to be chiral in order to recognize the chirality of the analyte, this will create attractive forces between the bonds and also form inclusion complexes.

Advantages / Disadvantages

Liquid-solid column chromatography is an effective separation technique when all

appropriate parameters and equipment are used. This method is especially effective when the compounds within the mixture are colored, as this gives the scientist the ability to see the separation of the bands for the components in the sample solution. Even if the bands are not visible, certain components can be observed by other visualization methods. One method that may work for some compounds is irradiation with ultraviolet light. This makes it relatively easy to collect samples one after another. However, if the components within the solution are not visible by any of these methods, it can be difficult to determine the efficacy of the separation that was performed. In this case, separate collections from the column are taken at specified time intervals. Since the human eye is the primary detector for this procedure, it is most effective when the bands of the distinct compounds are visible.

Liquid-solid column chromatography is also a less expensive procedure than other methods of separation (HPLC, GC, etc.). This is because the most basic forms of column chromatography do not require the help of expensive machinery like high pressure solvent pumps used in HPLC. In methods besides flash chromatography, the flow of the mobile phase, the detection of each separation band, and the collection of each component, are all done manually by the scientist. Although this introduces many potential instances of experimental error, this method of separation can be very effective when done correctly. Also, the glass wear used for liquid-solid column chromatography is relatively inexpensive and readily available in many laboratories. Burette are commonly used as the separating column, which in many cases will work just as well as an expensive pre-prepared column. For smaller scale chromatography, Pasteur pipettes are often used.

Flash chromatography has the potential to be more costly than the previous methods of separation, especially when sophisticated air pumps and vacuum pumps are needed. When these pieces of machinery are not needed, however, a vacuum line can be instead connected to an aspirator on a water faucet. Also, home-made pressurized air flow controllers can be made as shown previously.

7.7 High performance liquid chromatography

High Performance Liquid Chromatography (HPLC) is an analytical technique used for the separation of compounds soluble in a particular solvent.

History of HPLC

Liquid chromatography was initially discovered as an analytical technique in the early twentieth century and was first used as a method of separating colored compounds. This is where the name chromatography chroma means color, graphy means writing, was derived. A Russian botanist named Mikhail S. Tswett used a rudimentary form of chromatographic separation to purify mixtures of plant pigments into the pure constituents. He separated the pigments based on their interaction with a stationary phase, which is essential to any chromatographic separation. The stationary phase he used was powdered chalk and alumina, the mobile phase in his separation was the solvent. After the solid stationary phase was packed into a glass column (essentially a long, hollow, glass tube) he poured the mixture of plant pigments and solvent in the top of the column. He then poured additional solvent into the column until the samples were eluted at the bottom of the column. The result of this process most crucial to his investigation was that the plant pigments separated into bands of pure components as they passed through the stationary phase. Modern high performance liquid chromatography or HPLC has its roots in this separation, the first form of liquid chromatography. The chromatographic process has been significantly improved over the last hundred years, yielding greater separation efficiency, versatility and speed.

Affinities for Mobile and Stationary Phases

All chromatographic separations, including HPLC operate under the same basic principle; every compound interacts with other chemical species in a characteristic manner. Chromatography separates a sample into its constituent parts because of the difference in the relative affinities of different molecules for the mobile phase and the stationary phase used in the separation.

7.8 Retention Factor

Since K_c is a factor that is wholly dependent on a particular column and solvent flow rate, a quantitative measure of the affinity of a compound for a particular set of mobile and stationary phases that does not depend on the column geometry is useful. The retention factor, k, can be derived from K_c and is independent of the column size and the solvent flow rate.

$k_C = K_C V_S / V_M$

The retention factor is calculated by multiplying the distribution constant by the volume of stationary phase in the column and dividing by the volume of mobile phase in the column.

Instrumentation

Apparatus

Specialized apparatus is required for an HPLC separation because of the high pressures and low tolerances under which the separation occurs. If the results are to be reproducible, then the conditions of the separation must also be reproducible. Thus HPLC equipment must be of high quality; it is therefore expensive.

Solvent

The mobile phase, or solvent, in HPLC is usually a mixture of polar and non-polar liquid components whose respective concentrations are varied depending on the composition of the sample. As the solvent is passed through a very narrow bore column, any contaminants could at worst plug the column, or at the very least add variability to the retention times during repeated different trials. Therefore HPLC solvent must be kept free of dissolved gases, which could come out of solution mid-separation, and particulates.

Column

In the HPLC column, the components of the sample separate based on their differing interactions with the column packing. If a species interacts more strongly with the stationary phase in the column, it will spend more time adsorbed to the column's adsorbent and will therefore have a greater retention time. Columns can be packed with solids such as silica or alumina; these columns are called homogeneous columns. If stationary phase in the column is a liquid, the column is deemed a bonded column. Bonded columns contain a liquid stationary phase bonded to a solid support, which is again usually silica or alumina. The value of the constant C described in the van Demeter equation is proportional, in HPLC, to the diameter of the particles that constitute the column's packing material.

Pump

The HPLC pump drives the solvent and sample through the column. To reduce

variation in the elution, the pump must maintain a constant, pulse free, flow rate; this is achieved with multi-piston pumps. The presence of two pistons allows the flow rate to be controlled by one piston as the other recharges. A syringe pump can be used for even greater control of flow rate; however, the syringe pump is unable to produce as much pressure as a piston pump, so it cannot be used in all HPLC applications.

Detector

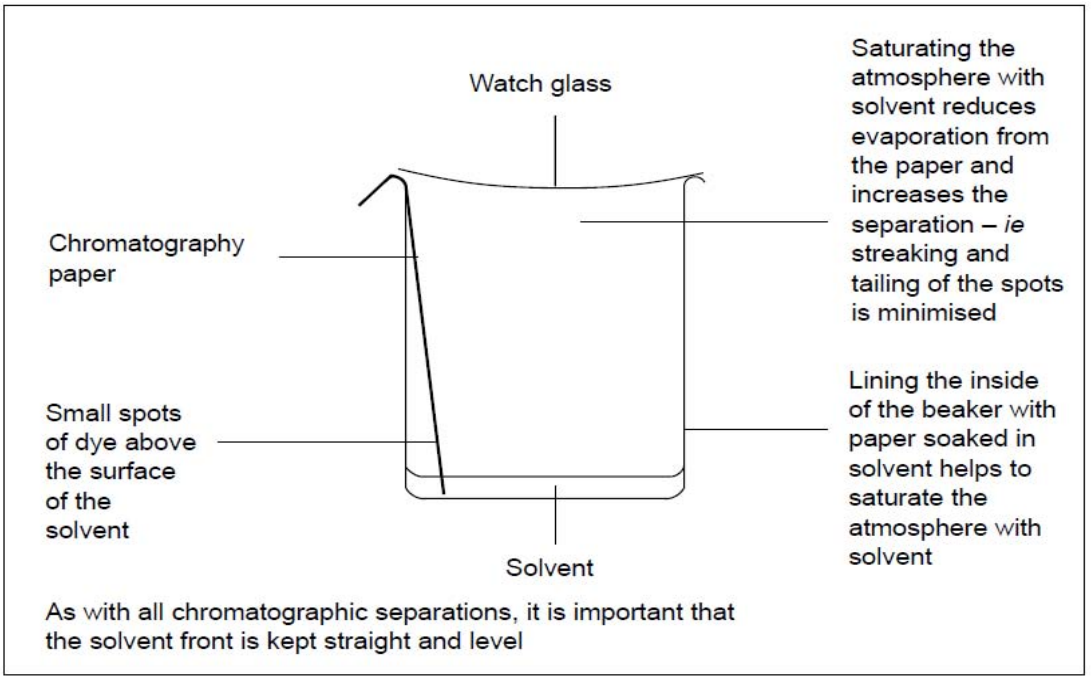
The HPLC detector, located at the end of the column, must register the presence of various components of the sample, but must not detect the solvent. For that reason there is no universal detector that works for all separations. A common HPLC detector is a UV absorption detector, as most medium to large molecules absorb UV radiation. Detectors that measure fluorescence and refractive index are also used for special applications. A relatively new development is the combination of an HPLC separation with an NMR detector. This allows the pure components of the sample to be identified and quantified by nuclear magnetic resonance after having been separated by HPLC, in one integrated process.

Applications

HPLC can be used in both qualitative and quantitative applications, that is for both compound identification and quantification. Normal phase HPLC is only rarely used now, almost all HPLC separation can be performed in reverse phase. Reverse phase HPLC is ineffective in for only a few separation types; it cannot separate inorganic ions.

Solid Chromatography

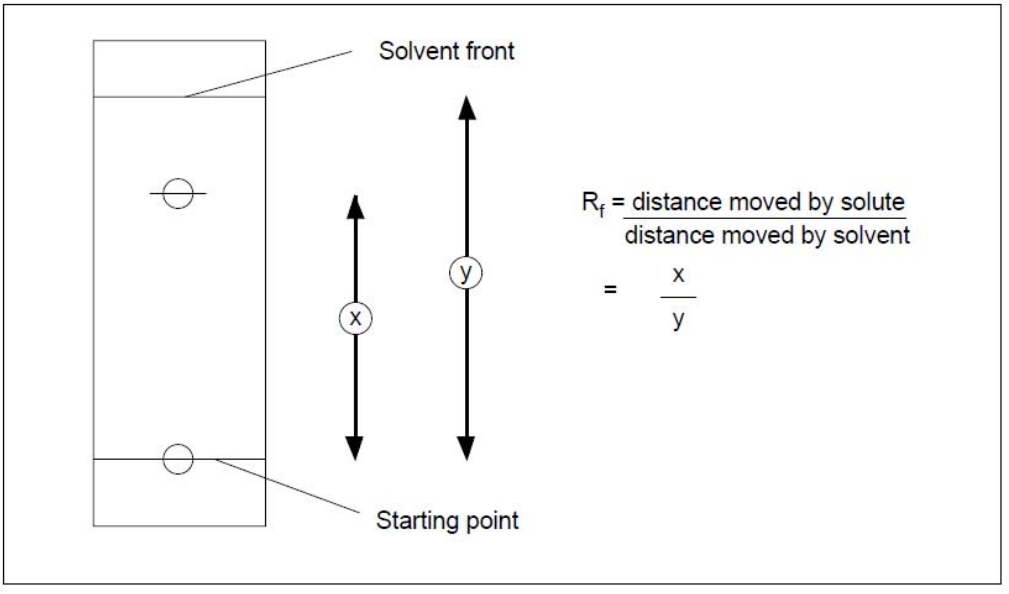
Paper chromatography



This is probably the first, and the simplest, type of chromatography that people meet. A drop of a solution of a mixture of dyes or inks is placed on a piece of chromatography paper and allowed to dry. The mixture separates as the solvent front advances past the mixture. Filter paper and blotting paper are frequently substituted for chromatography paper if precision is not required. Separation is most efficient if the atmosphere is saturated in the solvent vapour Some simple materials that can be separated by using this method are inks from fountain and fibre-tipped pens, food colourings and dyes. The components can be regenerated by dissolving them out of the cut up paper. The efficiency of the separation can be optimized by trying different solvents, and this remains the way that the best solvents for industrial separations are discovered (some experience and knowledge of different solvent systems is advantageous). Paper chromatography works by the partition of solutes between water in the paper fibres (stationary phase) and the solvent (mobile phase). Common solvents that are used include pentane, propanone and ethanol. Mixtures of solvents are also used, including aqueous solutions, and solvent systems with a range of polarities can be made. A mixture useful for separating the dyes on Smarties is a 3:1:1 mixture (by volume) of butan-1-ol:ethanol:0.880 ammonia solution. As each solute

distributes itself (equilibrates) between the stationary and the mobile phase, the distance a solute moves is always the same fraction of the distance moved by the solvent. This fraction is variously called the retardation factor or the retention ratio, and is given the symbol R or Rf:

Rf = distance moved by solute / distance moved by solvent



So as long as the correct solvent and type of chromatography paper are used, a component can be identified from its retention ratio It is possible that two solutes have the same Rf values using one solvent, but different values using another solvent (eg this occurs with some amino acids). This means that if a multi component system is not efficiently separated by one solvent the chromatogram can be dried, turned through 900, and run again using a second solvent.

Thin layer chromatography (TLC)

Thin layer chromatography is similar to paper chromatography, but the stationary phase is a thin layer of a solid such as alumina or silica supported on an inert base such as glass, aluminum foil or insoluble plastic. The mixture is 'spotted' at the bottom of the TLC plate and allowed to dry. The plate is placed in a closed vessel containing solvent (the mobile phase) so that the liquid level is below the spot. TLC has

advantages over paper chromatography in that its results are more reproducible, and that separations are very efficient because of the much smaller particle size of the stationary phase. The solvent ascends the plate by capillary action, the liquid filling the spaces between the solid particles. This technique is usually done in a closed vessel to ensure that the atmosphere is saturated with solvent vapour and that evaporation from the plate is minimised before the run is complete. The plate is removed when the solvent front approaches the top of the plate and the position of the solvent front recorded before it is dried (this allows the Rf value to be calculated). TLC has applications in industry in determining the progress of a reaction by studying the components present; and in separating reaction intermediates. In the latter case a line of the reaction mixture is 'painted' across the TLC plate instead of a single spot, and the line of product after separation is cut out of the plate and dissolved in an appropriate solvent.

7.9 References and suggested readings

1. chemwiki.ucdavis.edu
2. chemwiki.ucdavis.edu
3. http://media.rsc.org/Modern%20chemical%20techniques/MCT5%20Chromatography.pdf
4. chemwiki.ucdavis.edu

Unit - 8 : Gas Chromatography

Structure of Unit

8.0 Objective

At the end of the unit learner will be able to

- What is gas chromatography
- Different types of chromatography and related principles
- Liquid chromatography, types and its applications
- Solid chromatography, types and its applications

8.1 Introduction

Gas Chromatography

Gas chromatography is a term used to describe the group of analytical separation techniques used to analyze volatile substances in the gas phase. In gas chromatography, the components of a sample are dissolved in a solvent and vaporized in order to separate the analytes by distributing the sample between two phases: a stationary phase and a mobile phase. The mobile phase is a chemically inert gas that serves to carry the molecules of the analyte through the heated column. Gas chromatography is one of the sole forms of chromatography that does not utilize the mobile phase for interacting with the analyte. The stationary phase is either a solid adsorbant, termed gas-solid chromatography (GSC), or a liquid on an inert support, termed gas-liquid chromatography (GLC).

Introduction

In early 1900s, Gas chromatography (GC) was discovered by Mikhail Semenovich Tsvett as a separation technique to separate compounds. In organic chemistry, liquid-solid column chromatography is often used to separate organic compounds in solution. Among the various types of gas chromatography, gas-liquid chromatography is the method most commonly used to separate organic compounds. The combination of gas chromatography and mass spectrometry is an invaluable tool in the identification of molecules. A typical gas chromatograph consists of an injection port, a column, carrier gas flow control equipment, ovens and heaters for maintaining temperatures of the injection port and the column, an integrator chart recorder and a detector.

To separate the compounds in gas-liquid chromatography, a solution sample that contains organic compounds of interest is injected into the sample port where it will be vaporized. The vaporized samples that are injected are then carried by an inert gas, which is often used by helium or nitrogen. This inert gas goes through a glass column packed with silica that is coated with a liquid. Materials that are less soluble in the liquid will increase the result faster than the material with greater solubility.The purpose of this module is to provide a better understanding on its separation and measurement techniques and its application.

In GLC, the liquid stationary phase is adsorbed onto a solid inert packing or immobilized on the capillary tubing walls. The column is considered packed if the glass or metal column tubing is packed with small spherical inert supports. The liquid phase adsorbs onto the surface of these beads in a thin layer. In a capillary column, the tubing walls are coated with the stationary phase or an adsorbant layer, which is capable of supporting the liquid phase. However, the method of GSC, has limited application in the laboratory and is rarely used due to severe peak tailing and the semi-permanent retention of polar compounds within the column. Therefore, the method of gas-liquid chromatography is simply shortened to gas chromatography and will be referred to as such here.The purpose of this module is to provide a better understanding on its separation and measurement techniques and its application.

Instrumentation

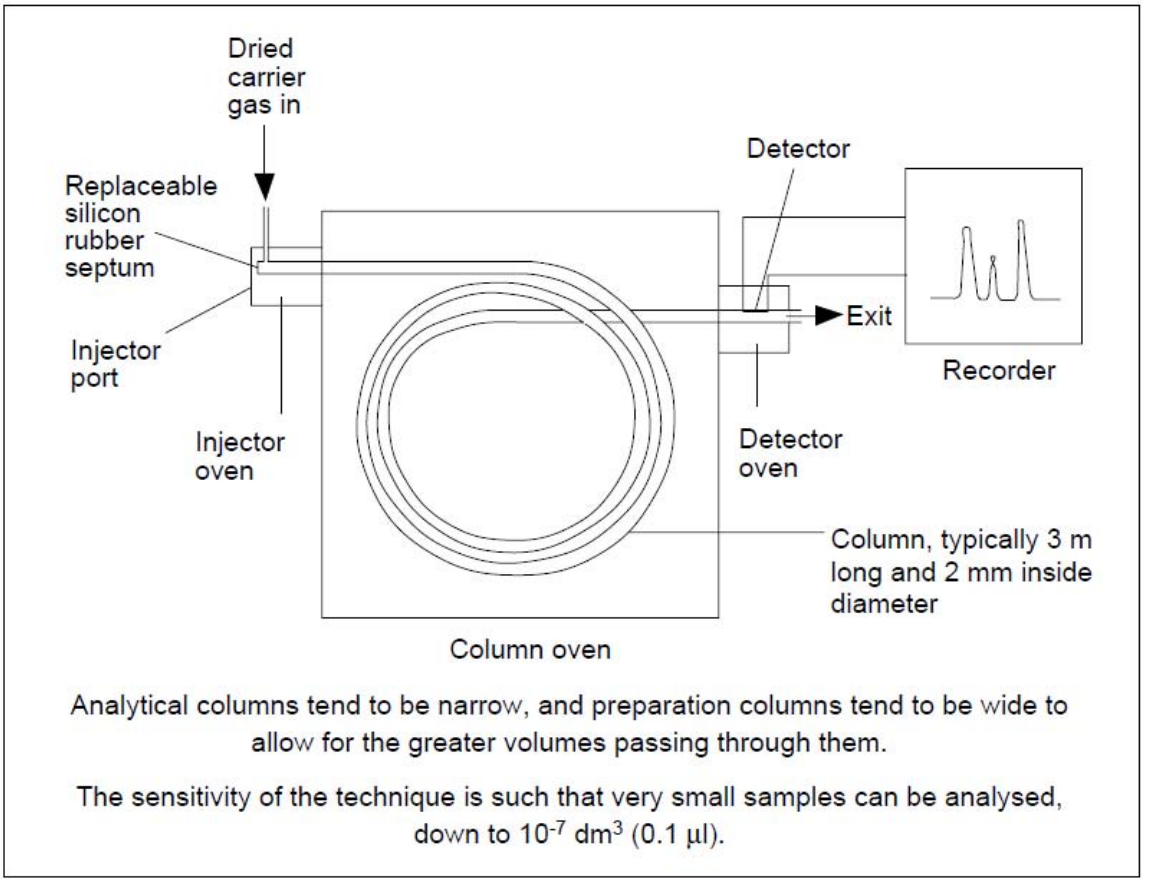
Sample Injection

A sample port is necessary for introducing the sample at the head of the column. Modern injection techniques often employ the use of heated sample ports through which the sample can be injected and vaporized in a near simultaneous fashion. A calibrated microsyringe is used to deliver a sample volume in the range of a few microliters through a rubber septum and into the vaporization chamber. Most separations require only a small fraction of the initial sample volume and a sample splitter is used to direct excess sample to waste. Commercial gas chromatographs often allow for both split and splitless injections when alternating between packed columns and capillary columns. The vaporization chamber is typically heated 50 °C above the lowest boiling point of the sample and subsequently mixed with the carrier gas to transport the sample into the column.

8.3 Carrier Gas

The carrier gas plays an important role, and varies in the GC used. Carrier gas must be dry, free of oxygen and chemically inert mobile-phase employed in gas chromatography. Helium is most commonly used because it is safer than, but comparable to hydrogen in efficiency, has a larger range of flow rates and is compatible with many detectors. Nitrogen, argon, and hydrogen are also used depending upon the desired performance and the detector being used. Both hydrogen and helium, which are commonly used on most traditional detectors such as Flame Ionization(FID), thermal conductivity (TCD) and Electron capture (ECD), provide a shorter analysis time and lower elution temperatures of the sample due to higher flow rates and low molecular weight. For instance, hydrogen or helium as the carrier gas gives the highest sensitivity with TCD because the difference in thermal conductivity between the organic vapor and hydrogen/helium is greater than other carrier gas. Other detectors such as mass spectroscopy, uses nitrogen or argon which has a much better advantage than hydrogen or helium due to their higher molecular weights, in which improve vacuum pump efficiency.

All carrier gasses are available in pressurized tanks and pressure regulators, gages and flow meters are used to meticulously control the flow rate of the gas. Most gas supplies used should fall between 99.995% - 99.9995% purity range and contain a low levels (< 0.5 ppm) of oxygen and total hydrocarbons in the tank. The carrier gas system contains a molecular sieve to remove water and other impurities. Traps are another option to keep the system pure and optimum sensitive and removal traces of water and other contaminants. A two stage pressure regulation is required to use to minimize the pressure surges and to monitor the flow rate of the gas. To monitor the flow rate of the gas a flow or pressure regulator was also require onto both tank and chromatograph gas inlet. This applies different gas type will use different type of regulator. The carrier gas is preheated and filtered with a molecular sieve to remove impurities and water prior to being introduced to the vaporization chamber. A carrier gas is typically required in GC system to flow through the injector and push the gaseous components of the sample onto the GC column, which leads to the detector



Analytical columns tend to be narrow, and preparation columns tend to be wide to allow for the greater volumes passing through them.

The sensitivity of the technique is such that very small samples can be analysed, down to 10^{-7} dm^3 (0.1 µl).

Column Oven

The thermostatted oven serves to control the temperature of the column within a few tenths of a degree to conduct precise work. The oven can be operated in two manners: isothermal programming or temperature programming. In isothermal programming, the temperature of the column is held constant throughout the entire separation. The optimum column temperature for isothermal operation is about the middle point of the boiling range of the sample. However, isothermal programming works best only if the boiling point range of the sample is narrow. If a low isothermal column temperature is used with a wide boiling point range, the low boiling fractions are well resolved but the high boiling fractions are slow to elute with extensive band broadening. If the temperature is increased closer to the boiling points of the higher boiling components, the higher boiling components elute as sharp peaks but the lower boiling components elute so quickly there is no separation.

In the temperature programming method, the column temperature is either increased continuously or in steps as the separation progresses. This method is well suited to separating a mixture with a broad boiling point range. The analysis begins at a low temperature to resolve the low boiling components and increases during the separation to resolve the less volatile, high boiling components of the sample. Rates of 5-7 °C/minute are typical for temperature programming separations.

Open Tubular Columns and Packed Columns

Open tubular columns, which are also known as capillary columns, come in two basic forms. The first is a wall-coated open tubular (WCOT) column and the second type is a support-coated open tubular (SCOT) column. WCOT columns are capillary tubes that have a thin later of the stationary phase coated along the column walls. In SCOT columns, the column walls are first coated with a thin layer (about 30 micrometers thick) of adsorbant solid, such as diatomaceous earth, a material which consists of single-celled, sea-plant skeletons. The adsorbant solid is then treated with the liquid stationary phase. While SCOT columns are capable of holding a greater volume of stationary phase than a WCOT column due to its greater sample capacity, WCOT columns still have greater column efficiencies.

Most modern WCOT columns are made of glass, but T316 stainless steel, aluminum, copper and plastics have also been used. Each material has its own relative merits depending upon the application. Glass WCOT columns have the distinct advantage of chemical etching, which is usually achieved by gaseous or concentrated hydrochloric acid treatment. The etching process gives the glass a rough surface and allows the bonded stationary phase to adhere more tightly to the column surface.

One of the most popular types of capillary columns is a special WCOT column called the fused-silica wall-coated (FSWC) open tubular column. The walls of the fused-silica columns are drawn from purified silica containing minimal metal oxides. These columns are much thinner than glass columns, with diameters as small as 0.1 mm and lengths as long as 100 m. To protect the column, a polyimide coating is applied to the outside of the tubing and bent into coils to fit inside the thermostatted oven of the gas chromatography unit. The FSWC columns are commercially available and currently

replacing older columns due to increased chemical inertness, greater column efficiency and smaller sampling size requirements. It is possible to achieve up to 400,000 theoretical plates with a 100 m WCOT column, yet the world record for the largest number of theoretical plates is over 2 million plates for 1.3 km section of column.

Packed columns are made of a glass or a metal tubing which is densely packed with a solid support like diatomaceous earth. Due to the difficulty of packing the tubing uniformly, these types of columns have a larger diameter than open tubular columns and have a limited range of length. As a result, packed columns can only achieve about 50% of the efficiency of a comparable WCOT column. Furthermore, the diatomaceous earth packing is deactivated over time due to the semi-permanent adsorption of impurities within the column. In contrast, FSWC open tubular columns are manufactured to be virtually free of these adsorption problems.

Detection Systems

The detector is the device located at the end of the column which provides a quantitative measurement of the components of the mixture as they elute in combination with the carrier gas. In theory, any property of the gaseous mixture that is different from the carrier gas can be used as a detection method. These detection properties fall into two categories: bulk properties and specific properties. Bulk properties, which are also known as general properties, are properties that both the carrier gas and analyte possess but to different degrees. Specific properties, such as detectors that measure nitrogen-phosphorous content, have limited applications but compensate for this by their increased sensitivity.

Each detector has two main parts that when used together they serve as transducers to convert the detected property changes into an electrical signal that is recorded as a chromatogram. The first part of the detector is the sensor which is placed as close the the column exit as possible in order to optimize detection. The second is the electronic equipment used to digitize the analog signal so that a computer may analyze the acquired chromatogram. The sooner the analog signal is converted into a digital signal, the greater the signal-to-noise ratio becomes, as analog signal are easily susceptible to many types of interferences.

An ideal GC detector is distinguished by several characteristics. The first requirement is adequate sensitivity to provide a high resolution signal for all components in the mixture. This is clearly an idealized statement as such a sample would approach zero volume and the detector would need infinite sensitivity to detect it. In modern instruments, the sensitivities of the detectors are in the range of 10-8 to 10-15 g of solute per second. Furthermore, the quantity of sample must be reproducible and many columns will distort peaks if enough sample is not injected. An ideal column will also be chemically inert and and should not alter the sample in any way. Optimized columns will be able to withstand temperatures in the range of -200 °C to at least 400 °C. In addition, such a column would have a short linear response time that is independent of flow rate and extends for several orders of magnitude. Moreover, the detector should be reliable, predictable and easy to operate.

Understandably, it is not possible for a detector meet all of these requirements. The next subsections will discuss some of the more common types of gas chromatography detectors and the relative advantages and/or disadvantages of each.

Type of Detector:	**Used for:**
Mass Spectrometer (MS)	Tunable for any sample
Flame Ionization (FID)	Hydrocarbons
Thermal Conductivity (TCD)	Universal
Electron-Capture (ECD)	Halogenated hydrocarbons
Atomic Emission (AED)	Element-selective
Chemiluminescence (CS)	Oxidizing reagent
Photoionization (PID)	Vapor and gaseous Compounds

Mass Spectrometry Detectors

Mass Spectrometer (MS) detectors are most powerful of all gas chromatography detectors. In a GC/MS system, the mass spectrometer scans the masses continuously throughout the separation. When the sample exits the chromatography column, it is passed through a transfer line into the inlet of the mass spectrometer . The sample is then ionized and fragmented, typically by an electron-impact ion source. During this process, the sample is bombarded by energetic electrons which ionize the molecule by

causing them to lose an electron due to electrostatic repulsion. Further bombardment causes the ions to fragment. The ions are then passed into a mass analyzer where the ions are sorted according to their m/z value, or mass-to-charge ratio. Most ions are only singly charged.

The Chromatogram will point out the retention times and the mass spectrometer will use the peaks to determine what kind of molecules are exist in the mixture. The figure below represents a typical mass spectrum of water with the absorption peaks at the appropriate m/z ratios.

Flame Ionization Detectors

Flame ionization detectors (FID) are the most generally applicable and most widely used detectors. In a FID, the sample is directed at an air-hydrogen flame after exiting the column. At the high temperature of the air-hydrogen flame, the sample undergoes pyrolysis, or chemical decomposition through intense heating. Pyrolized hydrocarbons release ions and electrons that carry current. A high-impedance picoammeter measures this current to monitor the sample's elution.

It is advantageous to used FID because the detector is unaffected by flow rate, noncombustible gases and water. These properties allow FID high sensitivity and low noise. The unit is both reliable and relatively easy to use. However, this technique does require flammable gas and also destroys the sample.

Thermal Conductivity Detectors

Thermal conductivity detectors (TCD) were one the earliest detectors developed for use with gas chromatography. The TCD works by measuring the change in carrier gas thermal conductivity caused by the presence of the sample, which has a different thermal conductivity from that of the carrier gas. Their design is relatively simple, and consists of an electrically heated source that is maintained at constant power. The temperature of the source depends upon the thermal conductivities of the surrounding gases. The source is usually a thin wire made of platinum, or gold. The resistance within the wire depends upon temperature, which is dependent upon the thermal conductivity of the gas.

TCDs usually employ two detectors, one of which is used as the reference for the carrier gas and the other which monitors the thermal conductivity of the carrier gas and

sample mixture. Carrier gases such as helium and hydrogen has very high thermal conductivities so the addition of even a small amount of sample is readily detected.

The advantages of TCDs are the ease and simplicity of use, the devices' broad application to inorganic and organic compounds, and the ability of the analyte to be collected after separation and detection. The greatest drawback of the TCD is the low sensitivity of the instrument in relation to other detection methods, in addition to flow rate and concentration dependency.

Electron-capture Detectors

Electron-capture detectors (ECD) are highly selective detectors commonly used for detecting environmental samples as the device selectively detects organic compounds with moieties such as halogens, peroxides, quinones and nitro groups and gives little to no response for all other compounds. Therefore, this method is best suited in applications where traces quantities of chemicals such as pesticides are to be detected and other chromatographic methods are unfeasible.

The simplest form of ECD involves gaseous electrons from a radioactive emitter in an electric field. As the analyte leaves the GC column, it is passed over this emitter, which typically consists of nickle-63 or tritium. The electrons from the ? emitter ionize the nitrogen carrier gas and cause it to release a burst of electrons. In the absence of organic compounds, a constant standing current is maintained between two electrodes. With the addition of organic compounds with electronegative functional groups, the current decreases significantly as the functional groups capture the electrons.

The advantages of ECDs are the high selectivity and sensitivity towards certain organic species with electronegative functional groups. However, the detector has a limited signal range and is potentially dangerous owing to its radioactivity. In addition, the signal-to-noise ratio is limited by radioactive decay and the presence of O_2 within the detector.

Atomic Emission Detectors

Atomic emission detectors (AED), one of the newest addition to the gas chromatographer's arsenal, are element-selective detectors that utilize plasma, which is a partially ionized gas, to atomize all of the elements of a sample and excite their

characteristic atomic emission spectra. AED is an extremely powerful alternative that has a wider applicability due to its based on the detection of atomic emissions.There are three ways of generating plasma: microwave-induced plasma (MIP), inductively coupled plasma (ICP) or direct current plasma (DCP). MIP is the most commonly employed form and is used with a positionable diode array to simultaneously monitor the atomic emission spectra of several elements.

GC Chemiluminescence Detectors

Chemiluminescence spectroscopy (CS) is a process in which both qualitative and quantitative properties can be be determined using the optical emission from excited chemical species. It is very similar to AES, but the difference is that it utilizes the light emitted from the energized molecules rather than just excited molecules. Moreover, chemiluminescence can occur in either the solution or gas phase whereas AES is designed for gaseous phases. The light source for chemiluminescence comes from the reactions of the chemicals such that it produces light energy as a product. This light band is used instead of a separate source of light such as a light beam.

Photoionization Detectors

Another different kind of detector for GC is the photoionization detector which utilizes the properties of chemiluminescence spectroscopy. Photoionization detector (PID) is a portable vapor and gas detector that has selective determination of aromatic hydrocarbons, organo-heteroatom, inorganice species and other organic compounds. PID comprise of an ultrviolet lamp to emit photons that are absorbed by the compounds in an ionization chamber exiting from a GC column. Small fraction of the analyte molecules are actually ionized, nondestructive, allowing confirmation analytical results through other detectors. In addition, PIDs are available in portable hand-held models and in a number of lamp configurations. Results are almost immediate. PID is used commonly to detect VOCs in soil, sediment, air and water, which is often used to detect contaminants in ambient air and soil. The disavantage of PID is unable to detect certain hydrocarbon that has low molecular weight, such as methane and ethane.

8.4 Applications

Gas chromatography is a physical separation method in where volatile mixtures are separated. It can be used in many different fields such as pharmaceuticals, cosmetics and even environmental toxins. Since the samples have to be volatile, human breathe, blood, saliva and other secretions containing large amounts of organic volatiles can be easily analyzed using GC. Knowing the amount of which compound is in a given sample gives a huge advantage in studying the effects of human health and of the environment as well.

Air samples can be analyzed using GC. Most of the time, air quality control units use GC coupled with FID in order to determine the components of a given air sample. Although other detectors are useful as well, FID is the most appropriate because of its sensitivity and resolution and also because it can detect very small molecules as well.

GC/MS is also another useful method which can determine the components of a given mixture using the retention times and the abundance of the samples. This method be applied to many pharmaceutical applications such as identifying the amount of chemicals in drugs. Moreover, cosmetic manufacturers also use this method to effectively measure how much of each chemical is used for their products.

8.5 Ion exchange chromatography

Ion exchange chromatography is used to remove ions of one type from a mixture and replace them by ions of another type. The column is packed with porous beads of a resin that will exchange either cations or anions. There is one type of ion on the surface of the resin and these are released when other ions are bound in their place eg. a basic anion exchange resin might remove nitrate(V) ions (NO_3^-) from a solution and replace them with hydroxide ions (OH^-).

1. This is the basis of ion exchange chromatography. The example above is termed "anion exchange" because the inert surface is interacting with anions
2. If the immobile surface was coated with anions, then the chromatography would be termed "cation exchange" chromatography and cations would selectively bind and be removed from the solution flowing through the column.

3. Strength of binding can be affected by pH, and salt concentration of the buffer. The ionic species "stuck" to the column can be removed (i.e. "eluted") and collected by changing one of these conditions. For example, we could lower the pH of the buffer and protonate anions. This would eliminate their electrostatic attraction to the immobilized cation surface. Or, we could increase the salt concentration of the buffer, the anions in the salt would "compete off" bound anions on the cation surface.

Acid/base character of exchange site groups

Character

Strongly acidic	$–SO_3^- H^+$
Weakly acidic	$–R–COO^- H^+$
Weakly basic	$–CH_2NH(CH_3)_2^+Cl^-$
Strongly basic	$–CH_2N(CH_3)_3^+OH^-$

Ion exchange equilibrium

If two ions are competing for the binding sites of a resin an equilibrium will be established. For example, a cation–exchange resin used to remove ammonium ions and replace them with sodium ions would have the equilibrium:

$$Resin–Na^+ + NH_4^+ \text{ ----------> } Resin–NH_4^+ + Na^+$$

This equilibrium can be described by an equilibrium constant (K) which is called the selectivity coefficient:

$$\text{Selectivity coefficient} = [Resin–NH_4][Na^+] / [Resin–Na^+][NH_4^+]$$

The equilibrium position can be changed in either direction by changing the concentration of ions in the aqueous phase. A column might remove relatively small amounts of ammonium ions almost quantitatively from a solution, but they can be liberated from the column equally efficiently by passing an excess of a concentrated solution of sodium ions through the column. The removal occurs despite the fact that

ammonium ions are preferentially bound to the resin, and this principle is useful in regenerating the column. Once a column's exchange capacity is approached, it is regenerated simply by passing a concentrated solution of sodium ions through it. This shifts the equilibrium back to the left hand side.

Under most circumstances absorption and release of ions is effectively quantitative, so it is possible to remove selected ions and determine their concentrations by titration – eg if calcium ions are removed from a sample of hard water and are replaced by hydrogen ions from the acidic form of a resin, then the concentration of hydrogen ions can be determined by titrating the eluate with a standard alkaline solution. Macromolecules can also be exchanged by using resins with larger pore sizes. The resins are generally derived from proteins or polysaccharides such as cellulose, and the exchange sites are bound to the OH groups of the saccharide units. The sites can be either weakly basic or weakly acidic, with polar covalent groups (eg amines); or they can be strongly acidic or strongly basic, with ionic groups (eg carboxylic or sulphonic acids).

Ion exchange applications

The solubility product of some partially soluble substances can be determined by sing exchange methods. For example, a saturated calcium sulphate solution can be passed down a cation exchange column that replaces the calcium ions with hydrogen ions:

$Ca^{2+}(aq) + 2(Resin–H^{+})$ ------> $Ca^{2+}(Resin–)_2 + 2H^{+}(aq)$

The hydrogen ions liberated can then be determined by titration using a standard sodium hydroxide solution (phenolphthalein as indicator). Once Ca^{2+} has been calculated from [H+], the solubility product of the salt can be calculated. By passing a water sample through two columns, one a cationic exchanger and the other an anionic exchanger, it is possible to remove any ionic impurities. Tap water, for example, can be passed through one column where the metal ions present, such as Mg^{2+} and Ca^{2+}, are replaced by H^{+}; then the anions present, such as F^{-}, Cl^{-} and NO_3^{-}, are replaced by OH^{-} in the second column. The product is deionised water.

8.6 Separation by electrolysis or electrochromatography

Electrochromatography is a chemical separation technique in analytical chemistry, biochemistry and molecular biology used to resolve and separate mostly large biomolecules such as proteins. It is a combination of size exclusion chromatography and gel electrophoresis. These separation mechanisms operate essentially in superposition along the length of a gel filtration column to which an axial electric field gradient has been added. The molecules are separated by size due to the gel filtration mechanism and by electrophoretic mobility due to the gel electrophoresis mechanism. Additionally there are secondary chromatographic solute retention mechanisms.

size exclusion chromatography + gel electrophoresis = Electrochromatography

Or

Gel Filtration Chromatography + Capillary Electrophoresis = Electrochromatography

Size-exclusion chromatography (SEC) is a chromatographic method in which molecules in solution are separated by their size, and in some cases molecular weight. It is usually applied to large molecules or macromolecular complexes such as proteins and industrial polymers. Typically, when an aqueous solution is used to transport the sample through the column, the technique is known as **gel-filtration chromatography**, versus the name **gel permeation chromatography**, which is used when an organic solvent is used as a mobile phase.

Gel electrophoresis is a method for separation and analysis of macromolecules (DNA, RNA and proteins) and their fragments, based on their size and charge.

Capillary electrophoresis (CE) is a family of electrokinetic separation methods performed in submillimeter capillaries and in micro- and nanofluidic channels. There are six types of capillary electroseparation available:

1. capillary zone electrophoresis (CZE),
2. capillary gel electrophoresis (CGE),
3. micellar electrokinetic capillary chromatography (MEKC),
4. capillary electrochromatography (CEC),
5. capillary isoelectric focusing (CIEF),
6. capillary isotachophoresis (CITP).

Useful for the separation of large biomolecules

1. separated by size due to the gel filtration mechanism
2. separated by electrophoretic mobility (gel electrophoresis)
3. Also other chromatographic solute retention mechanisms
4. widely applied for purification and analysis of synthetic or bio-polymers

8.7 Summary

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. Ion-exchange chromatography (or ion chromatography) is a process that allows the separation of ions and polar molecules based on their affinity to the ion exchanger. It can be used for almost any kind of charged molecule including large proteins, small nucleotides and amino acids. The solution to be injected is usually called a sample, and the individually separated components are called analytes. It is often used in protein purification, water analysis, and quality control.

8.8 Reference

1. Electrochromatography - Wikipedia, the free encyclopedia en.wikipedia.org
2. Gel electrophoresis - Wikipedia, the free encyclopedia en.wikipedia.org
3. http://www.unimicrotech.com/products_CEC_instrument.htm

B. Mathematics for Chemists

Unit - 9 : Vectors, dot, cross and triple products etc. gradient, divergence and curl, Vector Calculus, Gauss'theorem, divergence theorem etc.

Structure of Unit:

9.0 Objective

At the end of the unit learner will be able to

- Define vectors,
- Understand and apply vector products on many physical problems

9.1 Introduction

Vector is a quantity having both magnitude and direction e.g. displacement, velocity, force, acceleration, momentum, angular momentum.

A Vector is represented Geometrically by an arrow and written as $\vec{A}$ or A. The length of the arrow gives the magnitude of the vector and the direction of the arrow, the direction of the vector.

Two vectors are said to be equal if they have the same magnitude and direction.

Properties:-

Let $\vec{A}$, $\vec{B}$ and $\vec{C}$ be any three vectors and m, n are scalars the

(i) Associate law of addition

$$\vec{A}+(\vec{B}+\vec{C})=(\vec{A}+\vec{B})+\vec{C}$$

(ii) Null Vector- A null vector is where all the components of the vector are zero.

$$\vec{A}+\vec{0}=\vec{0}+\vec{A}=\vec{A}$$

(iii) For every vector $\vec{A}$, there exist a $-\vec{A}$ which has the same magnitude as $\vec{A}$ but opposite direction to $\vec{A}$

(iv) Commutative law for addition

$$\vec{A}+\vec{B}=\vec{B}+\vec{A}$$

(v) $m\vec{A}$ is defined as a vector having magnitude $|m||\vec{A}|$ and same direction as $\vec{A}$

$$m\vec{A}=\vec{A}m$$

(vi) $(m+n)\vec{A}=m\vec{A}+n\vec{A}$ and $m(\vec{A}+\vec{B})=m\vec{A}+m\vec{B}$

Example: Find equation f a straight line passing through two points A and B having position vector $\vec{a}$ and $\vec{b}$ with respect to an origin O.

Sol. Let $\vec{r}$ be the position vector at any point on the line then. $\vec{r}-\vec{a}$ is parallel to $(\vec{b}-\vec{a})$, so,

$$\vec{r}-\vec{a}=\lambda(\vec{b}-\vec{a})$$

Where λ is a constant.

$\vec{r} = (1-\lambda)\vec{a} + \lambda\vec{b}$ is the equation of a straight line.

Example Find the angle between $\vec{A} = 2\hat{\imath} + 2\hat{\jmath} - \hat{k}$ and $\vec{B} = 6\hat{\imath} - 3\hat{\jmath} + 2\hat{k}$.

Sol. $\vec{A} \cdot \vec{B} = AB\cos\theta$

So, $12 - 6 - 2 = \sqrt{2^2 + 2^3 + 1^2} \times \sqrt{6^2 + 3^2 + 2^2}\cos\theta$

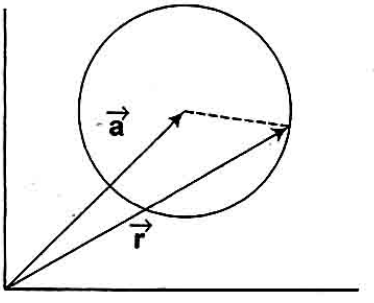
So, $Cos\,\theta = \frac{4}{\sqrt{9}\sqrt{49}} = \frac{4}{3\times 7} = \frac{4}{21}$

Example Find the equation of a sphere of radius R centered at $\vec{a}$.

Sol. Let

$\vec{r}$ be any point on the sphere

$|\vec{\mathbf{r}} - \vec{\mathbf{a}}| = R$



Therefore $(\vec{r} - \vec{a}).(\vec{r} - \vec{a}) = R^2$

This gives the equation of a sphere.

Example Find the projection of a vector $\vec{A} = \hat{\imath} - 2\hat{\jmath} + \hat{k}$ on the vector $\vec{B} = 4\hat{\imath} - 4\hat{\jmath} + 7\hat{k}$.

Sol. The projection of a vector $\vec{A}$ on the vector $\vec{B}$ is defined as $A\cos\theta$, where θ is the angle between $\vec{A}$ and $\vec{B}$.

Hence $A\cos\theta = \frac{AB\cos\theta}{B} = \frac{\vec{A}.\vec{B}}{B}$

$= \frac{4+8+7}{\sqrt{4^2+4^2+7^2}} = \frac{19}{9}$

Example 1 : Find the direction cosines of the line joining the points (3, 2, - 4) and (1, - 1, 2)

Sol. The direction cosines of a line is the cosines of the angles made by the line with each coordinate axes. So we first from the vector

$$= (3, 2, -4) - (1, -1, 2)$$

$$= (2, 3, -6)$$

Or $$\vec{v} = 2\hat{\imath} + 3\hat{\jmath} - 6\hat{k}$$

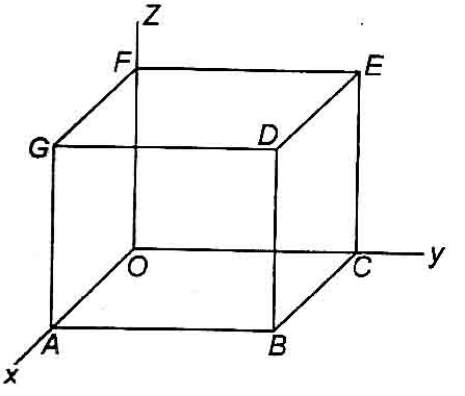
The cosines of the angles made by this vector with the three axes respectively

$$\cos\alpha = \frac{\vec{v}.\hat{\imath}}{v} = \frac{2}{\sqrt{2^2+3^2+6^2}}\frac{2}{7}$$

$$\cos\beta = \frac{\vec{v}.\hat{\imath}}{v} = \frac{3}{7}$$

$$\cos\gamma = -\frac{6}{7}$$

Example 2 : Find the acute angles formed by the diagrams of a cube.



Sol. Let $ABCD$ be a cube of edge length a. The vertex D has the coordinates (a, a, a)

Therefore, $\overrightarrow{OD} = a\hat{\imath} + a\hat{\jmath} + a\hat{k}$

B and F has the respective coordinates

(a, a, a) and $(0, 0, 0)$

$$\overrightarrow{BF} = (0,0,a) - (a,a,0)$$
$$= (-a,-a,a)$$

The cosine of the angle between $\overrightarrow{OD}$ and $\overrightarrow{BF}$ is :

$$\cos\alpha = \frac{(a\hat{\imath}+a\hat{\jmath}+a\hat{k})(-a\hat{\imath}-a\hat{\jmath}+a\hat{k})}{\sqrt{3a^2}\sqrt{3a^2}}$$
$$= \frac{-a^2-a^2+a^2}{3a^2} = -\frac{1}{3}$$

So, $$\alpha = cos^{-1}\left(-\frac{1}{3}\right)$$

9.2 Vector Products

The Dot or Scalar Product

The dot or the scalar product of two vectors $\overrightarrow{A}$ and $\overrightarrow{B}$ is defined as the product of their magnitudes and the cosine of the angle between them.

$$\overrightarrow{A}.\overrightarrow{B} = \left|\overrightarrow{A}\right|.\left|\overrightarrow{B}\right|\cos\theta \qquad 0 \leq \theta \leq \pi$$

$\overrightarrow{A}.\overrightarrow{B}$ is a scalar quantity.

Therefore $$\hat{\imath}.\hat{\imath} = \hat{\jmath}.\hat{\jmath} = \hat{k}.\hat{k} = 1$$

and $$\hat{\imath}.\hat{\jmath} = \hat{\jmath}.\hat{k} = \hat{k}.\hat{\imath} = 0$$

Therefore it can be easily proved that

$$\overrightarrow{A}.\overrightarrow{B} = A_1B_1 + A_2B_2 + A_3B_3$$

Where $$\overrightarrow{A} = A_1\hat{\imath} + A_2\hat{\jmath} + A_3\hat{k}$$

and $$\overrightarrow{B} = B_1\hat{\imath} + B_2\hat{\jmath} + B_3\hat{k}$$

The Cross or Vector Product

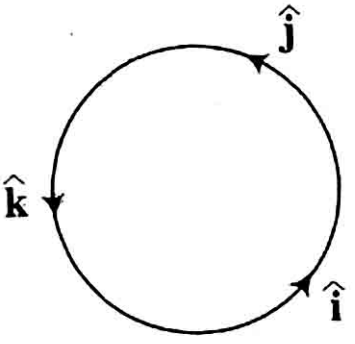
The cross or vector product of two vectors $\overrightarrow{A}$ and $\overrightarrow{B}$ taken in that order is define as the $AB\sin\theta\,\hat{n}$ where θ is the angle between $\overrightarrow{A}$ and $\overrightarrow{B}$ and $\hat{n}$ is a unit vector

perpendicular to the plane formed by $\overrightarrow{A}$ and $\overrightarrow{B}$ and $\overrightarrow{A}$, $\overrightarrow{B}$, $\hat{n}$ from a right handed system.

$$\overrightarrow{A} \times \overrightarrow{B} = AB \sin\theta\, \hat{n}\,(0 \leq \theta \leq \pi)$$

$$\hat{\imath} \times \hat{\imath} = \hat{\jmath} \times \hat{\jmath} = \hat{k} \times \hat{k} = 0$$

$$\hat{\imath} \times \hat{\jmath} = \hat{k}, \hat{\jmath} \times \hat{k} = \hat{\imath}, \hat{k} \times \hat{\imath} = \hat{\jmath}$$



Any two vectors taken r in that order.

If $\overrightarrow{A} \times \overrightarrow{B} = 0$ and $\overrightarrow{A}$ and $\overrightarrow{B}$ are not null vectors then $\overrightarrow{A}$ and $\overrightarrow{B}$ are parallel.

It can be easily show that

$$\overrightarrow{A} \times \overrightarrow{B} = \begin{vmatrix} \hat{\imath}\hat{\jmath}\hat{k} \\ A_1 A_2 A_3 \\ B_1\, B_2 B_3 \end{vmatrix}$$

Where $\overrightarrow{A} = (A_1, A_2, A_3), \overrightarrow{B} = (B_1, B_2, B_3)$

Product of Three Vectors

The triple product of the three vectors $\overrightarrow{A}$, $\overrightarrow{B}$ and $\overrightarrow{C}$ which will be explained are those of the form $\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C}$ and $\overrightarrow{A} \times (\overrightarrow{B} \times \overrightarrow{C})$. Other triple product such as $(\overrightarrow{A} . \overrightarrow{B})\, \overrightarrow{C}$, etc.

$\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C}$ is called the **scalar triple product** and $\overrightarrow{A} \times (\overrightarrow{B} \times \overrightarrow{C})$, the **vector triple product**. It can be easily shown that

$$\overrightarrow{A} . (\overrightarrow{B} \times \overrightarrow{C}) = \overrightarrow{B} . (\overrightarrow{A} \times \overrightarrow{C}) = \overrightarrow{C} . (\overrightarrow{A} \times \overrightarrow{B})$$

We may even write $\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C}$ having the bracket between $\overrightarrow{B}$ and $\overrightarrow{C}$ with the understanding that the cross product is between $\overrightarrow{B}$ and $\overrightarrow{C}$ first.

Vector product using the alternating tensor.

We define a symbol

$$\mathcal{E}_{ijk} = \begin{cases} 1 & i,j,k \text{ occur in cyclic order} \\ -1 & i,j,k, \text{occur in anti cycle order} \\ 0 & \text{ant two induces equal} \end{cases}$$

In terms of $\mathcal{E}_{ijk}, \overrightarrow{A} \times \overrightarrow{B}$ reads

$$\left(\overrightarrow{A} \times \overrightarrow{B}\right)_i = \mathcal{E}_{ijk} = A_j B_j$$

Where i on the left side means the ith component of $\overrightarrow{A} \times \overrightarrow{B}$, and we have used the Einstein's summation convention.

We may use this to form the scalar triple product.

$$\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C} = A_i \ \mathcal{E}_{ijk} B_j C_k = \mathcal{E}_{ijk} A_i B_j C_k$$
$$= \mathcal{E}_{ijk} B_j A_i C_k = \overrightarrow{B} . \overrightarrow{C} \times \overrightarrow{A}$$

$\mathcal{E}$ is unchanged by a cyclic change similarly

$$\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C} = \overrightarrow{C} . \overrightarrow{A} \times \overrightarrow{B}$$

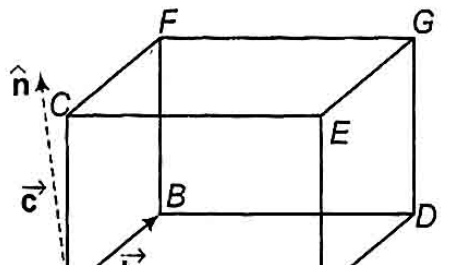
also $$\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C} = \begin{vmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{vmatrix}$$

as can be easily seen by expanding the determinant.

The geometrical significance of a vector product of $\overrightarrow{A}$ and $\overrightarrow{B}$ is that $\left|\overrightarrow{A} \times \overrightarrow{B}\right|$ gives the area of a parallelogram having $\overrightarrow{A}$ and $\overrightarrow{B}$ along the two adjacent sides.

Also, it implies that if $\overrightarrow{A}$ and $\overrightarrow{B}$ represent two vector along two adjacent sides of a triangle, then $\frac{1}{2}\left|\overrightarrow{A} \times \overrightarrow{B}\right|$ is the area of the triangle.

We may show that $\overrightarrow{A} . \overrightarrow{B} \times \overrightarrow{C}$ is the volume of parallelepiped having $\overrightarrow{A}, \overrightarrow{B}, \overrightarrow{C}$ vectors along adjacent sides having a common vertex.



Let $\vec{a}, \vec{b}, \vec{c}$ be the three vectors along three adjacent sides of a parallelepiped having a common vertex.

Then area of $OADB$ is $\left|\vec{a} \times \vec{b}\right|$

The direction of $\vec{a} \times \vec{b}$ is along $\hat{n}$ perpendicular to the plane formed by $\vec{a}$ and $\vec{b}$. Hence, volume of the parallelepiped is area of base times perpendicular

or $$V = \left|\vec{a} \times \vec{b}\right| \vec{c}.\hat{n} = \left(\vec{a} \times \vec{b}\right).\vec{c}$$

Example Prove that

$$\vec{A} \times \left(\vec{B} \times \vec{C}\right) = \left(\vec{A} \times \vec{B}\right) \times \vec{C}$$

If $\left(\vec{A} \times \vec{C}\right) \times \vec{B} = 0$

Sol. Let $$\vec{A} \times \left(\vec{B} \times \vec{C}\right) = \left(\vec{A} \times \vec{B}\right) \times \vec{C}$$

$$\left(\vec{A}.\vec{C}\right)\vec{B} - \left(\vec{A}.\vec{B}\right)\vec{C} = \left(\vec{A}.\vec{C}\right)\vec{B} - \left(\vec{B}.\vec{C}\right)\vec{A}$$

or $$\left(\vec{A}.\vec{B}\right)\vec{C} - \left(\vec{B}.\vec{C}\right)\vec{A} = 0$$

or $$\left(\vec{A} \times \vec{B}\right) \times \vec{B} = 0$$

Example The set of vectors $\vec{a}, \vec{b}, \vec{c}$ and a', b', c' are said to be reciprocal sets or systems of vectors, if

$$\vec{a}.\vec{a'} = \vec{b}.\vec{b'} = \vec{c}.\vec{c'} = 1$$

And $$\vec{a'}.\vec{b} = \vec{a'}.\vec{c} = \vec{b'}.\vec{a}$$

$$= \vec{b'}.\vec{c} = \vec{c'}.\vec{a} = \vec{a}.\vec{c}.\vec{b} = 0$$

$\vec{a}, \vec{b}, \vec{c}$ and a', b', c' are reciprocal set iff

$$\vec{a'} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{b'} = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{c'} = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

where $\vec{a} \cdot \vec{b} \times \vec{c} \neq 0$

Sol. If $\vec{a'} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{b'} = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{c'} = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}}$

Then it is easily seen that

$$\vec{a'} \cdot \vec{a} = \vec{b'} \cdot \vec{b} = \vec{c'} \cdot \vec{c} = 1$$

and $$\vec{a'} \cdot \vec{b} = \vec{a'} \cdot \vec{c} = 0, \text{ etc}$$

Now, we have to prove the converse if $\vec{a'}, \vec{b'}, \vec{c'}$ constitute a reciprocal set of vector then

$$\vec{a'} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{b'} = \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot \vec{b} \times \vec{c}}, \vec{c'} = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

It is given that $\vec{a'} \cdot \vec{a} = 1$ and $\vec{a'} \cdot \vec{b} = \vec{a'} \cdot \vec{c} = 0$

$\vec{a'}$ is perpendicular to the plane of $\vec{b}$ and $\vec{c}$ so,

$$\vec{a'} \parallel \vec{b} \times \vec{c}$$

Let $\vec{a'} = \lambda (\vec{b} \times \vec{c})$ where λ is a constant $\vec{a'} \cdot \vec{a} = 1$

So, $\lambda(\vec{a} \cdot \vec{b} \times \vec{c}) = 1$

So, $$\lambda = \frac{1}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

So, $$\vec{a} = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot \vec{b} \times \vec{c}}$$

Similarly all other relations may be proved.

9.3 Vector Calculus

There may be functions which are themselves scalars but depends on a variable which is a vectors and functions which are vectors but whose independent variables may be either scalar or vectors. Let us first consider a vector function $\overrightarrow{R}(u)$which depends on a scalar variable u.

For a small change in u, $\overrightarrow{R}\ (u)$ becomes $\overrightarrow{R}(u+\Delta u)$, then form the ratio

$$\frac{\Delta\,\vec{R}}{\Delta\,u}=\frac{\overrightarrow{R}(u+\Delta u)-\ \overrightarrow{R}\ (u)}{\Delta\,u}$$

If this ratio exist in the limit $\Delta u\ \to 0$, then we denote it as $\frac{d\overrightarrow{R}}{du}$and is the derivative of $\overrightarrow{R}$ with respect to u.

Similarly higher order derivatives may be defined.

If $\overrightarrow{A}, \overrightarrow{B}, \overrightarrow{C}$ are differentiable vector functions of a scalar variable u and ϕ is a differentiable scalar function of u, then

1. $\frac{d}{du}\left(\overrightarrow{A}\pm\overrightarrow{B}\right)=\frac{d\overrightarrow{A}}{du}\pm\frac{d\,\overrightarrow{B}}{du}$
2. $\frac{d}{du}\left(\overrightarrow{A}.\ \overrightarrow{B}\right)=\frac{d\overrightarrow{A}}{du}.\overrightarrow{B}+\overrightarrow{A}.\ \frac{d\,\overrightarrow{B}}{du}$
3. $\frac{d}{du}\left(\overrightarrow{A}\times\overrightarrow{B}\right)=\frac{d\overrightarrow{A}}{du}\times\overrightarrow{B}+\overrightarrow{A}\times\frac{d\,\overrightarrow{B}}{du}$
4. $\frac{d}{du}\left(\phi\overrightarrow{A}\right)=\frac{d\phi}{du}\overrightarrow{A}+\ \phi\pm\frac{d\,\overrightarrow{A}}{du}$
5. $\frac{d}{du}\left(\overrightarrow{A}\ .\ \overrightarrow{B}\ \times\ \overrightarrow{C}\right)=\frac{d\overrightarrow{A}}{du}\overrightarrow{B}\ \times\ \overrightarrow{C}+\overrightarrow{A}\ .\ \frac{d\,\overrightarrow{B}}{du}\times\overrightarrow{C}+\overrightarrow{A}.\ \overrightarrow{B}\ .\ \frac{d\,\overrightarrow{C}}{du}$
6. $\frac{d}{du}\left(\overrightarrow{A}\ \times(\overrightarrow{B}\ \times\ \overrightarrow{C})\right)=\frac{d\overrightarrow{A}}{du}\times\left(\overrightarrow{B}\ \times\ \overrightarrow{C}\right)+\overrightarrow{A}\ \times\left[\frac{d\,\overrightarrow{B}}{du}\times\overrightarrow{C}\right]+\overrightarrow{A}\ \times\ \left[\overrightarrow{B}\ \times\ \frac{d\,\overrightarrow{C}}{du}\right]$

Partial Derivative

If $\overrightarrow{A}$, $\overrightarrow{B}$, $\overrightarrow{C}$ are vector functions depending on scalar variables such as x, y and z, then the partial derivative of $\overrightarrow{A}$ with respect to x is defined as

$\frac{\partial \overrightarrow{A}}{\partial x} = \lim_{\Delta x} \frac{\overrightarrow{A}(x+\Delta x,y,z) - \overrightarrow{A}\ (x,y,z)}{\Delta x}$ Provided the limit exists finitely.

Similarly other partial derivatives are similar to those of ordinary derivatives.

Space Curves

Let c be a curve which may be described in terms of a parameter u. Let $\overrightarrow{r}(u)$be the position vector of any point on the curve. Then as u varies, $\overrightarrow{r}$moves over the curve.

$$\overrightarrow{r}(u) = x\,(u)\hat{\imath} + y\,(u)\hat{\jmath} + z\,(u)\hat{k}$$

$x = x\,(u), \quad y = y\,(u), \quad z = z\,(u)$ gives the parametric equation of the curve/

Taking differential, $\delta\overrightarrow{r}$is a vector in the direction of the tangent

$\frac{d\,\overrightarrow{r}}{du} = \frac{dx}{du}\hat{\imath} + \frac{dy}{du}\hat{\jmath} + \frac{dz}{du}\hat{k}$ is the position vector of a particle as a function of time and $\frac{d\,\overrightarrow{r}}{qt}$ is its velocity.

Example A particle moves along the curve $x = 2t^2, y = t^2 - 4t, z = 3t - 5$ where t is the time. Find the velocity and acceleration at t – 1 in the direction of $\hat{\imath} - 3\hat{\jmath} + 2\hat{k}$.

Sol. The velocity components are given by

$$\frac{dx}{dt} = 4t, \frac{dy}{dt} = 2t - 4, \frac{dz}{dt} = 3$$

and the acceleration components are given by

$$\frac{d^2x}{dt^2} = 4, \qquad \frac{d^2y}{dt^2} = 2, \frac{d^2z}{dt^2} = 0$$

At t = 1 $\quad \overrightarrow{v} = 4\hat{\imath} - 2\hat{\jmath} + 3\hat{k}$

and $\quad \overrightarrow{a} = 4\hat{\imath} + 2\hat{\jmath}$

Now, the component of velocity in the direction of $\hat{\imath} - 3\hat{\jmath} + 2\hat{k}$ is

$$\frac{(4\hat{\imath} - 2\hat{\jmath} + 3\hat{k}).(\hat{\imath} - 3\hat{\jmath} + 2\hat{k})}{\sqrt{1 + 3^2 + 2^2}} = \frac{4 + 6 + 6}{\sqrt{14}} = \frac{16}{\sqrt{14}}$$

and the component of acceleration in the direction of $\hat{\imath} - 3\hat{\jmath} + 2\hat{k}$

$$= \frac{(4\hat{\imath} + 2\hat{\jmath}).(\hat{\imath} - 3\hat{\jmath} + 2\hat{k})}{\sqrt{1 + 3^2 + 2^2}} = \frac{4 - 6}{\sqrt{14}} = \frac{-2}{\sqrt{14}}$$

Example If

$\phi(x, y, z) = xy^2z$ and $\overrightarrow{A} = xz\hat{\imath} + x\,y^2\hat{\jmath} + y\,z^3\hat{k}$

Then find $\frac{\partial(\phi\vec{A})}{\partial x^2 \partial y}$ at the point (1, 1, -1)

Sol. $\frac{\partial^2(\phi\vec{A})}{\partial x^2 \partial y} = \frac{\partial^2}{\partial x^2}\frac{\partial(\phi\vec{A})}{\partial y}$

$$= \frac{\partial^2}{\partial x^2}\{2xyz\overrightarrow{A} + xy^2z\,(-2xy\hat{\jmath} + z^2\hat{k})\}$$

$$= \frac{\partial}{\partial x}\{2yz\overrightarrow{A} + 2xy\,(z\hat{\imath} + y^2\hat{\jmath}) - 4xy^3z\hat{\jmath} + y^2z^3\hat{k}\}$$

$$= 2yz(z\hat{\imath} + y^2\hat{\jmath}) + 2y\,(z\hat{\imath} - y^2\hat{\jmath}) - 4y^2z\hat{\jmath}$$

$$\frac{\partial^2(\phi\vec{A})}{\partial x^2 \partial y}|(1, 1, -1) \quad = 2\,(1)(-1)(\hat{\imath} - \hat{\jmath}) + 2\,(-\hat{\imath} - \hat{\jmath}) + 4\hat{\jmath}$$

$$2\hat{\imath} + 2\hat{\jmath} - 2\hat{\imath} - 2\hat{\jmath} + 4\hat{\jmath} = 4\hat{\jmath}$$

Example Find A unit tangent to any point on the curve $x = \cos\omega t, y = a\sin\omega t, z = bt$ Where a, b, ω are constants.

Sol. Let $\overrightarrow{r} = x\hat{\imath} + y\hat{\jmath} + z\hat{k}$

$\frac{d\vec{r}}{dt}$ is a vector tangent to the curve.

$$\frac{d\vec{r}}{dt} = -a\omega \sin \omega t\, \hat{\imath} + a\omega \cos \omega t\, k\hat{\jmath} + b\hat{k}$$

A unit tangent, therefore is given by

$$\vec{r} = \frac{\frac{d\,\vec{r}}{dt}}{\left|\frac{d\,\vec{r}}{dt}\right|} = \frac{-a\omega \sin \omega t\, \hat{\imath} + a\omega \cos \omega t\, k\hat{\jmath} + b\hat{k}}{\sqrt{a^2\omega^2 + b^2}}$$

Example Find the integral $\int \vec{r} \times \frac{d^2\vec{r}}{dt}\, dt$

Sol. We note that

$$\frac{d}{dt}\left(\vec{r}\frac{d\vec{r}}{dt}\right) = \frac{d\,\vec{r}}{dt} \times \frac{d\,\vec{r}}{dt} + \vec{r} \times \frac{d^2\vec{r}}{dt^2}$$

So, $\int \vec{r} \times \frac{d^2\vec{r}}{dt^2}\, dt = \vec{r} \times \frac{d\,\vec{r}}{dt}$

9.4 The Gradient, Divergence and Curl

Here, we will discuss the important concepts of the gradient, divergence and curl. In fact, vector calculus is mainly gradient, divergence and curl and their related integral theorems.

First we defined the del operator (or rabla) which is a vector differential operator written as

$$\vec{\nabla} = \hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

It acts like a vector and also like a differential operator. Therefore, it will obey the rules relating to vectors as well as for differential operators. The expression for $\vec{\nabla}$ given above is given in the Cartesian coordinate system. It may be expressed in any coordinate system. Using the del operator, we define gradient, divergence and curl.

The Gradient

Let $\phi(x, y, z)$ be a scalar function of x, y, z coordinates and ϕ, is defined and differentiable at each point in a certain region of space. Then the gradient of ϕ is

$$\vec{\nabla}\phi = \hat{\imath}\frac{\partial\phi}{\partial x} + \hat{\jmath}\frac{\partial\phi}{\partial y} + \hat{k}\frac{\partial\phi}{\partial z}$$

$\vec{\nabla}\phi$ is no longer an operator. It is a vector field, that is, it has a value at every point in space. $\vec{\nabla}\phi$ is a vector and component of $\vec{\nabla}\phi$in the direction of another vector $\vec{a}$ is $\frac{\vec{\nabla}\phi \,.\, \vec{a}}{|\vec{a}|}$ and is called directional derivative of ϕ in the direction of $\vec{a}$. It is the rate of change of ϕ in the direction of $\vec{a}$.

Theorem If $\phi(x, y, z) = a$ is a surface then $\vec{\nabla}\phi$ is a vector perpendicular to the surface.

Proof$\phi(x, y, z) = a$ defines a surface taking gradient on both sides. We get

$$\frac{\partial\phi}{\partial x}\,dx + \frac{\partial\phi}{\partial y}\,dy + \frac{\partial\phi}{\partial z}\,dz = 0$$

or $$\vec{\nabla}\phi \,.\, d\,\vec{r} = 0$$

where $d\,\vec{r} = dx\vec{\imath} + dy\hat{\jmath} + dz\hat{k}$

$(x, y, z)$is any point on the surface $\phi = c.$ A near by point on the surface is $(x + \delta x, y + \partial y, z + \partial z).$

The vector $\partial\vec{r}$is tangent to the surface where $\delta x, \partial y, \partial z$ becomes infinitesimal. Now, since d $\vec{r}$ is tangent to the surface and $\vec{\nabla}\phi \,.\, d\,\vec{r} = 0$

Therefore $\vec{\nabla}\phi$ is normal to the surface.

Theorem The greatest changes of ϕtakes place e direction of $\vec{\nabla}\phi$.

Proof The differential of ϕ is given

$$d\phi = \frac{\partial \phi}{\partial x}\, dx + \frac{\partial \phi}{\partial y}\, dy + \frac{\partial \phi}{\partial z}\, dz$$

$$d\phi = \vec{\nabla}\phi \,.\, d\,\vec{r}$$

What we are doing amount to taking nearby point (x, y, z) and $(x + dx, y + dy\,, z + dz)$ and comparing the value of ϕ at the two nearby points? $d\phi$ is maximum when $\vec{\nabla}\phi$ and $d\,\vec{r}$ are in the same direction, that is of we chose $(x + dx, y + dy\,, z + dz)$ in the direction of $\vec{\nabla}\phi$, from (x, y, z) then $d\phi$is maximum. Hence, $\frac{d\phi}{ds}$ is maximum in the direction of $\vec{\nabla}\phi$.

Example If $\phi(x, y, z) = 2xz^4 - x^2y$, find $\vec{\nabla}\phi$ at the point (2, -2, -1).

Sol. $\vec{\nabla}\phi = (2z^4 - 2xy)\hat{\imath} - x^2\hat{\jmath} + 8z^2\hat{k}$

At the point (2, -2, -1)

$$\vec{\nabla}\phi\big|(2, -2, -1) = (2 + 8)\hat{\imath} - 4\hat{\jmath} - 16\hat{k}$$

$$= 10\hat{\imath} - 4\hat{\jmath} - 16\hat{k}$$

Example Find $\vec{\nabla}|\vec{r}|^3$

Sol. Let us find the x-component of $\vec{\nabla}|\vec{r}|^3$

The x-component is

$$\frac{\partial}{\partial x}|\vec{r}|^3 = \frac{\partial}{\partial x}(x^2 + y^2 + z^2)^{\frac{3}{2}}$$

$$= \frac{1}{2}(x^2 + y^2 + z^2)^{1/2}\, 2x = 3xr$$

Similarly, y-component is 3yr, etc.

So, $$\vec{\nabla}|\vec{r}|^3 \; 3r\left(x\hat{\imath} + y\hat{\jmath} + z\hat{k}\right) = \; 3r\,\vec{r}$$

Example If $\overrightarrow{A}$ is a constant vector, then prove that $\vec{\nabla}\left(\vec{r}\,.\,\overrightarrow{A}\right) = \overrightarrow{A}$

Sol. For rotational simplicity let us write $\vec{\nabla}$as $\sum_{k=1}^{3} \hat{\imath}_k \frac{\partial}{\partial x_k}$we may even suppress. The summation sign using the summation convention

$$\vec{\nabla}\left(\vec{r}\,.\,\overrightarrow{A}\right) = \hat{\imath}_k \frac{\partial}{\partial x_k}(x_i A_i)$$

$$= \hat{\imath}_k \frac{\partial x_i}{\partial x_k} A_i = \; \hat{\imath}_k \, \partial_{ik} A_i$$

$$= \; \hat{\imath}_k \, A_k = \; \overrightarrow{A}$$

The Divergence

Let $\overrightarrow{A}$ be defined, and differentiable at each point (x, y, z) in a certain region of space. The divergence of $\overrightarrow{A}$ is defined as

$$\vec{\nabla}.\overrightarrow{A} = \; \frac{\partial A_x}{\partial x} + \; \frac{\partial A_y}{\partial y} + \; \frac{\partial A_z}{\partial z}$$

$$= \; \sum \frac{\partial A_k}{\partial x_k}$$ using summation convention.

We may even shorter the rotation by writing ∂_k in place of $\frac{\partial}{\partial x_k}$.

Thus $$\vec{\nabla}\,.\overrightarrow{A} = \; \partial_k \, A_k$$

Theorem $\vec{\nabla}.\left(\overrightarrow{A} + \; \overrightarrow{B}\right) = \; \vec{\nabla}\,.\overrightarrow{A} + \; \vec{\nabla}\,.\overrightarrow{B}$

Proof

$$\vec{\nabla}.\left(\overrightarrow{A} + \; \overrightarrow{B}\right) = \partial_k \, (A_k + \; B_k)$$

$$= \partial_k \, A_k + \; \partial_k \, B_k$$

$$= \vec{\nabla}.\overrightarrow{A} + \vec{\nabla}.\overrightarrow{B}$$

Theorem $\vec{\nabla}.\left(\phi\,\overrightarrow{A}\right) = \vec{\nabla}\,\phi\,.\,\overrightarrow{A} + \phi\,\vec{\nabla}\,.\,\overrightarrow{A}$

Proof

$$\vec{\nabla}.\left(\phi\,\overrightarrow{A}\right) = \partial_k\,(\phi\,A_k) = \phi\,\partial_k A_k + (\partial_k \phi)A_k$$
$$= \vec{\nabla}\,\phi\,.\overrightarrow{A} + \vec{\nabla}\,\phi\,.\overrightarrow{A}$$
$$= \vec{\nabla}.\overrightarrow{A} + \vec{\nabla}.\overrightarrow{B}$$

Example Prove $\vec{\nabla}=\left(\frac{\vec{r}}{r^3}\right) = 0$

Sol. $\vec{\boldsymbol{\nabla}}.\frac{\vec{r}}{r^3} = \frac{1}{r^3}\vec{\boldsymbol{\nabla}}.\vec{r} + \vec{r}\,.\vec{\boldsymbol{\nabla}}\frac{1}{r^3}$

$$= \left(\frac{3}{r^3}\right) + \vec{r}\,.\left(\frac{-3\,\vec{r}}{r^5}\right) = \frac{3-3}{r^3} = \mathbf{0}$$

Example Prove $\phi\nabla^2\psi - \psi\,\nabla^2\phi = \nabla^2\,.\left(\phi\,\vec{\nabla}\,\psi - \psi\,\vec{\nabla}\,\phi\right)$

Sol. $\vec{\nabla}\left(\phi\,\vec{\nabla}\,\psi - \psi\,\vec{\nabla}\,\phi\right)$

$$= \vec{\nabla}\,\phi\,.\vec{\nabla}\,\psi - \vec{\nabla}\psi\,.\vec{\nabla}\phi + \phi\,\nabla^2\,\psi - \psi\,\nabla^2\phi$$
$$= \boldsymbol{\phi\,\nabla^2\,\psi - \psi\,\nabla^2\,\phi}$$

Example Evaluate $\vec{\nabla}\,.\left(2x^2z\hat{\imath} - xy^2z\hat{\jmath} + 3yz^2\hat{k}\right)$

Sol. $\vec{\nabla}\,.\left(2x^2z\hat{\imath} - xy^2z\hat{\jmath} + 3yz^2\hat{k}\right)$

$$= \frac{\partial}{\partial x}(2x^2z) - \frac{\partial}{\partial y}(x\,y^2z) + \frac{\partial}{\partial z}(3yz^2)$$
$$= 4xz - 2xyz + 6yz$$

Example If $\overrightarrow{\omega}$ is a constant vector and $\overrightarrow{v} = \overrightarrow{\omega} \times \overrightarrow{r}$.

Prove that $div\,\overrightarrow{v} = 0$

Sol. $\vec{\boldsymbol{\nabla}}\,.\,\overrightarrow{\boldsymbol{v}} = \vec{\boldsymbol{\nabla}}\,.(\overrightarrow{\omega} \times \overrightarrow{\boldsymbol{r}}) = \boldsymbol{\partial_i}(\overrightarrow{\omega} \times \overrightarrow{\boldsymbol{r}})_{\boldsymbol{i}} = \boldsymbol{\varepsilon_{ijk}\,\delta_{ik}}$

To make it clearer we may expand the cross product,

$$\vec{\omega} \times \vec{r} = (\omega_y z - \omega_z y)\hat{\imath} + (\omega_z x - \omega_x z)\,\hat{\jmath} + (\omega_x y - \omega_y x)\,\hat{k}$$

$$\frac{\partial}{\partial x}(\omega_y z - \omega_z y) + \frac{\partial}{\partial y}(\omega_z x - \omega_z z) + \frac{\partial}{\partial}(\omega_x y - \omega_y x) = 0$$

A vector $\vec{v}$ whose divergence is zero is called solenoidal. A vector field is said to be either a some field or a sink field according to as its divergence is positive or negative.

The Curl

If $\vec{A}$ is differentiable vector field, then the curl or rotation of $\vec{A}$ written as $\vec{\nabla} \times \vec{A}$, curl $\vec{A}$ is defined as

$$\vec{\nabla} \times \vec{A} = \left(\frac{\partial A_3}{\partial y} - \frac{\partial A_2}{\partial z}\right)\hat{\imath} + \left(\frac{\partial A_1}{\partial z} - \frac{\partial A_3}{\partial x}\right)\hat{\jmath} + \left(\frac{\partial A_2}{\partial x} - \frac{\partial A_1}{\partial y}\right)\hat{k}$$

where $\vec{A} = A_1\hat{\imath} + A_2\hat{\jmath} + A_3\hat{k}$

$$\vec{\nabla} \times \vec{A} = \begin{vmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_1 & A_2 & A_3 \end{vmatrix}$$

or $\varepsilon_{ijk}\,\partial_j\,A_k$, the ith component of $\vec{\nabla} \times \vec{A}$.

Theorem Prove the following identities

(i) $\vec{\nabla} \times (\vec{A} \times \vec{B}) = \vec{\nabla} \times \vec{A} + \vec{\nabla} \times \vec{B}$

(ii) $\vec{\nabla} \times (\phi\,\vec{A}) = (\vec{\nabla}\phi) \times \vec{A} + \phi\,(\vec{\nabla} \times \vec{A})$

Proof (i) Consider $\vec{\nabla} \times (\vec{A} \times \vec{B})$. Its ith components is

$$\varepsilon_{ijk}\,\partial_j\,(A + B)_k = \varepsilon_{ijk}\,\partial_j\,A_k + \varepsilon_{ijk}\,\partial_j\,B_k$$

$$= \vec{\nabla} \times \vec{A} + \vec{\nabla} \times \vec{B}$$

$$= \vec{\nabla} \times (\vec{A} \times \vec{B}) = \vec{\nabla} \times \vec{A} + \vec{\nabla} \times \vec{B}$$

(ii) The ith component of $\vec{\nabla} \times (\phi \overrightarrow{A})$

$$\boldsymbol{\varepsilon_{ijk}}\, \partial_j (\phi\, A)_k = \boldsymbol{\varepsilon_{ijk}}\, \partial_j (\phi\, A_k)$$

$$= \boldsymbol{\varepsilon_{ijk}}\, \partial_j\, \phi\, A_k + \boldsymbol{\varepsilon_{ijk}}\, \boldsymbol{\phi}\, \partial_j\, A_k$$

$$= \left(\vec{\boldsymbol{\nabla}}\, \boldsymbol{\phi}\right) \times \overrightarrow{\boldsymbol{A}} + \boldsymbol{\phi}\, \vec{\boldsymbol{\nabla}} \times \overrightarrow{\boldsymbol{A}}$$

$$= \vec{\boldsymbol{\nabla}} \times \left(\boldsymbol{\phi}\, \overrightarrow{\boldsymbol{A}}\right) = \left(\vec{\boldsymbol{\nabla}}\, \boldsymbol{\phi}\right) \times \overrightarrow{\boldsymbol{A}} + \boldsymbol{\phi}\, \vec{\boldsymbol{\nabla}} \times \overrightarrow{\boldsymbol{A}}$$

Theorem Prove $\vec{\nabla}.\left(\overrightarrow{A} \times \overrightarrow{B}\right) = \overrightarrow{B}\ .\ \vec{\nabla} \times \overrightarrow{A} - \overrightarrow{A}\ .\ \vec{\nabla} \times \overrightarrow{B}$

Where $\overrightarrow{A}\ and\ \overrightarrow{B}$ are differentiable vector fields.

Proof $\vec{\nabla}.\left(\overrightarrow{A} \times \overrightarrow{B}\right) = \partial_i (A_i \times B_i)$

$$= \partial_i \epsilon_{ijk}\, A_j B_k$$

$$= \epsilon_{ijk} \left(\partial_i A_j\right) B_k + \epsilon_{ijk}\, A_j\, \partial_i B_k$$

$$= B_k \epsilon_{kij}\ \partial_i\, A_j + A_j \epsilon_{jki}\ \partial_i B_k$$

$$= \overrightarrow{B}\ .\ \vec{\nabla} \times \overrightarrow{A} - A_j \epsilon_{jik}\ \partial_i B_k \qquad (Since\ \epsilon_{jki} = -\epsilon_{jik})$$

$$= \overrightarrow{B}\ .\ \vec{\nabla} \times \overrightarrow{A} - \overrightarrow{A}\ .\ \vec{\nabla} \times \overrightarrow{B}$$

Theorem Prove that

$$\vec{\nabla} \times \left(\vec{\mathrm{A}} \times \overrightarrow{B}\right) = \left(\overrightarrow{B}.\vec{\nabla}\right)\overrightarrow{A} - \overrightarrow{B}\left(\vec{\nabla}.\ \overrightarrow{A}\right) - \vec{\mathrm{A}}\left(\vec{\nabla}.\ \overrightarrow{B}\right) + \vec{\mathrm{A}}\left(\vec{\nabla}.\ \overrightarrow{\mathrm{B}}\right)$$

Theorem Prove that

$$\vec{\nabla}\left(\vec{\mathrm{A}}.\ \overrightarrow{B}\right) = \left(\overrightarrow{B}.\vec{\nabla}\right)\overrightarrow{A} + \left(\overrightarrow{A}\ .\ \vec{\nabla}\right)\overrightarrow{B} + \overrightarrow{B}\left(\vec{\nabla}.\ \overrightarrow{A}\right) + \vec{\mathrm{A}} \times \left(\vec{\nabla} \times\ \overrightarrow{\mathrm{B}}\right)$$

Proof We start with $\overrightarrow{\mathrm{B}} \times \left(\vec{\nabla} \times\ \overrightarrow{\mathrm{A}}\right)$

$\vec{\nabla}$ acts on $\overrightarrow{A}$, so we may write $\vec{\nabla}_A$.

Using the box product rule we write

$$\overrightarrow{B} \times \left(\vec{\nabla} \times\ \overrightarrow{A}\right) = \vec{\nabla}_A\left(\overrightarrow{A}.\overrightarrow{\mathrm{B}}\right) - \left(\overrightarrow{B}\ .\ \vec{\nabla}_A\right)\overrightarrow{A}$$

Also $\overrightarrow{A} \times \left(\vec{\nabla} \times\ \overrightarrow{B}\right) = \vec{\nabla}_B\left(\overrightarrow{A}.\overrightarrow{\mathrm{B}}\right) - \left(\overrightarrow{A}\ .\ \vec{\nabla}_B\right)\overrightarrow{B}$

Adding the above two equations, we get

$$\overrightarrow{B} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) + \overrightarrow{A} \times \left(\vec{\nabla} \times \overrightarrow{B}\right)$$
$$= \vec{\nabla}_A\left(\overrightarrow{A}.\vec{\mathrm{B}}\right) + \vec{\nabla}_B\left(\overrightarrow{A}.\vec{\mathrm{B}}\right) - \left(\overrightarrow{B}.\vec{\nabla}\right)\overrightarrow{A} - \left(\overrightarrow{A} \times \vec{\nabla}\right)\overrightarrow{B}$$

We dropped the subscripts on the last two expression because $\vec{\nabla}_A$ any way acts $\overrightarrow{A}$ and $\vec{\nabla}_B$ acts on $\overrightarrow{B}$.

In the expression, $\vec{\nabla} \times \left(\overrightarrow{A}.\overrightarrow{B}\right)$, $\vec{\nabla}$ acts on $\overrightarrow{A}$ as well as $\overrightarrow{B}$.

So, we may write

$$\vec{\nabla}\left(\vec{\mathrm{A}}.\overrightarrow{B}\right) = \vec{\nabla}_A\left(\overrightarrow{A}.\vec{\mathrm{B}}\right) + \vec{\nabla}_B\left(\overrightarrow{A}.\overrightarrow{B}\right)$$

So,
$$\vec{\mathrm{B}} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) + \overrightarrow{A} \times \left(\vec{\nabla} \times \vec{\mathrm{B}}\right)$$
$$= \vec{\nabla}\left(\overrightarrow{\mathrm{A}}.\overrightarrow{B}\right) - \left(\overrightarrow{B}.\vec{\nabla}\right)\vec{\mathrm{A}} - \left(\overrightarrow{A} \times \vec{\nabla}\right)\vec{\mathrm{B}}$$
$$= \vec{\nabla}\left(\overrightarrow{\mathrm{A}}.\overrightarrow{B}\right) = \left(\overrightarrow{B}.\vec{\nabla}\right)\vec{\mathrm{A}} + \left(\overrightarrow{A}.\vec{\nabla}\right)\vec{\mathrm{B}} + \vec{\mathrm{B}} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) + \overrightarrow{A}\left(\vec{\nabla} \times \vec{\mathrm{B}}\right)$$

Note If $\overrightarrow{\mathrm{A}} = \overrightarrow{B}$, then

$$2\vec{\mathrm{A}} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) = \vec{\nabla}A^2 - 2\left(\overrightarrow{A}.\vec{\nabla}\right)\vec{\mathrm{A}}$$
$$\left(\vec{\mathrm{A}}.\vec{\nabla}\right)\overrightarrow{A} = \frac{1}{2}\vec{\nabla}A^2 - \vec{\mathrm{A}} \times \left(\vec{\nabla} \times \vec{\mathrm{A}}\right)$$

Theorem Prove that

$$\vec{\nabla} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) = -\nabla^2\vec{\mathrm{A}} + \vec{\nabla}\left(\vec{\nabla}.\overrightarrow{A}\right)$$

Proof We first present the heuristic approach. The first $\vec{\nabla}$ acts. the second $\vec{\nabla}$ and also on $\overrightarrow{A}$. So, we may write $\vec{\nabla} \times \left(\vec{\nabla} \times \overrightarrow{A}\right)$

$$\vec{\nabla} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) = \vec{\nabla}\left(\vec{\nabla}.\overrightarrow{A}\right) - \nabla^2\vec{\mathrm{A}}$$

Hence the proof.

The formal proof is given below.

The ith component $\vec{\nabla} \times \left(\vec{\nabla} \times \overrightarrow{A}\right)$ is

$$\varepsilon_{ijk}\partial_j\left(\vec{\nabla} \times \overrightarrow{A}\right)_k = \varepsilon_{ijk}\partial_j(\varepsilon_{klm}\partial_l A_m)$$
$$= \varepsilon_{kij}\varepsilon_{klm}\partial_j(\partial_l A_m)$$

$$= \left(\partial_{im}\partial_{jl} - \partial_{im}\partial_{jl}\right)\partial^2{}_{jl}A_m$$

$$= \partial_m\partial_i\partial_m - \left(\partial_j\partial_j\right)A_i$$

$$\vec{\nabla} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) = \vec{\nabla}\left(\vec{\nabla} . \overrightarrow{A}\right) - \nabla^2\vec{A}$$

or we may prove it as

$$\hat{\imath}\,\partial_x \times \left(\vec{\nabla} \times \overrightarrow{A}\right) = \partial_x \times \left(\vec{\nabla}A_x \times \partial_x\overrightarrow{A}\right)$$

$$= \vec{\nabla}(\partial_x A_x) - \partial_x\partial_x\overrightarrow{A}$$

$$\vec{\nabla} \times \left(\vec{\nabla} \times \overrightarrow{A}\right) = \sum \hat{\imath}\,\partial_x \times \left(\vec{\nabla} \times \overrightarrow{A}\right)$$

$$= \vec{\nabla} \times \left(\vec{\nabla} . \overrightarrow{A}\right) - \nabla^2\vec{A}$$

9.5 Vector Integration

Line Integrals

Let c be a given curve which is given by $\vec{r}(u) = x(u)\hat{\imath} + y(u)\hat{\jmath} + z(u)\hat{k}$ where u is a parameter, from point P_1 to Point P_2.

Let A be vector function defined and having continues derivative along c. Then the line Integral of $\overrightarrow{A}$ from P_1 to P_2 is denied as

$$\int_{P_1}^{P_2} \overrightarrow{A} \,.dx\,\vec{r} = \int_c (A_1 dx + A_2 dy + A_3 dz)$$

Surface Integrals

A typical surface integral is of the form $\int() \, ds$ where ( ) may be either vector functions or scalar functions and the integral is over a given surface. If the surface of integration is not a plane surface parallel to the coordinate planes, we may project the surface of integration planes and perform the integration.

For definiteness let us consider a surface of integration in the first quadrant and project the surface onto xy the plane. Take any element any Δs of area, its projection into

xy-plane is $\frac{\Delta x\,\Delta y}{|\hat{n}\ .\ \hat{k}|}$ where $\hat{n}$ is the unit vector normal to the surface at the location of Δs. Thus, dx the integral $()\ ds$ reduces to $\int() \frac{dx\,dy}{|\hat{n}\ .\ \hat{k}|}$ the integration being in the $x - y$ plane.

Volume Integrals

Vector volume integrals are typically of the form $\int \vec{A}\ dv\ or\ \int \phi\, dv$, where $\vec{A}$ and ϕ are vector and scalar function respectively.

9.6 Transformation of Multiple Integrals

We are required to evaluate the double integrals $\int_R\ (x, y)dx\ dy.$

This can also be evaluated by considering a grid formed by a family of u and v curvilinear on R. A small region is ΔR which is equal to $\left|\left(\frac{\partial \vec{r}}{\partial u} \times \frac{\partial \vec{r}}{\partial v}\right)\right|\ du\ dv$ at the location (x, y) or equivalently (u, v)

$$\frac{\partial \vec{r}}{\partial u} \times \frac{\partial \vec{r}}{\partial v} = \begin{vmatrix} \hat{\imath}\hat{\jmath}\hat{k} \\ \frac{\partial x}{\partial u}\frac{\partial x}{\partial v}\ \ 0 \\ \frac{\partial y}{\partial u}\frac{\partial y}{\partial v}\ \ 0 \end{vmatrix} = \frac{\partial\ (x, y)}{\partial\ (u, v)}\hat{k}$$

So, $\int_R\ (x, y)dx\ dy$ is transformed into

$$\int_R\ F\ \{x\ (u, v), y\ (u, v)\} \left|\frac{\partial\ (x, y)}{\partial\ (u, v)}\right| du\ dv$$

Over a region R' which is mapped under the transformation $x\ =\ x\ (u, v), y\ =\ y\ (u, v).$

Similarly, for triple integrals it is transformed into $\int (u, v, w)$

$$\int_R (x,y,z)dx\ dy\ dz$$

$$\rightarrow \int_{R'} F\{x(u,v,w), y(u,v,w), z(u,v,w)\} \left|\frac{\partial(x,y,z)}{\partial(u,v,w)}\right| du\ dv\ dw$$

Integral Theorems

The Gauss's Divergence Theorem

If $\overrightarrow{A}$ is a vector function of position with continuous derivaties then $\int_V \vec{\nabla} \cdot \vec{A}\ dV = \int_S \overrightarrow{A} \cdot \hat{n}\ ds$ where V is the volume bounded by a closed s and $\hat{n}$ is the positive (outward) normal to s.

Stokes' Theorem

If S is an open, two sided surface bounded by a closed non intersecting curve C (simple closed curve) and $\overrightarrow{A}$ is a vector function having continuous derivatives, then

$$\oint_c \overrightarrow{A} \cdot d\overrightarrow{r} = \int_s \vec{\nabla} \times \overrightarrow{A}\hat{n}\ ds$$

The sense of direction of c is such that the surface area always lies to the left as one moves along the curve in that direction.

Green's Theorem

Let R be a closed region in the xy-plane bounded by a single closed curve C and M and N be continuous function of x and y, having continuous in R, then

$$\oint M\ dx + N\ dy + \int_R \left(\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y}\right) dx\ dy$$

Theorem (Green's first identity)

If ϕ and Ψ are scalar functions sufficiently differentiable then

$$\int_v \left(\phi\vec{\nabla}^2\Psi + \vec{\nabla}\phi.\vec{\nabla}\Psi\right)dV = \int_s \phi\vec{\nabla}\Psi.d\vec{s}$$

Proof We know

$$\vec{\nabla}.\left(\phi\vec{\nabla}\Psi\right) = \vec{\nabla}\phi.\vec{\nabla}\Psi + \phi\nabla^2\Psi$$

Integrating over a volume V and using the divergence theorem,

$$\int_s \phi\vec{\nabla}\Psi.d\vec{s} = \int_v (\phi\nabla^2\Psi + \vec{\nabla}\phi\vec{\nabla}\Psi)\,dV$$

Theorem (Green's second identity)

If ϕ and Ψ are scalar functions sufficiently differentiable, then,

$$\int_v (\phi\,\nabla^2\Psi - \Psi\,\nabla^2\phi)dV = \int_s \left(\phi\vec{\nabla}\Psi - \Psi\vec{\nabla}\phi\right).d\vec{s}$$

Proof Let us take div $(\phi\nabla\Psi - \Psi\nabla\phi)$

$$\vec{\nabla}.\left(\phi\vec{\nabla}\Psi - \Psi\vec{\nabla}\phi\right) = \phi\,\nabla^2\Psi - \Psi\,\nabla^2\phi$$

Integrating over a volume V and using the divergence theorem,

$$\int_s \left(\phi\vec{\nabla}\Psi - \Psi\vec{\nabla}\phi\right).d\vec{s} = \int_v (\phi\,\nabla^2\Psi - \Psi\,\nabla^2\phi)dV$$

Example Prove that $\int_V \vec{\nabla}\phi\,dV = \int_s \phi\hat{n}\,ds$.

Sol. By the divergence theorem,

$$\int \vec{\nabla}.\left(\vec{A}\phi\right)dV \int \vec{A}\phi.d\vec{s}$$

Now let us take $\vec{A}$ to be a constant vector.

So, $$\int \vec{A}.\,\vec{\nabla}\phi\,dV = \vec{A}\int \phi\hat{n}\,ds$$

or $$\overrightarrow{A}.\int \vec{\nabla}\phi\, dV = \overrightarrow{A}.\int \phi\hat{n}\ ds$$

$\overrightarrow{A}$ is an arbitrary vector

So, $$\int \vec{\nabla}\phi\, dV = \int \phi\hat{n}\ ds$$

Example Prove $\int_V \vec{\nabla} \times \overrightarrow{B}\, dV = \int_s \hat{n} \times \overrightarrow{B}\ ds$

Sol. Using the divergence theorem

$$\int \vec{\nabla}\,(\overrightarrow{B} \times \overrightarrow{C})\, dV = \int (\overrightarrow{B} \times \overrightarrow{C}).ds$$

Now let us take C to be a constant vector

So,

$$\int \vec{C}\ .\ \vec{\nabla} \times \overrightarrow{B}\, dV = \int \overrightarrow{C}.ds \times \overrightarrow{B}$$

or

$$\vec{C}\int \vec{\nabla} \times \overrightarrow{B}\, dV = \vec{C}\int \hat{n} \times \overrightarrow{B}\, ds$$

Since $\overrightarrow{C}$ is arbitrary

$$\int_V \vec{\nabla} \times \overrightarrow{B}\, dV = \int_s \hat{n} \times \overrightarrow{B}\, ds$$

Using the two examples we may define gradient ϕ and cur of a vector in a coordinate free form

$$\vec{\nabla}\phi = \lim_{\Delta v \to 0} \frac{\int_s \phi\hat{n}\, ds}{\Delta V}$$

$$\vec{\nabla} \times \overrightarrow{A} = \lim_{\Delta v \to 0} \frac{\int \hat{n} \times \overrightarrow{A}\, ds}{\Delta V}$$

In fact, the divergence theorem and Stokes's theorem be used (and are used) to define divergence and curl vector in a coordinate free form

$$\vec{\nabla}.\ \overrightarrow{A} = \lim_{\Delta v \to 0} \frac{\int_{\nabla s} \overrightarrow{A}\ .\ \hat{n}\, ds}{\Delta \nabla V}$$

where Δs is a closed surface bounding ∇V.

$$\hat{n}\ (\vec{\nabla} \times \overrightarrow{A}) = \lim_{\Delta s \to 0} \frac{\int_c \overrightarrow{A}\,.dt}{\Delta s}$$

where c is a closed single curve bounding Δs and $\hat{n}$ is normal to Δs.

Example Prove that $\oint_c \ \phi\, d\overrightarrow{r} = \int_s \ d\,\overrightarrow{s} \times \vec{\nabla}\phi$

Sol. Using Stokes' theorem

$$\oint_c \overrightarrow{A}\,\phi\,.\ d\overrightarrow{r} = \int_s \ \vec{\nabla} \times (\vec{\mathrm{A}}\phi)\,.d\overrightarrow{s}$$

Now let us take $\vec{\mathrm{A}}$to be constant vector.

$$\overrightarrow{A} \oint_c \ \phi\ d\overrightarrow{r} = \int_s \ \vec{\nabla}\phi \times \overrightarrow{A}\,.d\overrightarrow{s}$$

$$\overrightarrow{A}\ .\ \int_s \ d\,\overrightarrow{s} \times \vec{\nabla}\phi$$

Since $\overrightarrow{A}$ is arbitrary

$$\oint_c \ \phi\ d\overrightarrow{r} = \int_s \ d\,\overrightarrow{s} \times \vec{\nabla}\phi$$

Example Prove

$$\int_V \ \vec{\nabla}\phi\,.\ \vec{\mathrm{A}}dV = \int_s \ \phi\vec{\mathrm{A}}\ .\hat{n}\ ds - \int_V \ \phi\,.\ \vec{\nabla}\vec{\mathrm{A}}\,dV$$

Sol. We have,

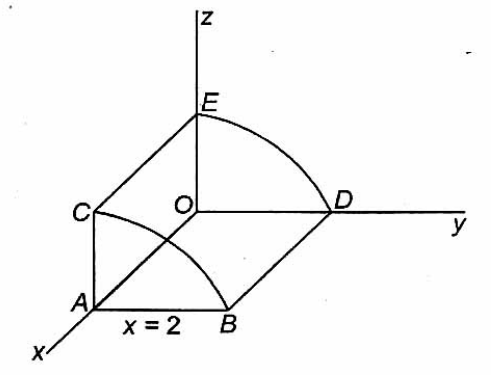
$$\vec{\nabla}\,.\left(\phi\vec{\mathrm{A}}\right) = \ \phi\vec{\nabla}\,.\,\overrightarrow{A} + \ \vec{\mathrm{A}}.\vec{\nabla}\phi$$

Integrating over a volume and using the divergence theorem,

$$\int_s \ \phi\vec{\mathrm{A}}\,.ds = \int_v \ \phi\vec{\nabla}\ .\ \overrightarrow{A}\ dV + \int \vec{\nabla}\phi\,.\ \vec{\mathrm{A}}\,dV$$

Example Verify the divergence theorem for $\overrightarrow{A} = \ 2x^2y\hat{\imath} - \ y^3\hat{\jmath} + \ 4xz^2\hat{k}$ taken over the first octant bounded by $y^2 + \ z^2 = 9$ and $x = 2.$

Sol. $\vec{\nabla} \cdot \overrightarrow{A} = 4xy - 2y + 8xz$



$$\int_V \vec{\nabla} \cdot \overrightarrow{A}\, dV = \int (4xy - 2y + 8xz)dx\, dy\, dz$$

$$= \int \left\{4xy - 2y)\ (z)_{z=0}^{z=\sqrt{9-y^2}} + 4x(z^2)_{z=0}^{z=\sqrt{9-y^2}}\right\} dx\, dy$$

$$= (2x^2 - 2x)\left\{2\int_0^3 y\sqrt{9 - y^2} + 2x^2\left\{2\int_0^3 (9 - y^2)dy\right.\right.$$

$$= 36 + 144 = 180.$$

Next let us evaluate the surface integral

$$\int \overrightarrow{A} \cdot \hat{n}\ d\vec{s}$$

$$\int_{ABC} \overrightarrow{A} \cdot \hat{n}\ ds = \int 2x^2 y\, dy\, dz = 8\int y\, dy\, dz$$

$$= 8\int_0^3 y\ \sqrt{9 - y^2}\ dy = 72$$

$$\int_{EOD} \overrightarrow{A} \cdot \hat{n}\ ds = -\int 2x^2 y\, dy\, dz = 0 \qquad since\ x = 0$$

$$\int_{ABDO} \overrightarrow{A} \cdot \hat{n}\ ds = -4\int zx^2\, dx\, dy = 0 \qquad since\ z = 0$$

$$\int_{CBDE} \overrightarrow{A} \cdot \hat{n}\ ds = \int y^2\, dx\, dz \qquad since\ y = 0$$

$$\int_{CBDE} \overrightarrow{A} \cdot \hat{n}\, ds = \int \overrightarrow{A} \cdot \frac{\left(v\hat{j} + z\hat{k}\right)}{3} \frac{dx\, dy}{\left|\hat{n} \cdot \hat{k}\right|}$$

$$= \int \frac{(-y^3 + 4xz^2)dx\, dy}{z}$$

$$= \int \frac{4x\,(9 - y^2)^{\frac{3}{2}} - y^3}{\sqrt{9 - y^2}}\, dx\, dy$$

$$= \int 4x\,(9 - y^2)dx\, dy - \int_0^3 \frac{y^3}{\sqrt{9 - y^2}}\, dx\, dy$$

$$= 144 - 36 = 108$$

So,

$$\int_z \overrightarrow{A} \cdot \hat{n}\, ds = 72 + 108 = 180.$$

Hence $\int_V \vec{\nabla} . \overrightarrow{A}\, dV = \int_s \overrightarrow{A} \cdot \hat{n}\, ds$

The divergence theorem is thus verified.

Example Using the divergence theorem, show that the volume V of a region R bounded by a surface S is $V = \int_s x\, dy\, dz = \int_s dz\, dx = \int_s z\, dx\, dy$

$$= \frac{1}{3}\int (x\, dy\, dz + y\, dz\, dx + z\, dx\, dy)$$

Sol. We know $dx\, dy = ds\, \hat{n} \cdot \hat{k} = \hat{k} \cdot d\vec{s}$

Therefore $x\, dy\, dz = x\, \hat{\imath} \cdot d\vec{s}$

Using the divergence theorem

$$\int_s x\, \hat{\imath} \cdot d\vec{s} = \int \vec{\nabla} \cdot (x\, \hat{\imath}) dV = \int dV = V$$

Similarly $\int y\, \hat{\jmath} \cdot d\vec{s} = V$

And $\int z\, \hat{k} \cdot d\vec{s} = V$

or $$3V = \int \vec{r} \,.\, ds$$

or $$V = \frac{1}{3}\int_s (x\, dy\, dz + y\, dz\, dx + z\, dx\, dy)$$

Example Evaluate

$$\int_s x^2\, dy\, dz + y^2\, dz\, dx + 2z\,(xy - x - y) dx\, dy$$

where S is the surface of the cube, $0 \le x \le 1, 0 \le y \le 1, 0 \le z \le 1$

Sol. Let $\vec{A} = x^2\hat{\imath} + y^2\hat{\jmath} + 2z\,(xy - x - y\,)\hat{k}$

$$\int_s \vec{A}.ds = \int x^2\, dydz + y^2 dzdx + 2z(xy - x - y)dxdy$$

By the divergence theorem

$$\int_s \vec{A}.ds = \int \vec{\nabla}.\vec{A}\, dv$$

$$= \int \{2x + 2y + 2(xy - x - y)\} dv$$

$$= \int 2xy\, dx\, dy\, dz$$

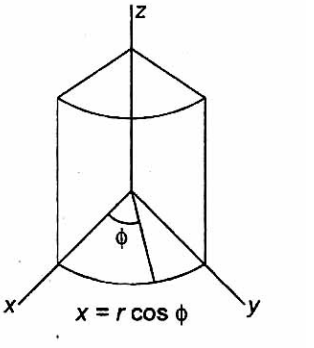
$$= x^2 \left\{ {}_0^1 \frac{x^2}{2} \right\{ {}_0^1 z \left\{ {}_0^1 = \frac{1}{2} \right.$$

Example Evaluate

$$\int_s (x^3\, dy\, dz + x^2\, y\, dz\, dx + x^2 z\, dx\, dy)$$

where S is the closed surface bounded by the planes $z = 0, z = b$ and $x^2 + y^2 = a^2$.

Sol. $\int_s (x^3\, dy\, dz + x^2\, y\, dz\, dx + x^2 z\, dx\, dy)$



$$\int (3x^2 + x^2 + x^2)\, dV$$

$$= 5 \int x^2\, dV \qquad \text{by divergence theorem}$$

$$= 5 \int x^2\, dx\, dy\, dz$$

$$= 5 \int x^2\, dx\, dy\, b$$

$$= 5b \int r^2 cos^2\phi\, r\, dr\, d\phi$$

$$= 5b \int_0^a r^3\, dr \int_0^{\frac{\pi}{2}} cos^2\phi\, d\phi$$

$$= 5b\, \frac{a^4}{d} \cdot \frac{\pi}{4} = \frac{5\pi}{16} a^4 b$$

Example Prove that $\oint_c \phi\, d\vec{r} = \int_s d\vec{s} \times \vec{\nabla}\phi$

Sol. By Stokes' theorem

$$\int_s \vec{\nabla} \times \vec{A}\,.\, \hat{n}\, ds = \oint_c \vec{A}\,.\, d\,\vec{r}$$

Let $\vec{A} = \phi\vec{C}$ where $\vec{C}$ is a constant vector

$$\vec{\nabla} \times \vec{A} = \vec{\nabla}\phi \times \vec{C}$$

So, $$\int \vec{\nabla}\,\phi \times \vec{C}\,.\, d\,\vec{s} = \oint \phi\vec{C}\,.\, d\,\vec{r}$$

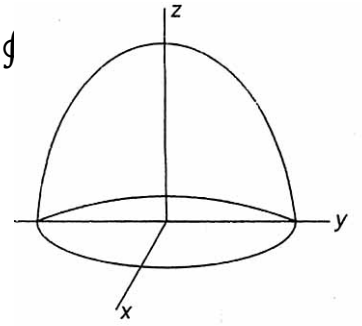
or $$\vec{C}.\int_s d\,\vec{s} \times \vec{\nabla}\phi = \vec{C}.\oint_s \phi\, d\,\vec{r}$$

$\vec{C}$ is an arbitrary vector.

Hence, $$\int_s d\,\vec{s} \times \vec{\nabla}\phi = \oint_c \phi\, d\,\vec{r}$$

Example Verify Stokes' theorem for $\overrightarrow{A} = y\hat{\imath} + z\hat{\jmath} + x\hat{k}$ and S is the upper half of the sphere $x^2 + y^2 + z^2 = 1$ and C is its boundary.

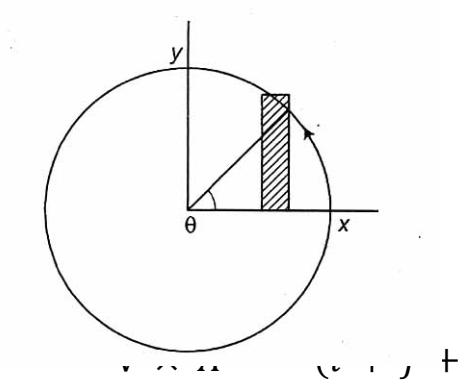
Sol. $\oint \vec{A} \cdot d\vec{r} = \oint$



$$= \oint y\, dx \qquad since\ z = 0$$

$$= \int_0^{2\pi} \sin\theta\ (\cos\theta)$$

$$= -\int_0^{2\pi} sin^2\,\theta\, d\theta = -\pi$$



$+ \hat{k})$

On the plane circular area of radius I

$$\int_S \vec{\nabla} \times \overrightarrow{A} \cdot \hat{n}\, ds = -\int dx\, dy = -\pi$$

Hence, the theorem is verified.

Green's Theorem in the Plane

$\oint M\,dx + N\,dy = \int_S \left(\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y}\right) dx\,dy$ is a special case of Stokes' theorem when the surface of integration over the $x - y$ plane.

Example Evaluate using Green's theorem $\oint_c (xy + y^2)\,dx + x^2\,dy$ where c is the closed cury bounded by $y = x, y = x^2$.

Sol. $\oint (xy + y^2)dx + x^2\,dy$

$$= \int_s \left\{\frac{\partial x^2}{\partial x} - \frac{\partial (xy + y^2)}{\partial y}\right\} dx\,dy$$

$$= \int \{2x - (x + 2y)\}dx\,dy = \int_s (x - 2y)\,dx\,dy$$

$$= \int (xy - y^2)\begin{cases} y = x \\ y = x^2 \end{cases} dx$$

$$= \int_{x-0}^{x=1} (x^4 - x^3)\,dx = -\frac{1}{2}$$

Also, $\oint (xy + y^2)dx + x^2 dy = \int_0^1 (x.x^2 + x^4)dx + x^2\,2x\,dx + \int_1^0 (x\,.\,x + x^2)dx + x^2\,dx = \frac{19}{20} - 1 = -\frac{1}{20}$

Example Show that the area bounded by simple closed curve c is given by

$$\frac{1}{2}\oint_c (x\,dy - y\,dx)$$

Sol. By Green's theorem in the plane

$$\oint_c M\,dx + N\,dy = \int_s \left(\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y}\right) dx\,dy$$

Let $M = -y, N = x$

So, $\int x\,dy - y\,dx = 2\int dx\,dy$

So, area $= \frac{1}{2}\oint (x\,dy - y\,dx)$

If we choose $M = 0, N = x$

then $\oint x\, dy = \int dx\, dy$

or area $= \oint x\, dy$

$$= \int_s \left\{ \frac{\partial(-2xy)}{\partial x} - \frac{\partial(x^2 + y^2)}{\partial y} \right\} = -4 \int y\, dx\, dy$$

$$= -2y^2 \Big|_{y=0}^{b} x \Big|_{-a}^{a} = -4ab^2$$

9.7 Different Types of Coordinate Systems

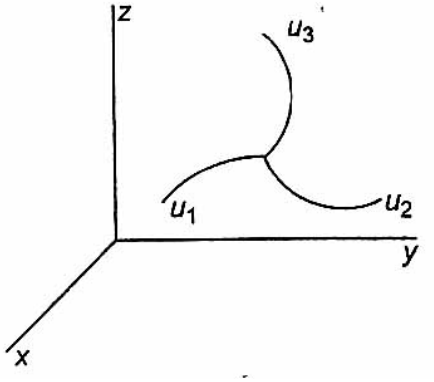
Curvilinear Coordinates

A point is defined by giving the rectangular coordinates (x, y, z) in the usual rectangular coordinate system. Sometimes it is more convenient and more natural to use other systems of coordinates than rectangular. Let $u_1 = u_1(x, y, z), u_2 = u_2(x, y, z), u_3 = u_3(x, y, z).$

These may be solved for x, y, z.

$$x = x\,(u_1, u_{2,} u_3), y = y\,(u_1, u_{2,} u_3), z = z\,(u_1, u_{2,} u_3)$$

Thus a point may be equally described by $(u_1, u_{2,} u_3)$coordinates. Just as the entire space may be filled by grids x = constant, y = constant, z = constant surfaces, the entire space may be assumed to be filled by the surfaces, u_1= constant, u_2 = constant, u_3 = consta[illegible] l case when the surfaces are mutually orthogonal.



The surface say $u_1 = c$, there exist two sets of unit vectors, one tangential to the surface given by $\frac{\partial \vec{r}}{\partial u_1} = h_1 \hat{e}_1$ and other, normal to the surface.

$\hat{E}_1 = \frac{\vec{\nabla} u_1}{|\vec{\nabla} u_1|}$ Any vector may be expanded in terms of $\hat{e}$.

Let $d\vec{r} = \frac{\partial r}{\partial u_1} du_1 + \frac{\partial \vec{r}}{\partial u_2} du_2 + \frac{\partial \vec{r}}{\partial u_3} du_3$

$= h_1 du_1 \hat{e}_1 + h_2 du_2 \hat{e}_2 + h_3 du_3 \hat{e}_3$

where $h_i = \left|\frac{\partial \vec{r}}{\partial u_1}\right|$ called scale factor.

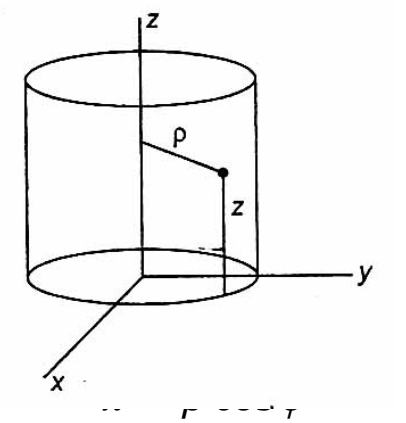
For orthogonal systems, an element of length dl is given by

$$dl^2 = h_1^2 du_1 + h_2^2 du_2 + h_3^2 du_3$$

and volume element dV

$$dV = h_1 h_2 h_3 du_1 du_2 du_3$$

Cylindrical coordinate system is defined by the transformation

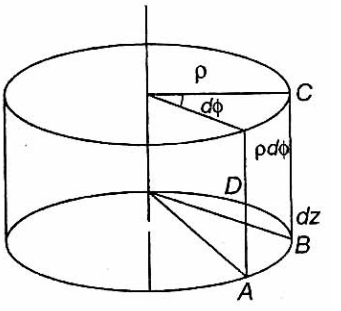


$$y = \rho \sin \phi$$

$$z = z$$

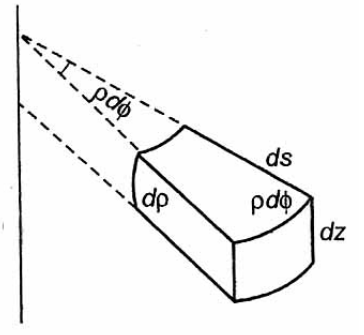
where $0 \leq \phi \leq 2\pi$ ρ is the distance of any point from the z −axis, ϕ is the angle rotated from the x −axis, and z is the height above the xy −plane. Using the figure, it is easily seen that an element of ds is given by

$$ds = AB \,.AD = \rho \, d\phi \, dz = \rho \, d\phi \, dz$$



and an element of volume is

$$dV = d\rho \, \rho \, d\phi \, dz = \rho \, d\rho \, d\phi \, dz$$



or formally as

$$dl^2 = dx^2 + dy^2 + dz^2$$

Since

$$x = \rho \cos\phi$$

$$y = \rho \sin\phi$$

$$z = z$$

$$dx = -\rho \sin\phi \; d\phi + \cos\phi \, d\phi$$

$$dy = \rho \cos\phi \; d\phi + \sin\phi \; dl$$

$$dz = dz$$

$$dl^2 = (d\rho)^2 + \rho^2 (d\phi)^2 + dz^2$$

So,

$$h_v = 1, \; h_\phi = \rho, \; h_z = 1$$

So, $$d\vec{r} = \hat{e}_\rho \, d\rho + \rho \, \hat{e}_\phi \, d\phi + \hat{e}_z \, dz$$

So, $$dV = \rho \; d\rho \; d\phi \; dz$$

Next we find the unit tangent vectors.

$$\hat{e}_\rho = \frac{1}{h_\rho}\frac{\partial \vec{r}}{\partial \rho} \; , \quad \hat{e}_\phi = \frac{1}{h_{\phi\rho}}\frac{\partial \vec{r}}{\partial \phi} \; , \qquad \hat{e}_z = \frac{1}{h_z}\frac{\partial \vec{r}}{\partial z}$$

$$\vec{r} = \rho \cos\phi \hat{\imath} + \rho \sin\phi \hat{\jmath} + z\,\hat{k}$$

$$\frac{\partial \vec{r}}{\partial \rho} = (\cos\phi \hat{\imath} + \sin\phi \hat{\jmath} + \hat{e}_\rho = \hat{\rho}$$

$$\therefore \frac{\partial \vec{r}}{\partial \phi} = \rho \, (-\sin\phi \hat{\imath} + \cos\phi \hat{\jmath} = \rho \; \hat{e}_\phi$$

$$\frac{\partial \vec{r}}{\partial z} = \hat{k} = \hat{e}_z$$

We may verify

$$\frac{d}{dt}\hat{e}_\rho = \phi \hat{e}_{\phi'} \qquad \frac{d}{dt}\hat{e}_\phi = \phi \hat{e}_{\phi\rho}$$

Spherical Coordinates

A spherical coordinate system is defined by

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

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

$$z = r\cos\theta$$

Hence, $\vec{r} = r\sin\theta\,(\cos\phi\hat{\imath} + \sin\phi\hat{\jmath}) + r\cos\theta\,\hat{k}$

$$= \frac{\partial \vec{r}}{\partial r} = \sin\theta\,(\cos\phi\hat{\imath} + \sin\phi\hat{\jmath}) + r\,\cos\theta\,\hat{k} = \hat{e}_r$$

$$= \frac{\partial \vec{r}}{\partial \theta} = r\,\{\cos\theta\,(\cos\phi\hat{\imath} + \sin\phi\hat{\jmath}) - \sin\theta\hat{k}\} = r\,\hat{e}_\theta$$

and

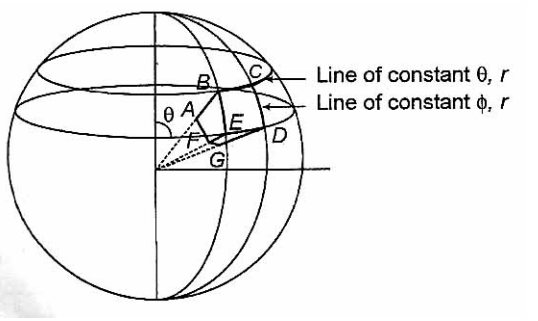
$$= \frac{\partial \vec{r}}{\partial \theta} = r\ \sin\theta\ (-\sin\phi\hat{\imath} + \cos\phi\hat{\jmath} = \ r\sin\theta\ \hat{e}_{\phi}$$

So, $h_r = 1, \quad h_\theta = r, \ \ h_\phi = r\sin\theta,$

So, $dl^2 = \ (dr)^2 + \ r^2(d\theta)^2 + \ r^2 sin^2\theta\ (d\phi)^2$

$$d_r = r^2\sin\theta\ dr\ d\theta\ d\phi$$

For greater clarity please refer to the figure given below



Clearly from the figure,

Area of $BCDE\ = \ r\ d\theta\ .r\sin\theta\ d\phi$

$$= \ r^2\sin\theta\ d\theta\ d\phi$$

Area of $ABEF\ = \ dr\ .r\ d\theta = r\ dr\ d\theta$

Area of $FEDG = \ dr\ .r\sin\theta\ \ d\phi = r\sin\theta\ \ dr\ d\phi$

And volume element $dV = AB\ \times area\ of\ BCDE$

$$= dr.r^2\sin\theta\ d\theta\ d\phi$$

$$dV = \ r^2\sin\theta\ dr\ d\theta\ d\phi$$

Gradient, Divergence and Curl in Curvilinear Orthogonal Coordinates

The Gradient

We start with

$$d\phi = \frac{\partial \phi}{\partial u_1} u_1 + \frac{\partial \phi}{\partial u_2} u_2 + \frac{\partial \phi}{\partial u_3} u_3$$

And $d\vec{r} = h_1 \hat{e}_1 du_1 + h_2 \hat{e}_2 du_2 + h_3 \hat{e}_3 du_3$

Also we know

$$d\phi = \vec{\nabla}\phi . \, d\vec{r}$$

If we write $\vec{\nabla}\phi = f_1 \hat{e}_1 + f_2 \hat{e}_2 + f_3 \hat{e}_3$

$$d\phi = \sum h_i f_i du_i$$

$$= \sum \frac{\partial \phi}{\partial u_1} \, du_1$$

Comparing $f_1 = \frac{1}{h_i} \frac{\partial \phi}{\partial u_1}$ $(no\ summation)$

Hence,

$$\vec{\nabla}\phi = \frac{1}{h_i} \frac{\partial \phi}{\partial u_1} \hat{e}_1 \qquad (Summation\ convention)$$

Using this we may $d\phi$ in cylindrical or spherical coordinate system as :

$$\vec{\nabla}\phi = \frac{\partial \phi}{\partial \rho} \hat{e}_\rho + \frac{1}{\rho} \frac{\partial \phi}{\partial \theta} \hat{e}_\theta + \frac{\partial \phi}{\partial z}$$

and $$\vec{\nabla}\phi = \frac{\partial \phi}{\partial r} \hat{e}_r + \frac{\partial \phi}{r \, \partial \theta} \hat{e}_\theta + \frac{1}{r \sin\theta \, \partial \phi} \frac{\partial \phi}{\partial \phi} \hat{e}_\phi$$

The Divergence

First we show that $\hat{e}_1 = h_2 h_3 \vec{\nabla} u_2 \times \vec{\nabla} u_3$

In the expression for gradient we put $\phi = u_1$

So, $$\vec{\nabla} u_1 = \frac{1}{h_1} \frac{\partial u_1}{\partial u_1} \hat{e}_1 \frac{\hat{e}_1}{h_1}$$

So, $$\hat{e}_1 = h_1 \vec{\nabla} u_1$$

Similarly for $\hat{e}_2$ and $\hat{e}_3$.

$$\vec{\nabla}u_2 \times \vec{\nabla}u_3 = \frac{1}{h_2 h_3}\hat{e}_2 \times \hat{e}_3 = \frac{\hat{e}_1}{h_2 h_3}$$

So, $$\hat{e}_1 = h_2 h_3 \vec{\nabla}u_2 \times \vec{\nabla}u_3$$

We first find $\vec{\nabla}.\ A_1\hat{e}_1$

$$\vec{\nabla}.\ A_1\hat{e}_1 = \vec{\nabla}.\left(A_1 h_2 h_3 \vec{\nabla}u_2 \times \vec{\nabla}u_3\right)$$

$$= \vec{\nabla}A_1 h_2 h_3 \left(\vec{\nabla}u_2 \times \vec{\nabla}u_3\right) + A_1 h_2 h_3 .\ \vec{\nabla}\left(\vec{\nabla}u_2 \times \vec{\nabla}u_3\right)$$

$$= \frac{1}{h_1 h_2 h_3}\frac{\partial(A_1 h_2 h_3)}{\partial u_1} + 0$$

$$\vec{\nabla}.\ A_1\hat{e}_1 = \frac{1}{h_1 h_2 h_3}\frac{\partial(A_1 h_2 h_3)}{\partial u_1}$$

So, $$\vec{\nabla}.\ A_1 = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial(A_1 h_2 h_3)}{\partial u_1} + \frac{\partial(A_2 h_3 h_1)}{\partial u_2} + \frac{\partial(A_3 h_1 h_2)}{\partial u_3}\right]$$

From this divergence and curl in cylindrical (or spherical) coordinates immediately follows

$$\vec{\nabla}.\overrightarrow{A} = \frac{1}{\rho}\frac{\partial(\rho A_\rho)}{\partial\rho} + \frac{\partial A_\phi}{\rho\partial\phi} + \frac{1}{\rho}\frac{\partial(\rho A_z)}{\partial z}$$

$$\vec{\nabla}.\overrightarrow{A} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2.\ A_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}$$

$$\left(\sin\theta\ \frac{\partial A_\theta}{\partial\theta}\right) + \frac{1}{r\sin\theta}\frac{\partial A_\phi}{\partial\phi}\quad respectively$$

The Curl

We first find $\vec{\nabla}\times\ A_1\hat{e}_1$

$$\vec{\nabla}\times A_1\hat{e}_1 = \vec{\nabla}\times A_1\, h_1\vec{\nabla}u_1 = \vec{\nabla}A_1\, h_1 \times\vec{\nabla}\, u_1$$

$$= \frac{\hat{e}_2}{h_3\, h_1}\frac{\partial(A_1\, h_1)}{\partial u_3} - \frac{\hat{e}_3}{h_1\, h_2}\frac{\partial(A_1\, h_1)}{\partial u_2}$$

Similarly for the other components

$$\vec{\nabla} \times \vec{\mathrm{A}} = \frac{1}{h_1\, h_2\, h_3}\begin{vmatrix} h_1\hat{e}_1 h_2\hat{e}_2 & h_3\hat{e}_3 \\ \partial_1\partial_2\partial_3 & \\ A_1\, h_1\, A_2\, h_2 A_3\, h_3 & \end{vmatrix}$$

The curl in cylindrical and spherical coordinates is respectively.

$$\vec{\nabla} \times \vec{\mathrm{A}} = \frac{1}{\rho}\left(\frac{\partial A_z}{\partial \phi} - \frac{\partial\left(\rho\, A_\phi\right)}{\partial z}\right)\hat{e}_\rho + \left(\rho\frac{\partial A_\rho}{\partial z} - \rho\,\frac{\partial(\rho\, A_z)}{\partial \rho}\right)\hat{e}_\phi + \left(\frac{\partial(A_\phi)}{\partial \rho} - \rho\,\frac{\partial\left(\rho\, A_\phi\right)}{\partial \phi}\right)\hat{e}_z$$

$$\vec{\nabla} \times \vec{\hat{\mathrm{e}}} = \frac{1}{r^2 \sin\theta}\left[\left\{\hat{e}_r + \frac{\partial A_r}{\partial \phi} - \frac{\partial}{\partial r}\,(r \sin\theta\, A_\phi)\right\} r\, \hat{e}_\theta + \left\{\frac{\partial}{\partial r}(r\, A_\theta) - \frac{\partial A_r}{\partial \theta}\right\}\right] \left\{\frac{\partial}{\partial \theta}\,(r \sin\theta\, A_\theta) - \frac{\partial}{\partial \phi}\,(r\, A_\theta)\right\} r \sin\theta\ \hat{e}_\phi]$$

Laplacian Operator

The Laplacian operator defined as $\vec{\nabla}\,.\,(\vec{\nabla}\phi)$

So,
$$\vec{\nabla}^2\phi = \vec{\nabla}\,.\vec{\nabla}\phi$$
$$= \vec{\nabla}.\left[\frac{1}{h_1}\frac{\partial\phi}{\partial u_1}\hat{e}_1 + \frac{1}{h_2}\frac{\partial\phi}{\partial u_2}\hat{e}_2 + \frac{1}{h_3}\frac{\partial\phi}{\partial u_3}\hat{e}_3\right]$$

So,

$$\vec{\nabla}^2 = \frac{1}{h_1 h_2 h_3}\left[\partial_1\left(\frac{h_2 h_3}{h_1}\partial_1\right)\partial_2\left(\frac{h_1 h_3}{h_2}\partial_{21}\right)\partial_3\left(\frac{h_1 h_2}{h_3}\partial_{13}\right)\right]$$

Hence, the Laplacian operator in cylindrical and spherical coordinates is given respectively as

$$\nabla^2 = \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial}{\partial \rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 sin^2\,\theta}\frac{\partial^2}{\partial \theta^2}$$

9.8 Self Assessment Test

1. Write down Greens theorem and derive Greens first and second identity.

2. Write Gradient, Divergence and curl in spherical coordinate.

9.9 Reference Books

1. Schaum's Outline of Vector Analysis, 2ed by Murray Spiegel, Seymour Lipschutz.

2. Mathematical Physics with Classical Mechanics by Satya Prakash.

3. Mathematical Physics by H.K. Das.

Unit-10: Matrices

Structure of Unit:

10.1 Introduction

The term matrix was apparently coined by Sylvester about 1850, but was introduced by Cayley in 1860. There is rich and wide theory of matrices which has a broad area of applications to the real world. Matrices find application in solution of system of linear equations, probability, and quantum mechanics etc. In this chapter we will discuss the basic concepts and types of matrices and some important matrix operations which will help to the reader to understand further application of matrices.

10.2 Matrix Algebra

Linear algebra includes the theory and application of linear systems of equations, vector spaces, inner product spaces & eigen value problems, as they arise, for instance, from electrical networks, Fourier analysis, frame works in machine, curve fitting etc. The central problem of linear algebra is the solution of linear equations. Linear algebra makes systematic use of matrices and vectors and to a lesser extent, determinants. This requires the study of properties of matrices as a central task by itself.

10.2.1 Matrix : A Matrix is a rectangular array of numbers enclosed in brackets. These numbers are called elements or entries of matrix.

Example 1: $\begin{bmatrix}1 & 2\\3 & 4\end{bmatrix}, \begin{bmatrix}5\\6\end{bmatrix}, [x_1 \quad x_2 \quad x_3], \begin{bmatrix}Sinx & Cosx\\-Cosx & Sinx\end{bmatrix}$

The size or order of matrix is described in terms of rows(horizontal lines) & columns(vertical lines).

Example 2: $\begin{bmatrix}1 & 1 & 2\\3 & 1 & 2\end{bmatrix}$ It has 2 rows and 3 columns. So its order is 2x3.

Example 3 : $\begin{bmatrix}1 & 4\\5 & 6\end{bmatrix}$ It has 2 rows and 2 columns. So its order is 2x2or called square matrix.

A matrix having same no. of rows and columns is called ***Square Matrix***.

10.2.2 Operations on Matrix : For applications of matrices, it is desirable to develop an "arithmetic of matrices" in which matrices can be added, subtracted and multiplied.

$A = [a_{ij}] = \begin{bmatrix}a_{11} & a_{12} \ldots . & a_{1m}\\a_{21} & a_{22} \ldots . & a_{2m}\\a_{n1} & a_{n2} \ldots . & a_{nm}\end{bmatrix}$ i = 1,2,….n&j = 1,2,….m

This is basic notation, where "n" denotes the number of rows and "m" denotes number of columns.

[I] Matrix Addition : Addition of matrices $A = [a_{ij}]$ and $B = [b_{ij}]$ is possible if and only if A=B, i.e. order of both matrices is the same. Then addition is obtained by adding corresponding entries of both matrices.

For example:

(1) $A = \begin{bmatrix}1 & 1\\a_{ij} & a_{ij}\\2 & 1\\a_{ij} & a_{ij}\end{bmatrix}, B = \begin{bmatrix}3 & 1\\b_{ij} & b_{ij}\\4 & 1\\b_{ij} & b_{ij}\end{bmatrix}$

$$A + B = \begin{bmatrix}a_{ij}+b_{ij} & a_{ij}+b_{ij}\\1+3 & 1+1\\2+4 & 1+1\\a_{ij}+b_{ij} & a_{ij}+b_{ij}\end{bmatrix} = \begin{bmatrix}4 & 2\\6 & 2\end{bmatrix}$$

(2) $A = \begin{bmatrix}1 & 1 & 3\\5 & 1 & 2\\4 & 1 & 3\end{bmatrix}$ $B = \begin{bmatrix}1 & 2\\3 & 1\end{bmatrix}$

A + B is not defined because order of A is 3*3 and of B is 2*2.

(3) C = $\begin{bmatrix}1 & 2 & 3\end{bmatrix}$ D = $\begin{bmatrix}4 & 5 & 6\end{bmatrix}$

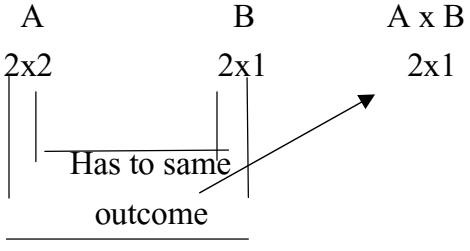
C + D = $\begin{bmatrix}1+4 & 2+5 & 3+6\end{bmatrix} = \begin{bmatrix}5 & 7 & 9\end{bmatrix}$

Matrix Multiplication : Multiplication or product of two matrices is possible if and only if, number of columns of first matrix in multiplication is equal to number of rows of second matrix in multiplication order. That is, let order of A is m x n and order of B is l x r, then multiplication AB is possible if and only if n=l and result of AB if m x r.

Example 4 : Consider A = $\begin{bmatrix}1 & 2\\ 3 & 1\end{bmatrix}$ B = $\begin{bmatrix}1\\ 3\end{bmatrix}$ Find A x B?

Solution : Since order of A is 2x2 and of B is 2x1. So A x B is possible and outcome will be 2 x 1.

Lets check it by flow chart.



A x B = $\begin{bmatrix}1 & 2\\ 3 & 1\end{bmatrix}\begin{bmatrix}1\\ 3\end{bmatrix} = \begin{bmatrix}1*1 & + & 2*3\\ 3*1 & + & 1*3\end{bmatrix} = \begin{bmatrix}7\\ 6\end{bmatrix}$

(1) A = $\begin{bmatrix}a_{11}=1 & a_{12}=1 & a_{13}=2\\ a_{21}=3 & a_{22}=1 & a_{23}=2\\ a_{31}=2 & a_{23}=3 & a_{33}=1\end{bmatrix}$ B = $\begin{bmatrix}b_{11}=1 & b_{12}=2\\ b_{21}=2 & b_{22}=3\\ b_{31}=1 & b_{32}=3\end{bmatrix}$

Since order of A is 3x3 and of B is 3x2. So, AxB is possible and outcome is of the order 3x2.

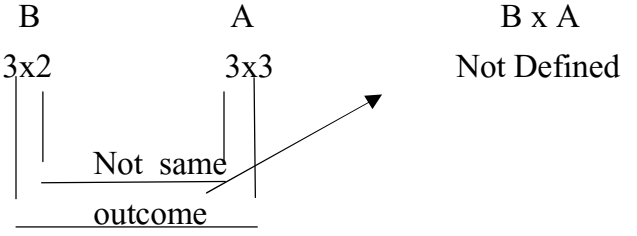
AxB = $\begin{bmatrix}1 & 1 & 2\\ 3 & 1 & 2\\ 2 & 3 & 1\end{bmatrix}$ x $\begin{bmatrix}1 & 2\\ 2 & 3\\ 1 & 3\end{bmatrix}$

=

$\begin{bmatrix}a_{11}=1*b_{11}=1+a_{12}=1*b_{21}=2+a_{13}=2*b_{31}=1 & a_{11}=1*b_{12}=2+a_{12}=1*b_{22}=3+a_{13}=2*b_{32}\\ a_{21}=3*b_{11}=1+a_{22}=1*b_{21}=2a_{23}=2*b_{31}=1 & a_{21}=3*b_{12}=2+a_{22}=1*b_{22}=3+a_{23}=2*b_{32}\\ a_{31}=2*b_{11}=1+a_{32}=3*b_{21}=2+a_{33}=1*b_{31}=1 & a_{31}=2*b_{12}=2+a_{32}=3*b_{22}=3+a_{33}=1*b_{32}\end{bmatrix}$

$$= \begin{bmatrix} 1+2+2 & 2+3+6 \\ 3+2+2 & 6+3+6 \\ 2+6+1 & 4+9+3 \end{bmatrix} = \begin{bmatrix} 5 & 11 \\ 7 & 15 \\ 9 & 16 \end{bmatrix}$$

But for same equation B x A is not satisfied.



10.3 Inverse of a Matrix

Let A = $\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$ be 3*3 matrix, so its inverse is obtained as follows:

10.3.1 Minor of an element of a matrix :

$$\det(A) = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

Then minor of all elements of A are as follows:

Minor of $a_{11} = \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix}$, Minor of $a_{21} = \begin{vmatrix} a_{12} & a_{13} \\ a_{32} & a_{33} \end{vmatrix}$, Minor of $a_{31} = \begin{vmatrix} a_{12} & a_{13} \\ a_{22} & a_{23} \end{vmatrix}$

Minor of $a_{12} = \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix}$, Minor of $a_{22} = \begin{vmatrix} a_{11} & a_{13} \\ a_{31} & a_{33} \end{vmatrix}$, Minor of $a_{32} = \begin{vmatrix} a_{11} & a_{13} \\ a_{21} & a_{23} \end{vmatrix}$

Minor of $a_{13} = \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$, Minor of $a_{23} = \begin{vmatrix} a_{11} & a_{12} \\ a_{31} & a_{32} \end{vmatrix}$, Minor of $a_{33} = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}$

10.3.2 Cofactor of an element of a Matrix :

Cofactor of an element a_{ij} of a determinant is the minor multiplied by $(-1)^{i+j}$

Cofactor of $a_{11} = (-1)^{1+1}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} = A_{11}$, Cofactor of $a_{21} = (-1)^{2+1}\begin{vmatrix} a_{12} & a_{13} \\ a_{32} & a_{33} \end{vmatrix} = A_{21}$,

Cofactor of $a_{12} = (-1)^{1+2}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} = A_{12}$, Cofactor of $a_{22} = (-1)^{2+2}\begin{vmatrix} a_{11} & a_{13} \\ a_{31} & a_{33} \end{vmatrix} = A_{22}$,

Cofactor of $a_{13} = (-1)^{1+3}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix} = A_{13}$, Cofactor of $a_{23} = (-1)^{2+3}\begin{vmatrix} a_{11} & a_{12} \\ a_{31} & a_{32} \end{vmatrix} = A_{23}$,

Cofactor of $a_{31} = (-1)^{3+1}\begin{vmatrix} a_{12} & a_{13} \\ a_{22} & a_{23} \end{vmatrix} = A_{31}$, Cofactor of $a_{32} = (-1)^{3+2}\begin{vmatrix} a_{11} & a_{13} \\ a_{21} & a_{23} \end{vmatrix} = A_3$

Cofactor of $a_{33} = (-1)^{3+3}\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = A_{33}$

10.4 Adjoint of a Matrix

The matrix obtained by cofactors of elements of matrix A is as follows:

$$\text{Cofactor (A)} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix}$$

The matrix obtained by taking transpose (i.e. Converting rows into columns) of above matrix Cofactor(A) is called adjoint of A.

$$\text{adjA} = \begin{bmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{bmatrix}$$

Example 5 : Find adjoint of the Matrix A = $\begin{bmatrix} 2 & 3 & 1 \\ 1 & 2 & 3 \\ 3 & 1 & 2 \end{bmatrix}$

Solution: The cofactors of elements of A are:

$A_{11} = (-1)^{1+1}\begin{bmatrix} 2 & 3 \\ 1 & 2 \end{bmatrix} = 1$, $A_{12} = (-1)^{1+2}\begin{bmatrix} 1 & 3 \\ 3 & 2 \end{bmatrix} = 7$

$A_{13} = (-1)^{1+3}\begin{bmatrix} 1 & 2 \\ 3 & 1 \end{bmatrix} = -5$, $A_{21} = (-1)^{2+1}\begin{bmatrix} 3 & 1 \\ 1 & 2 \end{bmatrix} = -5$

$A_{22} = (-1)^{2+2}\begin{bmatrix} 2 & 1 \\ 3 & 2 \end{bmatrix} = 1$, $A_{23} = (-1)^{2+3}\begin{bmatrix} 2 & 3 \\ 3 & 1 \end{bmatrix} = -7$

$A_{31} = (-1)^{3+1}\begin{bmatrix} 3 & 1 \\ 2 & 3 \end{bmatrix} = 7$, $A_{32} = (-1)^{3+2}\begin{bmatrix} 2 & 1 \\ 1 & 3 \end{bmatrix} = -5$

$A_{33} = (-1)^{3+3}\begin{bmatrix} 2 & 3 \\ 1 & 2 \end{bmatrix} = 1$

$$\text{Cofactor(A)} = \begin{bmatrix} 1 & 7 & -5 \\ -5 & 1 & 7 \\ 7 & -5 & 1 \end{bmatrix} 3$$

$$\text{Adj(A) = Transpose of Cofactor(A)imply (Cofactor A)}^{T} = \begin{bmatrix} 1 & -5 & 7 \\ 7 & 1 & -5 \\ -5 & 7 & 1 \end{bmatrix}.$$

10.5 Transpose of a matrix

Let A = $\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$, so transpose of A is obtained by writing rows as columns or columns as rows. It is denoted by A^T.

Example 6 : Obtain transpose of matrix A = $\begin{bmatrix} 1 & 2 & 3 \\ 2 & 3 & 4 \\ 6 & 1 & 7 \end{bmatrix}$

Solution: Transpose of any matrix is obtained by writing columns of a matrix as rows or rows as columns.

Trans(A) = $\begin{bmatrix} 1 & 2 & 6 \\ 2 & 3 & 1 \\ 3 & 4 & 7 \end{bmatrix}$ = A^T

Inverse of matrix A by determinant method: It is obtained by $A^{-1} = \frac{1}{\det(A)}\ adj\ A$

Theorem 1 : The necessary and sufficient condition for a square matrix A to possess an inverse is that det(A) $\neq$ 0 i.e. A is non-singular.

Example 7 : Find inverse of A = $\begin{bmatrix} 1 & 1 & 2 \\ 3 & 1 & 2 \\ 1 & 1 & 3 \end{bmatrix}$

Solution : The cofactor of elements of A is

$A_{11} = (-1)^{1+1}\begin{bmatrix} 1 & 2 \\ 1 & 3 \end{bmatrix} = 1$, $A_{12} = (-1)^{1+2}\begin{bmatrix} 3 & 2 \\ 1 & 3 \end{bmatrix} = -(7) = -7$

$A_{13} = (-1)^{1+3}\begin{bmatrix} 3 & 1 \\ 1 & 1 \end{bmatrix} = 2$, $A_{21} = (-1)^{2+1}\begin{bmatrix} 1 & 2 \\ 1 & 3 \end{bmatrix} = -(1) = -1$

$A_{22} = (-1)^{2+2}\begin{bmatrix} 1 & 2 \\ 1 & 3 \end{bmatrix} = 1$, $A_{23} = (-1)^{2+3}\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} = 0$

$A_{31} = (-1)^{3+1}\begin{bmatrix} 1 & 2 \\ 1 & 2 \end{bmatrix} = 0$, $A_{32} = (-1)^{3+2}\begin{bmatrix} 1 & 2 \\ 3 & 2 \end{bmatrix} = -(-4) = 4$

$A_{33} = (-1)^{3+3}\begin{bmatrix} 1 & 1 \\ 3 & 1 \end{bmatrix} = -2$

Cofactor(A) = $\begin{bmatrix} 1 & -7 & 2 \\ -1 & 1 & 0 \\ 0 & 4 & -2 \end{bmatrix}$ and Adj(A) = Transpose of Cofactor(A)

= $\begin{bmatrix} 1 & -1 & 0 \\ -7 & 1 & 4 \\ 2 & 0 & -2 \end{bmatrix}$ = $(\text{Cofactor}(A))^T$

Determinant of A = det(A) = $\begin{vmatrix} 1 & 1 & 2 \\ 3 & 1 & 2 \\ 1 & 1 & 3 \end{vmatrix}$ = 1(3-2)-1(9-2)+2(3-1) = 1-7+4 = -2

A^{-1} = Inverse of A = $\frac{adj(A)}{\det(A)} = \frac{\begin{bmatrix} 1 & -1 & 0 \\ -7 & 1 & 4 \\ 2 & 0 & -2 \end{bmatrix}}{-2} = \frac{-1}{2}\begin{bmatrix} 1 & -1 & 0 \\ -7 & 1 & 4 \\ 2 & 0 & -2 \end{bmatrix}$

10.6 Special Matrices

10.6.1 Symmetric Matrix : A square matrix $A = (a_{ij})_{m\times n}$ is called Symmetric matrix if $A = (a_{ij})_{n\times n} = (a_{ji})_{n\times n} = A^T$ i.e. matrix is equal to its transpose.

For example $A = \begin{pmatrix} 2 & -1 \\ -1 & 0 \end{pmatrix}$. Its transpose $A^T = \begin{pmatrix} 2 & -1 \\ -1 & 0 \end{pmatrix}$, So $A = A^T$ which says that A is symmetric matrix.

10.6.2 Skew Symmetric Matrix : A square matrix $A = (a_{ij})_{m\times n}$ is called Skew-Symmetric matrix if $A = (a_{ij})_{n\times n} = (-a_{ji})_{n\times n} = -A^T$.

For example $A = \begin{pmatrix} 0 & 1 & -1 \\ -1 & 0 & 3 \\ 1 & -3 & 0 \end{pmatrix}$. Its transpose $A^T = \begin{pmatrix} 0 & -1 & 1 \\ 1 & 0 & -3 \\ -1 & 3 & 0 \end{pmatrix} = -\begin{pmatrix} 0 & 1 & -1 \\ -1 & 0 & 3 \\ 1 & -3 & 0 \end{pmatrix} = -A^T$, So $A = -A^T$ which says that A is Skew- symmetric matrix.

Note : Every square matrix can be uniquely expressed as the sum of a symmetric matrix and a skew symmetric matrix..

10.6.3 Conjugate Matrix : Let $A = (a_{ij})_{m\times n}$ be a matrix with complex entries, like $a \pm ib$. Then conjugate of A is obtained by taking complex conjugate of each entry A and is denoted by $\bar{A} = (\overline{a_{ij}})_{m\times n}$.

10.6.4 Conjugate transposed Matrix : Let $A = (a_{ij})_{m\times n}$ be a matrix with complex entries. Then $(\bar{A})^T or\ \overline{(A^T)}$ is called conjugate transpose of A and is denoted by A^θ.

For example :$A = \begin{bmatrix} 1+3i & -2i & 1-i \\ 5 & 3-i & 1+2i \end{bmatrix}$ Then conjugate of A is $\bar{A} = \begin{bmatrix} 1-3i & 2i & 1+i \\ 5 & 3+i & 1-2i \end{bmatrix}$.

Now $A^{\theta} = (\bar{A})^{T} = \overline{(A^{T})} = \begin{bmatrix} 1-3i & 5 \\ 2i & 3+i \\ 1+i & 1-2i \end{bmatrix}$.

10.6.5 Hermitian Matrix :A square matrix $A = (a_{ij})_{n\times n}$ is called Hermitian matrix if $A = A^{\theta}$.

For example:$A = \begin{bmatrix} 1 & 2+3i & 3-4i \\ 2-3i & 0 & 2-7i \\ 3+4i & 2+7i & 2 \end{bmatrix}$.

Then$A^{\theta} = \begin{bmatrix} 1 & 2+3i & 3-4i \\ 2-3i & 0 & 2-7i \\ 3+4i & 2+7i & 2 \end{bmatrix}$, that is $A = A^{\theta}$. Hence A is Hermitian matrix.

10.6.6 Skew-Hermitian Matrix :-A square matrix $A = (a_{ij})_{n\times n}$ is called Skew-Hermitian matrix if $A = -A^{\theta}$.

For example :$A = \begin{bmatrix} 6i & -1-i \\ 1-i & -4i \end{bmatrix}$. Then $A^{\theta} = \begin{bmatrix} -6i & 1+i \\ -1+i & 4i \end{bmatrix}$and $-A = \begin{bmatrix} -6i & 1+i \\ -1+i & 4i \end{bmatrix}$. Hence $A = -A^{\theta}$.

Note:- Every square matrix can be uniquely expressed as the sum of a Hermitian matrix and a skew Hermitian matrix..

Properties :1. If A is Hermitian matrix then all its principal diagonal entries are real.

2. When all entries are real in Hermitian matrix then it is symmetric matrix.
3. If A is Skew-Hermitian matrix then all its main diagonal entries are zero or purely imaginary numbers.

10.6.7 Unit matrix : A square matrix $A = (a_{ij})_{n\times n}$ is said to be unit matrix if $a_{ij} = \begin{cases} 1 & when\ i = j \\ 0 & otherwise \end{cases}$. It is denoted by I_n or I. For example : $I_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, I_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$.

10.6.8 Diagonal Matrix : Any non-zero square matrix $A = (a_{ij})_{n\times n}$ is called diagonal matrix if its all entries except diagonal entries are zero. It is denoted by $\mathrm{A} = \mathrm{diag}(\mathrm{a}_{11}, a_{22}, a_{33}, \dots, a_{nn})$.

For example : $A = \begin{bmatrix} 4 & 0 \\ 0 & 15 \end{bmatrix}, B = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 5 \end{bmatrix}$ are diagonal matrices.

10.6.9 Upper triangular matrix : A square matrix $A = (a_{ij})_{n\times n}$ is said to be upper triangular if all its entries below principal diagonal are zero.

For example : $A = \begin{bmatrix} 1 & 1 & 1 \\ 0 & 3 & 4 \\ 0 & 0 & 5 \end{bmatrix}, B = \begin{bmatrix} 1 & 2 \\ 0 & 3 \end{bmatrix}$.

10.6.10 Lower triangular matrix :A square matrix $A = (a_{ij})_{n\times n}$ is said to be lower triangular if all its entries abow principal diagonal are zero.

For example : $A = \begin{bmatrix} 1 & 0 & 0 \\ 2 & 3 & 0 \\ 3 & 4 & 5 \end{bmatrix}$.

10.6.11 Unitary Matrix :A square matrix $A = (a_{ij})_{n\times n}$ is said to be Unitary matrix id $A^{\theta}A = AA^{\theta} = I_n$.

If A is Unitary matrix then $A^{\theta} = A^{-1}$.

For example : $A = \begin{bmatrix} i/3 & 2/\sqrt{3} \\ 3/\sqrt{2} & i \end{bmatrix}$, $A^{\theta} = \begin{bmatrix} -i/3 & 3/\sqrt{2} \\ 2/\sqrt{3} & -i \end{bmatrix}$. $A^{-1} = \begin{bmatrix} -i/3 & 3/\sqrt{2} \\ 2/\sqrt{3} & -i \end{bmatrix}$. Thus $A = A^{-1}$.

10.7 Simultaneous System Of Linear Equations

Let us consider arbitrary system of m linear equations in n variables $x_1, x_2, x_3, \ldots, x_n$ is a set of equations of the form

$$a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = b_1.$$
$$a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = b_2.$$
$$\vdots$$
$$a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n = b_m.$$

10.7.1 Matrix Equation : Matrix Equation of a linear system :

From system we get

$$A = \begin{bmatrix} a_{11} & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} & \ldots & a_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ a_{m1} & a_{m2} & \ldots & a_{mn} \end{bmatrix}_{m\times n}, X = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix}_{n\times 1}, \quad B = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_m \end{bmatrix}_{m\times 1}.$$

So matrix representation of above Linear system is AX=B.

The matrix A is called coefficient matrix, B and X are column matrix. The matrix $[A: B]$ is calledaugmented matrix.

10.7.2 Non-Homogeneous System : A system of equations AX=B is called non-homogeneous if B is non-zero matrix. Such system is called consistent if AX=B has solution. System AX=B can have unique solution, many solution or no solution.

System AX=B is consistent if it has unique of many solution and said to be inconsistent if system has no solution. So Non-Homogeneous system AX=B has

1. Unique solution (consistent system)
2. Many solution (consistent system)
3. No solution (inconsistent system).

Theorem 2 : Let $A = (a_{ij})_{m\times n}$ be a matrix with $m < n$ then system AX=B has no solution.

Theorem 3 : If $A = (a_{ij})_{m\times m}$ then following are equivalent

1. A is non-singular (i.e. $\det(A) \neq 0.$)
2. The non-homogeneous system AX=B has solution for each matrix B.

Non-Homogeneous system of equation can be solved by methods called

1. Gauss elimination method.
2. Gauss Jordon method.

Note :- In both the methods we can apply only row operations to solve system.

- **Gauss Elimination Method**

In this method final augmented matrix should satisfy following forms :

1. It has all zero rows below non-zero rows.
2. In all non-zero rows first non-zero entry falls to the right from first non-zero entry of its above row.

Example 7 : Solve the following system by Gauss elimination method

$$-x + 3y + 2z = 2,\ \ 2x - y + 5z = -1,\ \ -x + y + 3z = 3.$$

Solution : Required augmented matrix is

$$[A:B] = \left(\begin{array}{ccc|c} -1 & 3 & 2 & 2 \\ 2 & -1 & 5 & -1 \\ -1 & 1 & 3 & 3 \end{array}\right)$$

$(2)R_{12}$ (multiply row-1 by 2 and add to row-2)

$(-1)R_{13}$(multiply row-1 by -1 and add to row-3)

$$\sim \left(\begin{array}{ccc|c} -1 & 3 & 2 & 2 \\ 0 & 5 & 9 & 3 \\ 0 & -2 & 1 & 1 \end{array}\right)$$

$(\frac{2}{5})R_{23}$(multiply row-2 by 2/5 and add to row-3)

$$\sim \left(\begin{array}{ccc|c} -1 & 3 & 2 & 2 \\ 0 & 5 & 9 & 3 \\ 0 & 9 & \frac{23}{5} & \frac{11}{5} \end{array}\right)$$

Writing matrix again in form of equation

$$-x + 3y + 2z = 2$$
$$5y + 9z = 3$$
$$\frac{23}{5}z = \frac{11}{5}.$$

By back-substitution, z=11/23, $5y + 9 \times \frac{11}{3} = 3 \Rightarrow y = -\frac{6}{23}$

And $-x + 3\left(-\frac{6}{23}\right) + 2\left(\frac{11}{23}\right) = 2 \Rightarrow x = -\frac{42}{23}$.

Thus system has Unique solution $(x, y, z) = \left(-\frac{42}{23}, -\frac{6}{23}, \frac{11}{23}\right)$.

Example 8 : Solve the following system by Gauss elimination method

$$4x - 2y + 6z = 8$$
$$x + y - 3z = -1$$
$$15x - 3y + 9z = 21.$$

Solution : Required augmented matrix is $\left(\begin{array}{ccc|c} 4 & -2 & 6 & 8 \\ 1 & 1 & -3 & -1 \\ 15 & -3 & 9 & 21 \end{array}\right)$

$(-\frac{1}{4})R_{12}$, $(-\frac{15}{4})R_{13}$ $\sim \left(\begin{array}{ccc|c} 4 & -2 & 6 & 8 \\ 0 & \frac{3}{2} & -\frac{9}{2} & -3 \\ 0 & \frac{9}{2} & -\frac{27}{2} & -9 \end{array}\right)$ &

$(-3)R_{23} \sim \left(\begin{array}{ccc|c} 4 & -2 & 6 & 8 \\ 0 & 3/2 & -9/2 & -3 \\ 0 & 0 & 0 & 0 \end{array}\right)$

By Back substitution

$$4x - 2y + 6z = 8$$

$$\frac{3}{2}y - \frac{9}{2}z = -3.$$

Hence we get last row zero. So suppose z=t, we get $\frac{3}{2}y = -3 + \frac{9}{2}t \Rightarrow y = \frac{-6+9t}{3} \Rightarrow y = -2 + 3t$.

$$4x - 2(-2 + 3t) + 6t = 8 \Rightarrow x = 1.$$

Hence we get many solutions for different values of t, Hence system has many solution.

Note : In above both the sums we get unique solution and many solution respectively, hence both systems are consistent.

Example 9 : Solve the following system by Gauss elimination method

$$-2x + 4y + 3z = 5$$
$$3x + y - z = -3$$
$$4x + 6y + z = 1.$$

Solution : Required augmented matrix is $\left(\begin{array}{ccc|c} -2 & 4 & 3 & 5 \\ 3 & 1 & -1 & -3 \\ 4 & 6 & 1 & 1 \end{array}\right)$

$(\frac{3}{2})R_{12}$, $(2)R_{13}$ $\sim \left(\begin{array}{ccc|c} -2 & 4 & 3 & 5 \\ 0 & 7 & \frac{7}{2} & \frac{9}{2} \\ 0 & 14 & 7 & 11 \end{array}\right)$ and $(-2)R_{23}$ $\sim \left(\begin{array}{ccc|c} -2 & 4 & 3 & 5 \\ 0 & 7 & \frac{7}{2} & \frac{9}{2} \\ 0 & 0 & 0 & 2 \end{array}\right)$

By Backs substitution,

$$-2x + 4y + 3z = 5$$
$$7y + \frac{7}{2}z = \frac{9}{2}.$$
$$0 = 2.$$

Which is not possible, So system has no solution.

Note : Above example has no solution, so system is inconsistent.

- **Gauss Jordan Method**

  In this method final augmented matrix should satisfy following forms

  1. All zero-rows falls below non-zero rows.

2. In all non-zero rows first non-zero entry from right should be one, it is called leading one.
3. Leading one in each row should falls to right, from the leading one of its above row.
4. All the other entries in the column containing leading one should be zero.

Example 10 : Solve the following system by Gauss Jordan method

$$x + y + 2z = 8$$
$$-x - 2y + 3z = -1$$
$$3x - 7y + 4z = 10.$$

Solution : Required augmented matrix is $\sim \left(\begin{array}{ccc|c} 1 & 1 & 2 & 8 \\ -1 & -2 & 3 & 1 \\ 3 & -7 & 4 & 10 \end{array}\right)$

$(1)R_{12}$, $(-3)R_{13} \sim \left(\begin{array}{ccc|c} 1 & 1 & 2 & 8 \\ 0 & -1 & 5 & 9 \\ 0 & -10 & -2 & -14 \end{array}\right)$ and

$(-1)R_2 \sim \left(\begin{array}{ccc|c} 1 & 1 & 2 & 8 \\ 0 & 1 & -5 & -9 \\ 0 & -10 & -2 & -14 \end{array}\right)$

$(-1)R_{21}, (10)R_{23}$

$$\sim \left(\begin{array}{ccc|c} 1 & 0 & 7 & 17 \\ 0 & 1 & -5 & -9 \\ 0 & 0 & -52 & -104 \end{array}\right) \& R_3 \to \left(-\frac{1}{52}\right)R_3 \sim \left(\begin{array}{ccc|c} 1 & 0 & 7 & 17 \\ 0 & 1 & -5 & -9 \\ 0 & 0 & 1 & 2 \end{array}\right)$$

$$(5)R_{32}, (-7)R_{31} \sim \left(\begin{array}{ccc|c} 1 & 0 & 0 & 3 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 2 \end{array}\right)$$

By back substitution, x=2, y=1 and z=3, System has unique solution.

Example 11: Solve the following system by Gauss Jordan method

$$-2y + 3z = 1$$
$$3x + 6y - 3z = -2$$
$$6x + 6y + 3z = 5.$$

Solution : Required augmented matrix is $\left(\begin{array}{ccc|c} 0 & -2 & 3 & 1 \\ 3 & 6 & -3 & -2 \\ 6 & 6 & 3 & 5 \end{array}\right)$

$R_1 \leftrightarrow R_2$(Interchanging row-1 and row-2) $\sim \left(\begin{array}{ccc|c} 3 & 6 & -3 & -2 \\ 0 & -2 & 3 & 1 \\ 6 & 6 & 3 & 5 \end{array}\right)$

$$\left(\frac{1}{3}\right)R_1 \sim \left(\begin{array}{ccc|c} 1 & 2 & -1 & -2/3 \\ 0 & -2 & 3 & 1 \\ 6 & 6 & 3 & 5 \end{array}\right) \& (-6)R_{13} \sim \left(\begin{array}{ccc|c} 1 & 2 & -1 & -2/3 \\ 0 & -2 & 3 & 1 \\ 0 & -6 & 9 & 9 \end{array}\right)$$

$$(-1/2)R_2 \sim \left(\begin{array}{ccc|c} 1 & 2 & -1 & -2/3 \\ 0 & 1 & -3/2 & -1/2 \\ 0 & -6 & 9 & 9 \end{array}\right) \& (-2)R_{21}, (6)R_{23} \sim \left(\begin{array}{ccc|c} 1 & 2 & -1 & -2/3 \\ 0 & 1 & -3/2 & -1/2 \\ 0 & 0 & 0 & 6 \end{array}\right)$$

From last row we have $0x + 0y + 0z = 6$, which is not possible, hence system has no solution.

Example 12 : For which value of α and β following system has (1) many solutions, (2) Unique solution and (3) No solution. Solve by any method.

$$x + 2y + z = 8$$
$$2x + 2y + 2z = 13$$
$$3x + 4y + \alpha z = \beta.$$

Solution : Required augmented matrix is $\left(\begin{array}{ccc|c} 1 & 2 & 1 & 8 \\ 2 & 2 & 2 & 13 \\ 3 & 4 & \alpha & \beta \end{array}\right)$

Let's apply Gauss elimination method $(-2)R_{12}, (-3)R_{13}$

$$\sim \left(\begin{array}{ccc|c} 1 & 2 & 1 & 8 \\ 0 & -2 & 0 & -3 \\ 0 & -2 & \alpha - 3 & \beta - 24 \end{array}\right)$$

$$(-1)R_{23}$$

$$\sim \left(\begin{array}{ccc|c} 1 & 2 & 1 & 8 \\ 0 & -2 & 0 & -3 \\ 0 & 0 & \alpha - 3 & \beta - 21 \end{array}\right)$$

i. For $\alpha = 3$ and $\beta = 21$ system has many solutions.

ii. For $\alpha \neq 3$ and for any value of β system has unique solution.

iii. For $\alpha = 3$ and $\beta \neq 21$ system has no solution.

10.7.3 Homogeneous system of Equations :

A system of equations of the form AX=B is called Homogeneous system of equation if B is zero matrix. i.e.

$$a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = 0.$$
$$a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = 0.$$
$$\vdots$$
$$a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n = 0.$$

Writing in Matrix Equation form:

$$\begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ a_{m1} & a_{m2} & \dots & a_{mn} \end{bmatrix}_{m\times n} \cdot \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix}_{n\times 1} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}_{m\times 1}$$ i.e. AX=B.

Above system has two kind of solutions :

1. System has exactly one solution $x_1 = 0, x_2 = 0, \dots, x_n = 0.$ i.e. trivial solution.
2. System has infinite solutions, i.e. non-trivial solution.

Note : Above system can also be solve by following methods,

1. Gauss Elimination method
2. Gauss Jordan method

Example 13: Solve the following system by Gauss elimination method

$$3x - y - z = 0$$
$$x + y + 2z = 0$$
$$5x + y + 3z = 0.$$

Solution : Required augmented matrix is $\left(\begin{array}{ccc|c} 3 & -1 & -1 & 0 \\ 1 & 1 & 2 & 0 \\ 5 & 1 & 3 & 0 \end{array}\right)$

$(-1/3)R_{12}, (-5/3)R_{13} \sim \left(\begin{array}{ccc|c} 3 & -1 & -1 & 0 \\ 0 & 4/3 & 7/3 & 0 \\ 0 & 8/3 & 14/3 & 0 \end{array}\right)$ & $(-2)R_{23} \sim \left(\begin{array}{ccc|c} 3 & -1 & -1 & 0 \\ 0 & 4/3 & 7/3 & 0 \\ 0 & 0 & 0 & 0 \end{array}\right)$

Since all the entries are zero in last row, so z is free variable. Suppose z=t.

By back substitution, $\frac{4}{3}y + \frac{7}{3}t = 0 \Rightarrow y = -\frac{7}{4}t$ and $3x + \frac{7}{4}t - t = 0 \Rightarrow x = -\frac{1}{4}t.$

Hence system has non-trivial i.e. many solutions.

Example 14 : Solve the following system,

$$\begin{aligned} 2x + y + 3z &= 0 \\ x + 2y \quad &= 0 \\ y \quad + z &= 0. \end{aligned}$$

Solution : Since the method is not specify we can apply any method, let's apply Jordan method.

Required augmented matrix is $\left(\begin{array}{ccc|c} 2 & 1 & 3 & 0 \\ 1 & 2 & 0 & 0 \\ 0 & 1 & 1 & 0 \end{array}\right)$

$$R_{12} \sim \left(\begin{array}{ccc|c} 1 & 2 & 0 & 0 \\ 2 & 1 & 3 & 0 \\ 0 & 1 & 1 & 0 \end{array}\right) \& (-2)R_{12} \sim \left(\begin{array}{ccc|c} 1 & 2 & 0 & 0 \\ 0 & -3 & 3 & 0 \\ 0 & 1 & 1 & 0 \end{array}\right)$$

$$R_{23} \sim \left(\begin{array}{ccc|c} 1 & 2 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & -3 & 3 & 0 \end{array}\right) \& \ (-2)R_{21}, (3)R_{23} \sim \left(\begin{array}{ccc|c} 1 & 0 & -2 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 6 & 0 \end{array}\right)$$

$$\left(\frac{1}{6}\right)R_3 \sim \left(\begin{array}{ccc|c} 1 & 0 & -2 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 \end{array}\right) \& (-1)R_{32}, (2)R_{31} \sim \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{array}\right)$$

Hence system has unique trivial solution $(x, y, z) = (0,0,0).$

Example 15 : Find the possible values of $\alpha, \beta \ and \ \gamma,$ if system has trivial solution.

$$\begin{aligned} \sin\alpha + 2\cos\beta + 3\tan\gamma &= 0 \\ 2\sin\alpha + 5\cos\beta + 3\tan\gamma &= 0 \\ -\sin\alpha - 5\cos\beta + 5\tan\gamma &= 0 \end{aligned}$$

Solution : Required augmented matrix is

$$\left(\begin{array}{ccc|c} 1 & 2 & 3 & 0 \\ 2 & 5 & 3 & 0 \\ -1 & -5 & 5 & 0 \end{array}\right)$$

Since the method is not written we can apply any method, let's apply elimination method.

$$(-2)R_{12}, (1)R_{13} \sim \left(\begin{array}{ccc|c} 1 & 2 & 3 & 0 \\ 0 & 1 & -3 & 0 \\ 0 & -3 & 8 & 0 \end{array}\right) \& \ (3)R_{23} \sim \left(\begin{array}{ccc|c} 1 & 2 & 3 & 0 \\ 0 & 1 & -3 & 0 \\ 0 & 0 & -1 & 0 \end{array}\right)$$

By back substation

$$\sin\alpha = 0, \cos\beta = 0, \tan\gamma = 0.$$

Which implies

$$\alpha = 0, \pi, 2\pi; \qquad \beta = \frac{\pi}{2}, \frac{3\pi}{2}; \qquad \gamma = 0, \pi, 2\pi.$$

10.8 Linear Dependence and Independence

Let $\{V_1, V_2, V_3, \ldots \ldots V_n\}$ be set of vectors,such that $K_1V_1 + K_2V_2 + \cdots \ldots + K_nV_n = 0$, this is called linear combination of vectors $V_1, V_2, V_3, \ldots \ldots V_n$ and scalars $K_1, K_2, \ldots . . K_n$.

If system $K_1V_1 + K_2V_2 + \cdots \ldots + K_nV_n = 0$ has trivial solution (i:e $K_1 = K_2 = \cdots . . = K_n = 0$) than vectors are said to be linearly independent, otherwise linearly dependent.

Note:-

(i) If the coefficient matrix of the system $K_1V_1 + K_2V_2 + \cdots \ldots + K_nV_n = 0$, is A and if det(A)$\neq 0$ then vectors are linearly independent, otherwise dependent.

(ii) In this topic vectors can be in any form, like vectors in $R^n, vectors\ in\ from\ of\ polynimials\ in\ P_n, vectors\ in\ form\ of$

(iii) System $K_1V_1 + K_2V_2 + \cdots \ldots + K_nV_n = 0$ can be solve by any elimination method, until it is specified.

Example 16 : Check whether the vectors are linearly independent or dependent?

$$(4, -1, 2), (-4, 10, 2), (4, 0, 1).$$

Solution:- Since there are three vectors in R^3 ,$V_1 = (4, -1, 2), V_2 = (-4, 10, 2), V_3 = (4, 0, 1)$

Writing such vectors as linear combination with three scalars $K_1, K_2, K_3 \in R^3$ such that

$$K_1V_1 + K_2V_2 + K_3V_3 = 0$$
$$K_1(4,-1,2) + K_2(-4,10,2) + K_3(4,0,1) = (0,0,0)$$
$$4K_1 - 4K_2 + 4K_3 = 0$$
$$-K_1 + 10K_2 = 0$$
$$2K_1 + 2K_2 + K_3 = 0$$

Augmented form of system

$$\sim \left(\begin{array}{ccc|c} 4 & -4 & 4 & 0 \\ -1 & 10 & 0 & 0 \\ 2 & 2 & 1 & 0 \end{array}\right) \& \left(\frac{1}{4}\right)R_{12}, \left(-\frac{1}{2}\right)R_{13} \sim \left(\begin{array}{ccc|c} 4 & -4 & 4 & 0 \\ 0 & 9 & 1 & 0 \\ 0 & 4 & -1 & 0 \end{array}\right)$$

$$\left(-\frac{4}{9}\right)R_{23} \sim \left(\begin{array}{ccc|c} 4 & -4 & 4 & 0 \\ 0 & 9 & 1 & 0 \\ 0 & 0 & -\frac{13}{9} & 0 \end{array}\right)$$

By back substitution

$-13/9K_3 = 0 \Rightarrow K_3 = 0$

$9K_2 + 0 = 0 \Rightarrow K_2 = 0$

$4K_1 + 0 + 0 = 0 \Rightarrow K_1 = 0$

Since system has trivial solution so vectors V_1, V_2, V_3 are linearly independent.

Example 17 : Check whether the polynomials in R^2 are linearly independent or dependent?

$$2 + x + x^2, x + 2x^2, 2 + 2x + 3x^2.$$

Solution:- Let $P_1 = 2 + x + x^2, P_2 = x + 2x^2$ and $P_3 = 2 + 2x + 3x^2$ are polynomials in R^2 and $K_1, K_2, K_3 \in R^2$ are scalars, so linear combination is $K_1P_1 + K_2P_2 + K_3P_3 = 0$

$$K_1(2 + x + x^2) + K_2(x + 2x^2) + K_3(2 + 2x + 3x^2) = (0,0,0)$$

here we have to compare coefficient of x^2, x and constant to form a system

$$K_1 + 2K_2 + 3K_3 = 0$$
$$K_1 + K_2 + 2K_3 = 0$$
$$2K_1 + \quad + 2K_3 = 0$$

Augmented form of system $\sim \left(\begin{array}{ccc|c} 1 & 2 & 3 & 0 \\ 1 & 1 & 2 & 0 \\ 2 & 0 & 2 & 0 \end{array}\right)$

$$(-1)R_{12}, (-2)R_{13} \sim \left(\begin{array}{ccc|c} 1 & 2 & 3 & 0 \\ 0 & -1 & -1 & 0 \\ 0 & -4 & -4 & 0 \end{array}\right) \& \ (-4)R_{23} \sim \left(\begin{array}{ccc|c} 1 & 2 & 3 & 0 \\ 0 & -1 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{array}\right)$$

Since system has non-trivial solution i:e many solution, so $P_1, P_2, and\ P_3$ are linearly dependent.

Example 18 : Check whether the following matrices are linearly independent or dependent?

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}, \begin{bmatrix} 0 & 1 \\ 0 & 2 \end{bmatrix}.$$

Solution:- Let $\mathrm{A}_1 = \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}, \mathrm{A}_2 = \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}$ and $\mathrm{A}_3 = \begin{bmatrix} 0 & 1 \\ 0 & 2 \end{bmatrix}$ are matrices in M_{22} and K_1, K_2, K_3 are scalars in M_{22}.Its linear combination is

$$\mathrm{K}_1\mathrm{A}_1 + \mathrm{K}_2\mathrm{A}_2 + \mathrm{K}_3\mathrm{A}_3 = 0$$

$$\mathrm{K}_1 \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} + \mathrm{K}_2 \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} + \mathrm{K}_3 \begin{bmatrix} 0 & 1 \\ 0 & 2 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

$$K_1 + K_2 = 0 \ldots\ldots(i)$$
$$K_1 + K_3 = 0 \ldots\ldots(ii)$$
$$K_1 = 0 \ldots\ldots\ldots(iii)$$
$$K_1 + 2K_2 + 2K_3 = 0 \ldots.(iv)$$

Since $K_1 = 0$ from (iii)

$K_1 + K_2 = 0 \Rightarrow K_2 = 0$ from (i)

$K_1 + K_3 = 0 \Rightarrow K_3 = 0$

Since system has trivial solution so all matrices $A_1, A_2\ and\ A_3$ in M_{22} are linearly independent.

Example 19: Show that vectors $V_1 = (-2,0,1), V_2 = (3,2,5) and\ V_3 = (7,0,-2)$ are linearly independent.

Solution:- Since there are three vectors in R^3 $V_1 = (-2,0,1), V_2 = (3,2,5), \text{and } V_3 =$(7,0,-2)

Writing such vectors as linear combination with three scalars $K_1, K_2, K_3 \in R^3$ such that

$$K_1V_1 + K_2V_2 + K_3V_3 = 0$$
$$K_1(-2,0,1) + K_2(3,2,5) + K_3(7,0,-2) = (0,0,0)$$
$$-2K_1 + 3K_2 + 7K_3 = 0$$
$$2K_2 \quad = 0$$
$$K_1 + 5K_2 - 2K_3 \ = 0$$

Augmented form of system

$$\sim \left(\begin{array}{ccc|c} -2 & 3 & 7 & 0 \\ 0 & 2 & 0 & 0 \\ 1 & 5 & -2 & 0 \end{array}\right) = (A|B)$$

Det(A)= $\begin{vmatrix} -2 & 3 & 7 \\ 0 & 2 & 0 \\ 1 & 5 & -2 \end{vmatrix}$ = -2(-4)-3(0)+7(-2) = 8-14 = -6 $\neq 0$

Hence $V_1, V_2\ and\ V_3$ are linearly independent.

Example 20: For what values of $\propto$, vectors $V_1 = \left(\propto, -\frac{1}{2}, -\frac{1}{2}\right),\ V_2 = \left(-\frac{1}{2}, \propto, -\frac{1}{2}\right), V_3 = (-\frac{1}{2}, -\frac{1}{2}, \propto)$ in R^3 are linearly dependent?

Solution:- Since there are three vectors in R^3 ,$\mathrm{V}_1 = \left(\propto, -\frac{1}{2}, -\frac{1}{2}\right), \mathrm{V}_2 = \left(-\frac{1}{2}, \propto, -\frac{1}{2}\right), \text{and } \mathrm{V}_3 = (-\frac{1}{2}, -\frac{1}{2}, \propto)$

Writing such vectors as linear combination with three scalars $K_1, K_2, K_3 \in R^3$ such that

$$K_1V_1 + K_2V_2 + K_3V_3 = 0$$
$$\mathrm{K}_1\left(\propto, -\frac{1}{2}, -\frac{1}{2}\right) + \mathrm{K}_2\left(-\frac{1}{2}, \propto, -\frac{1}{2}\right) + \mathrm{K}_3(-\frac{1}{2}, -\frac{1}{2}, \propto) = (0,0,0)$$

$$\propto K_1 - \frac{1}{2}K_2 - \frac{1}{2}K_3 = 0$$

$$-\frac{1}{2}K_1 + \propto K_2 - \frac{1}{2}K_3 = 0$$

$$-\frac{1}{2}K_1 - \frac{1}{2}K_2 + \propto K_3 = 0$$

Augmented form of system

$$\sim \left(\begin{array}{ccc|c} \propto & -\frac{1}{2} & -\frac{1}{2} & 0 \\ -\frac{1}{2} & \propto & -\frac{1}{2} & 0 \\ -\frac{1}{2} & -\frac{1}{2} & \propto & 0 \end{array}\right) = (A|B)$$

Since it is given that $V_1, V_2 \; and \; V_3$ are linearly dependent so det(A)=0

$$\det(A) = \begin{vmatrix} \propto & -\frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \propto & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{1}{2} & \propto \end{vmatrix} = 0$$

$$\propto \left(\propto^2 - \frac{1}{4}\right) + \frac{1}{2}\left(-\frac{\propto}{2} - \frac{1}{4}\right) - \frac{1}{2}\left(\frac{1}{4} + \frac{\propto}{2}\right) = 0$$

$$\propto^3 - -\frac{\propto}{4} - \frac{\propto}{4} - \frac{1}{8} - \frac{1}{8} - \frac{\propto}{4} = 0$$

$$\Rightarrow \propto^3 - 3\frac{\propto}{4} - \frac{1}{4} = 0$$

By factorization of $\propto^3 - 3\frac{\propto}{4} - \frac{1}{4} = 0$ we get,

For $\propto = 1$ we get zero in last equation

$(\propto -1)(\propto^2 + \frac{1}{4} \propto) = 0$

$so \; we \; get \;\; \propto = 0, \propto = 1 and \;\; \propto$=-1/4

Hence for $\propto = 0, \propto = 1 and \;\; \propto$=-1/4 vectors $V_1, V_2 \; and \; V_3$ are linearly dependent.

Exercise

Q.1 : Matrix addition and scalar multiplication for following matrices.

$A=\begin{bmatrix}1 & 2\\ 3 & 1\end{bmatrix}$, $B=\begin{bmatrix}1 & -1\\ 2 & 3\end{bmatrix}$, $C=\begin{bmatrix}1 & 2 & 4\\ 1 & -1 & 3\end{bmatrix}$, $D=\begin{bmatrix}1 & -1 & 2\\ 2 & 3 & -2\end{bmatrix}$

Find following with reasons

i. A+B, B+A, A+B+C

ii. A+C, $(C^T)^T$, $C+C^T$

iii. 5D-3C, $5D^T-3C^T$

iv. $(\mathbf{B}^T - A^T)$, B-A, A- A^T

Q.2 : Multiplication of Matrices.

i. $A=\begin{bmatrix}2 & -1 & 0\end{bmatrix}$, $B=\begin{bmatrix}4\\ -1\\ 2\end{bmatrix}$. Find AB?

ii. $A=\begin{bmatrix}1 & 2\\ 2 & -1\end{bmatrix}$, $B=\begin{bmatrix}1 & 2\\ 3 & 4\end{bmatrix}$ Find AB and BA?

iii. $A=\begin{bmatrix}2 & 3\\ 1 & -1\end{bmatrix}$, $B=\begin{bmatrix}1 & 5 & 0\\ -2 & 1 & 4\end{bmatrix}$ Find AB?

Q.3 : Find inverse of following matrices.

$A=\begin{bmatrix}3 & 2 & 1\\ 2 & -1 & 0\\ 0 & 2 & 1\end{bmatrix}$, $B=\begin{bmatrix}0 & 1 & 2\\ 1 & 2 & 3\\ 3 & 1 & 1\end{bmatrix}$, $C=\begin{bmatrix}1 & 2 & 3\\ 2 & 5 & 3\\ 1 & 0 & 8\end{bmatrix}$

Q.4 : If $A=\begin{bmatrix}3 & -3 & 4\\ 2 & -3 & 4\\ 0 & -1 & 1\end{bmatrix}$, show that $A^3=A^{-1}$.

Q.5 : If $A=\begin{bmatrix}1 & 1 & 1\\ 1 & 2 & 3\\ 1 & 4 & 9\end{bmatrix}$ and $B=\begin{bmatrix}2 & 5 & 3\\ 3 & 1 & 2\\ 1 & 2 & 1\end{bmatrix}$, show that $(AB)^{-1} = B^{-1}A^{-1}$.

Q.6 : For which values of k and λ the following system have 1) No solution, 2) Unique solution, 3) An infinite solutions.

x+y+z=6

x+2y+3z=10

x+2y+kz=λ

Q.7 : Solve following system by gauss elimination method.

5x+3y+7z=4

$2x+26y+2z=9$

$7x+2y+10z=5$

Q.8 : Solve following system by gauss Jordan method.

$2x-3y+7z=5$

$3x+y-3z=13$

$2x+19y-47z=32$

Q.9 : Solve following system by gauss elimination method.

i. $2x_1+2x_2-x_3+x_5=0$
   $-x_1-x_2+2x_3-3x_4+x_5=0$
   $x_1+x_2-2x_3-x_5=0$
   $x_3+x_4+x_5=0$

ii. $x_1-3x_2+x_3=0$
   $2x_1-6x_2+2x_3=0$
   $3x_1-9x_2+3x_3=0$

Q.10 : Solve following system by gauss Jordan method.

i. $X-y+z=0$
   $X+2y+z=0$
   $2x+y+3z=0$

ii. $2x-y+3z=0$
   $3x+2y+z=0$
   $X-4y+5z=0$

Q.11 : Check whether following vectors are linearly dependent or independent.

i. $V_1=(1,0,1)$, $v_2=(1,1,0)$, $v_3=(1,-1,1)$, $v_4=(1,2,-3)$

ii. $P_1=1-t-t^3$, $P_2=-2+3t+t^2+2t^3$, $P_3=1+t^2+5t^3$

iii. $A_1=\begin{bmatrix}3\\0\\0\end{bmatrix}$, $A_2=\begin{bmatrix}4\\1\\0\end{bmatrix}$, $A_3=\begin{bmatrix}2\\5\\2\end{bmatrix}$

Answers:

Q.1

i. $\begin{bmatrix}2 & 1\\5 & 4\end{bmatrix}, \begin{bmatrix}2 & 1\\5 & 4\end{bmatrix}$,Not possible.

ii. Not possible, C = $\begin{bmatrix}1 & 2 & 4\\1 & -1 & 3\end{bmatrix}$, Not possible.

iii. $\begin{bmatrix}2 & -11 & -2\\7 & 18 & -19\end{bmatrix}, \begin{bmatrix}2 & 7\\-11 & 18\\-2 & -19\end{bmatrix}$

iv. $\begin{bmatrix}0 & -1\\-3 & 2\end{bmatrix}, \begin{bmatrix}0 & -3\\-1 & 2\end{bmatrix}, \begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$

Q.2

i.9

ii. $\begin{bmatrix}7 & 10\\-1 & 0\end{bmatrix}, \begin{bmatrix}5 & 0\\11 & 2\end{bmatrix}$

iii. $\begin{bmatrix}-4 & 13 & 12\\3 & 4 & -4\end{bmatrix}$

Q.3

i. $\begin{bmatrix}\frac{1}{3} & 0 & -\frac{1}{3}\\\frac{2}{3} & -1 & -\frac{2}{3}\\-\frac{4}{3} & 2 & \frac{7}{3}\end{bmatrix}$

ii. $\begin{bmatrix}1 & 0 & 0\\-\frac{1}{2} & 1 & 0\\\frac{3}{4} & -\frac{5}{2} & \frac{1}{2}\end{bmatrix}$

iii. $\begin{bmatrix}-40 & 16 & 9\\13 & -5 & -3\\5 & -2 & -1\end{bmatrix}$

Q.6

For k=3, $\lambda \neq 10$ *system has no solution.*

For k$\neq 3$ *system has unique solution.*

For k=3, λ10 system has many solutions.

Q.7

System has many solution.$x = \frac{7-16t}{11}, y = \frac{t+3}{11}, z = t$

Q.8

System is inconsistent.

Q.9

i. System has many solutions.$x_1 = -s - t, x_2 = s, x_3 = -t, x_4 = 0, x_5 = t.$

ii. System has many solutions.

Q.10

i. x=0,y=0,z=0.

ii. x=-t,y=t,z=t.

Q.11

i. Linearly Dependent.

ii. Linearly Independent.

iii. Linearly Independent.

Unit – 11: Eigen Values and Eigen Vectors

Structure of Unit:

11.1 Introduction

In this chapter, we started our discussion with the notion of vector spaces. Vector spaces play an important role in linear algebra with respect to some binary operations. Then we put our focus on Eigen value and Eigen vectors of matrices in continuation with previous unit. Eigen vectors are helpful to study of genetics, quantum machine population dynamics etc. then the discussion continues with the concept of determinants and we end up on tensor algebra.

11.2 Introduction of Vector Spaces

11.2.1 Vector Space : Let K be a given field and let V be a no empty set with rules of addition and scalar multiplication. Then V is Said to be a vector space if it satisfy following axioms :

I. Closure Axiom :

C_1 – for any vectors $u, v \in V \Rightarrow u + v \in V$

C_2 – for any vector $u \in V$ and for any scalar $k \in K \Rightarrow ku \in V$

II. Additive Axioms :

A_1 – for any vectors $u, v \in V \Rightarrow u + v = v + u$ (Commutative Law)

A_2 – for any vectors $u, v, w \in V \Rightarrow (u + v) + w = u + (v + w$ (Associative Law)

A_3 – Existence of Identity : for any vector $u \in V$ there exists $0 \in V$ such that

$$u + 0 = u = 0 + u$$

A_4 – Existence of Inverse : for any vector $u \in V$ there exists $-u \in V$ such that

$$u + (-u) = 0 = (-u) + u$$

III. Multiplicative Axioms :

M_1 – for any vectors $u, v \in V$ and for any scalar $k \Rightarrow k(u + v) = ku + kv$
M_2 – for any scalars $a, b \in K$ and $u \in V \Rightarrow (a + b)u = au + bu$
M_3 – for any scalars $a, b \in K$ and $u \in V \Rightarrow (a.b)u = a(b.u)$
M_4 – For $1 \in K$ and $u \in V \Rightarrow 1.u = u$.

11.2.2 Vector Subspace : Let W e subset of a vector space V over K , then W is said to be a subspace of V if W is itself a vector space over K.

Theorem 1 : (Alternate definition of subspace) W is a subspace of V if and only if (iff)

(i) W is a nonempty subset of V
(ii) for any vectors $u, v \in W \Rightarrow u + v \in W$
(iii) for any vector $u \in W$ and for any scalar $k \in K \Rightarrow ku \in W$

Theorem 2 : W is a subspace of V iff

(i) $W = \{\Phi\}$
(ii) for any vectors $u, v \in W$ and for any scalar $a, b \in K \Rightarrow au + bv \in W$.

Example1 : The set of all vectors in 3-dimensional Euclidean space is a real vector space: the vector space axioms in this case are familiar properties of vector algebra.

Example 2 : The set of all vectors in 3-dimensional Euclidean space is a real vector space: the vector space axioms in this case are familiar properties of vector algebra.

Example 3 : The field C of complex numbers can be viewed as a real vector space: the vector space axioms are satisfied when two complex numbers are added together in the normal fashion, and when complex numbers are multiplied by real numbers.

Example 4 : Show that the following set functions is subspace of a functional space F:

$$W = \{ f \ / \ f(0) = 0 \} \ldots\ldots\ldots\ldots\ldots(*)$$

Solution : By the definition it is clear that W is a nonempty set. Now

I. Let $f, g \in W \Rightarrow f(0) = 0, g(0) = 0$ (by (*))
Now consider
$(f+g)(0) = f(0) + g(0)$
$\Rightarrow \quad = 0 + 0$
$\Rightarrow \quad = 0$
$\Rightarrow \quad f+g \in W$ (by the definition of W)

II. Let $f \in W$ and for a scalar k and consider
$(kf)(0) = k(f(0))$

$= k\,0$

$= 0$

$\Rightarrow \quad kf \in W$ (by the definition of W)

Therefore W is a subspace of F.

11.2.3 Linear Combination and Linear Span : Let V be a vector space over a field K and let $v_1, v_2, \ldots, v_n \in V$. Any vector v in V of the form

$$v = a_1v_1 + a_2v_2 + \ldots + a_n v_n,$$

$$v = a_1v_1 + a_2v_2 + \ldots + a_n v_n,$$

where $a_1, a_2, \ldots, a_n$ are constants, is said be a *linear combination* of $v_1, v_2, \ldots, v_n$.

Let S = $\{ v_1, v_2, \ldots, v_n\}$ be a set of vectors then the set of linear combinations of vectors of S is called *linear span* and is denoted by L(S).

Example 5 : Let

$$e_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad e_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad e_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad v = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}.$$

Since

$$v = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = 1 \cdot \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} + 2 \cdot \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} + 3 \cdot \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = 1e_1 + 2e_2 + 3e_3,$$

v is a linear combination of e_1, e_2, e_3.

Example 6 : Is the vector $v = \begin{bmatrix} 3 \\ -4 \\ -6 \end{bmatrix}$ a linear combination of the vectors

$$v_1 = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}, v_2 = \begin{bmatrix} -1 \\ -1 \\ -2 \end{bmatrix}, v_3 = \begin{bmatrix} 1 \\ 4 \\ 5 \end{bmatrix}.$$

Solution : We need to find the constants c_1, c_2, c_3 such that

$$v = \begin{bmatrix} 3 \\ -4 \\ -6 \end{bmatrix} = c_1 \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} + c_2 \begin{bmatrix} -1 \\ -1 \\ -2 \end{bmatrix} + c_3 \begin{bmatrix} 1 \\ 4 \\ 5 \end{bmatrix} = c_1v_1 + c_2v_2 + c_3v_3 .$$

$\Leftrightarrow$ we need to solve for the linear system

$$A\begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 1 & -1 & 1 \\ 2 & -1 & 4 \\ 3 & -2 & 5 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 3 \\ -4 \\ -6 \end{bmatrix}.$$

$\Leftrightarrow$ The linear system has no solution.

$\Leftrightarrow$ v is not a linear combination of v_1, v_2, v_3.

Example 7 : Determine whether the vector $v = (3, 9, -4, -2)$ is a linear combination of $u_1 = (1, -2, 0, 3)$, $u_2 = (2, 3, 0, -1)$ and $u_3 = (2, -1, 2, 1)$ or not.

Solution : Consider

$$v = xu_1 + yu_2 + zu_3$$

$$(3, 9, -4, -2) = x(1, -2, 0, 3) + y(2, 3, 0, -1) + z(2, -1, 2, 1)$$

$$= (x+2y+2z, -2x+3y-z, 2z, 3x-y+z)$$

On comparing, we get

$$x+2y+2z = 3$$

$$-2x+3y-z = 9$$

$$2z = -4 \Rightarrow z = -2$$

$$3x-y+z = -2$$

On putting $z = -2$ in first two equations and with elimination method, we get

$x = 1$ and $y = 3$

since the system is consistence and have a unique solution and so v is a linear combination of given vectors.

11.2.3 Linear dependence and Linear Independence : The vectors

$\{ v_1, v_2, \ldots, v_k \}$ in a vector space V are said to linearly dependent if there exist constants, $c_1, c_2, \ldots, c_k$, not all 0, such that

$$c_1 v_1 + c_2 v_2 + \cdots + c_k v_k = 0.$$

$v_1, v_2, \ldots, v_k$ are linearly independent if

$$c_1 v_1 + c_2 v_2 + \cdots + c_k v_k = 0 \Rightarrow c_1 = c_2 = \cdots = c_k = 0.$$

The procedure to determine if $v_1, v_2, \ldots, v_k$ are linearly dependent or linearly independent:

Form equation $c_1v_1 + c_2v_2 + \cdots + c_kv_k = 0$, which lead to a homogeneous system.

1. If the homogeneous system has only the trivial solution, then the given vectors are linearly independent; if it has a nontrivial solution, then the vectors are linearly dependent.

Example 8 : If $e_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$, $e_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$, $e_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$, and $S = \{e_1, e_2, e_3\}$ .Are e_1, e_2 and e_3 linearly independent?

Solution :

$$c_1e_1 + c_2e_2 + c_3e_3 = c_1\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} + c_2\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} + c_3\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = 0$$

$\Rightarrow \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$. Therefore, e_1, e_2 *and* e_3 *are linearly independent.*

Example 9 : If $v_1 = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$, $v_2 = \begin{bmatrix} -2 \\ 1 \\ 1 \end{bmatrix}$, $v_3 = \begin{bmatrix} 8 \\ 6 \\ 10 \end{bmatrix}$.. Are v_1, v_2 and v_3 linearly independent?

Solution:

$$c_1v_1 + c_2v_2 + c_3v_3 = c_1\begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} + c_2\begin{bmatrix} -2 \\ 1 \\ 1 \end{bmatrix} + c_3\begin{bmatrix} 8 \\ 6 \\ 10 \end{bmatrix} = \begin{bmatrix} 1 & -2 & 8 \\ 2 & 1 & 6 \\ 3 & 1 & 10 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = 0$$

$$\Rightarrow \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = t\begin{bmatrix} 4 \\ -2 \\ -1 \end{bmatrix}, \; t \in R \; .$$

Therefore, v_1, v_2 and v_3 are linearly dependent.

Note : see chapter 10.

11.3 : Eigen Values and Eigen Vectors of a matrix

Let A be a square matrix of order n, then the following equation is known as ***characteristic equation*** or ***Secular equation*** of A and the determinant is known as ***Secular determinant.***

$$| A - \lambda I | = \begin{vmatrix} \lambda - a_{11} & -a_{12} & \cdots & -a_{1n} \\ -a_{21} & \lambda - a_{22} & \cdots & -a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ -a_{n1} & -a_{n2} & \cdots & \lambda - a_{nn} \end{vmatrix} = 0$$

The roots of the above equations are known as ***characteristic roots*** or ***latent roots*** or ***Eigen values*** of A.

Nate : 1. The sum of Eigen values = Trace(A) (sum of principal diagonal elements).\

The ***Eigenvectors*** of a square matrix are the non-zero vectors which, after being multiplied by the matrix, remain proportional to the original vector, i.e. any vector X that satisfies the equation:

$$\mathbf{A}X = \lambda X,$$

where $\mathbf{A}$ is the matrix in question, X is the Eigenvector and λ is the associated Eigen value.

Remarks : 1. If X is a solution of $\mathbf{A}X = \lambda X,$ then kX is also a solution , where k is any arbitrary constant.

2. The Eigen values of a Hermitian matrix are all real.

3. The Eigen values of a skew-Hermitian matrix are either zero or purely imaginary.

4. The Eigen values of an idempotent matrix are either zero or unity.

5. The Eigen values of a unitary matrix are of unit modulus.

Example 10 : Find the Eigen values and Eigenvectors of the matrix $\mathbf{A} = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$.

Solution : First we start by finding the Eigen values, using the equation derived above:

$$|\mathbf{A}-\lambda\mathbf{I}| = \left|\begin{pmatrix}2 & 1\\ 1 & 2\end{pmatrix}-\begin{pmatrix}\lambda & 0\\ 0 & \lambda\end{pmatrix}\right| = \begin{vmatrix}2-\lambda & 1\\ 1 & 2-\lambda\end{vmatrix}. = 0$$

$$(2-\lambda)(2-\lambda)-1\times 1 = \lambda^2-2\lambda+3 = 0.$$

We now need to find the roots of this quadratic equation in λ.

In this case the quadratic factorizes straightforwardly to:

$$\lambda^2-2\lambda+3 = (\lambda-3)(\lambda-1) = 0.$$

The solutions to this equation are $\lambda_1 = 1$ and $\lambda_2 = 3$. These are the Eigen values of the matrix $\mathbf{A}$. We will now solve for an Eigenvector corresponding to each Eigen value in turn. First we will solve for $\lambda = \lambda_1 = 1$:

To find the Eigenvector we substitute a general vector $\mathbf{x} = \begin{pmatrix}x_1\\ x_2\end{pmatrix}$ into the defining equation:

$$\mathbf{Ax} = \lambda\mathbf{x},$$

$$\begin{pmatrix}2 & 1\\ 1 & 2\end{pmatrix}\begin{pmatrix}x_1\\ x_2\end{pmatrix} = 1\times\begin{pmatrix}x_1\\ x_2\end{pmatrix}.$$

By multiplying out both sides of this equation, we form a set of simultaneous equations:

$$\begin{pmatrix}2x_1+x_2\\ x_1+2x_2\end{pmatrix} = \begin{pmatrix}x_1\\ x_2\end{pmatrix},$$

□

$$2x_1+x_2 = x_1,$$
$$x_1+2x_2 = x_2.$$

$$x_1+x_2 = 0,$$
$$x_1+x_2 = 0,$$

where, we have taken everything over to the LHS. It should be immediately clear that ,

$$x_2 = -x_1,$$

so our Eigenvector is produced by substituting this relationship into the general vector is $\mathbf{x} = \begin{pmatrix}x_1\\ -x_1\end{pmatrix}$. This is a valid answer to the question, however it is common practice to

put 1 in place of x_1 and give the answer: $\mathbf{x} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$. We continue the same procedure for the second Eigen value, $\lambda = \lambda_2 = 3$. First we write out the defining equation:

$$\mathbf{Ax} = \lambda\mathbf{x},$$

$$\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 3 \times \begin{pmatrix} x_1 \\ x_2 \end{pmatrix},$$

and multiply out to find a set of simultaneous equations:

$$2x_1 + x_2 = 3x_1,$$
$$x_1 + 2x_2 = 3x_2.$$

Taking everything over to the LHS we find:

$$-x_1 + x_2 = 0,$$
$$x_1 - x_2 = 0.$$

Once again we can find a relationship between x_1 and x_2, in this case $x_1 = x_2$, and form our general Eigenvector: $\mathbf{x} = \begin{pmatrix} x_1 \\ x_1 \end{pmatrix}$. As before, set $x_1 = 1$ to give: $\mathbf{x} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$.

Therefore solution is:

$$\lambda_1 = 1, \quad \mathbf{x}_1 = \begin{pmatrix} -1 \\ 1 \end{pmatrix};$$

$$\lambda_2 = 3, \quad \mathbf{x}_2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Example 11 : Find the Eigen values and Eigenvectors of the matrix

$$A = \begin{bmatrix} 5 & 4 & 2 \\ 4 & 5 & 2 \\ 2 & 2 & 2 \end{bmatrix}$$

Solution : $f(\lambda) = \det(\lambda I - A) = \begin{vmatrix} \lambda - 5 & -4 & -2 \\ -4 & \lambda - 5 & -2 \\ -2 & -2 & \lambda - 2 \end{vmatrix} = (\lambda - 1)^2 (\lambda - 10) = 0$

$\Rightarrow \quad (\lambda - 5)\{(\lambda - 5)(\lambda - 2) - 4\} - (-4)\{(\lambda - 2)(-4) - 4\} - 2\{8 - 2(\lambda - 5)\} = 0$

$\Rightarrow \quad \lambda^3 - 12\lambda^2 + 21\lambda - 10 = 0$

$\Rightarrow \qquad \lambda = 1, 1, \text{ and } 10.$

1. As $\lambda = 1$,

$$(1 \cdot I - A)x = \begin{bmatrix} -4 & -4 & -2 \\ -4 & -4 & -2 \\ -2 & -2 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = 0 \cdot$$

Clearly all the equation are multiple of $2x_1 + 2x_2 + x_3 = 0$. Since here only one equation and three unknowns (x_1, x_2, x_3) and so here 3-1 – 0 independent variables, so let $x_1 = k_1$ and $x_2 = k_2$ which imply $x_3 = -2k_1 - 2k_2$. Thus we have

$$X = \begin{bmatrix} k_1 \\ k_2 \\ -2k_1 - 2k_2 \end{bmatrix} = \begin{bmatrix} k_1 \\ 0 \\ -2k_1 \end{bmatrix} + \begin{bmatrix} 0 \\ k_2 \\ -2k_2 \end{bmatrix} = k_1 \begin{bmatrix} 1 \\ 0 \\ -2 \end{bmatrix} + k_2 \begin{bmatrix} 0 \\ 1 \\ -2 \end{bmatrix}$$

Therefore the Eigen vector for $\lambda = 1$ is a linear combination of two vectors

$$\text{i.e. } X_1 = \begin{bmatrix} 1 \\ 0 \\ -2 \end{bmatrix} \text{and} \quad X_2 = \begin{bmatrix} 0 \\ 1 \\ -2 \end{bmatrix}$$

2. As $\lambda = 10$,

$$(10 \cdot I - A)x = \begin{bmatrix} 5 & -4 & -2 \\ -4 & 5 & -2 \\ -2 & -2 & 8 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = 0$$

From first two rows and cross multiplication method, we get

$$X_3 = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 2k \\ 2k \\ k \end{bmatrix} = k \begin{bmatrix} 2 \\ 2 \\ 1 \end{bmatrix},$$

Thus, $\begin{bmatrix} 2 \\ 2 \\ 1 \end{bmatrix}$, are the Eigenvectors associated with Eigen value $\lambda = 10$.

Example 12 : Find the Eigen values and Eigen vectors of $A = \begin{pmatrix} -3 & 1 & -1 \\ -7 & 5 & -1 \\ -6 & 6 & -2 \end{pmatrix}$.

Solution : The Characteristic equation is

$$A - \lambda I_3 = \begin{pmatrix} -3-\lambda & 1 & -1 \\ -7 & 5-\lambda & -1 \\ -6 & 6 & -2-\lambda \end{pmatrix} \text{ and}$$

$$|A - \lambda I_3| = (-3-\lambda)\begin{vmatrix} 5-\lambda & -1 \\ 6 & -2-\lambda \end{vmatrix} - \begin{vmatrix} -7 & -1 \\ -6 & -2-\lambda \end{vmatrix} - \begin{vmatrix} -7 & 5-\lambda \\ -6 & 6 \end{vmatrix} = -\lambda^3 + 12\lambda + 16 = 0$$

Or $\lambda^3 - 12\lambda + 16 = 0$

On Solving we get λ = -2, -2, 4

To get the Eigenvectors associated with $\lambda_0 = -2$, we solve $(A+2I_3)u = 0$:

$$(A+2I_3)u = \begin{pmatrix} -1 & 1 & -1 \\ -7 & 7 & -1 \\ -6 & 6 & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \Leftrightarrow \begin{cases} -x_1 + x_2 - x_3 = 0 \\ -7x_1 + 7x_2 - x_3 = 0 \\ -6x_1 + 6x_2 = 0 \end{cases} \Leftrightarrow \begin{cases} x_1 = x_2 \\ x_3 = 0 \end{cases}.$$

Hence the Eigenvectors associated with the Eigen value $\lambda_0 = -2$ are of the form $k\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$.

To get the Eigenvectors associated with $\lambda_1 = 4$, we solve $(A-4I_3)u = 0$:

$$(A+2I_3)u = \begin{pmatrix} -7 & 1 & -1 \\ -7 & 1 & -1 \\ -6 & 6 & -6 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \Leftrightarrow \begin{cases} -7x_1 + x_2 - x_3 = 0 \\ -7x_1 + x_2 - x_3 = 0 \\ -6x_1 + 6x_2 - 6x_3 = 0 \end{cases} \Leftrightarrow \begin{cases} x_1 = 0 \\ x_2 = x_3 \end{cases}.$$

Hence the Eigenvectors associated with the Eigen value $\lambda_1 = 4$ are of the form $k\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$.

Example 13 : If λ be an Eigen value of a non-singular matrix A, then show that

(a) λ^{-1} is an Eigen value of A^{-1}.

(b) $|A|/\lambda$ is an Eigen value of adj(A).

Solution : (a) Let λ be an Eigen value of A

$\Rightarrow$ There exists a non zero matrix X such that $AX = \lambda X$

$\Rightarrow$ $X = A^{-1}(\lambda X)$ $\Rightarrow$ $X = \lambda(A^{-1}X)$

$\Rightarrow$ $\lambda^{-1} X = A^{-1}X$

$\Rightarrow$ λ^{-1} is an Eigen value of A^{-1}.

(b) Let λ be an Eigen value of A

$\Rightarrow$ There exists a non zero matrix X such that $AX = \lambda X$

$\Rightarrow$ $X = A^{-1}(\lambda X)$ $\Rightarrow$ $X = \lambda(A^{-1}X)$

$\Rightarrow$ $\lambda^{-1} X = A^{-1}X$

$\Rightarrow$ λ^{-1} is an Eigen value of A^{-1}.

(b) Let λ be an Eigen value of A

$\Rightarrow$ There exists a non zero matrix X such that $AX = \lambda X$

$\Rightarrow$ $adj(A)(AX) = adj(A)(\lambda X)$ $\Rightarrow$ $(adj(A)A)X = \lambda(adj(A))X$

$\Rightarrow$ $|A| X = \lambda(adj(A))X$ $\Rightarrow$ $(|A|/\lambda)X = (adj(A))X$

(since $(adj(A).\ A) = |A|$)

$\Rightarrow$ $|A|/\lambda$ is an Eigen value of adj(A).

11.4 : Diagonalization of a Matrix

Let A be a square matrix of order n and let $\lambda_1, \lambda_2, \ldots, \lambda_n$ be the Eigen values of A and $X_1, X_2, \ldots, X_n$ be the corresponding Eigen vectors, the there exists a matrix P such that $P^{-1}AP$ is a diagonal matrix.

2.4.1 Modal Matrix : Let A be a square matrix of order n then the non singular matrix P which diagonalizes A is called the modal matrix.

2.4.2 Spectral Matrix : Let A be a square matrix of order n and P be a modal matrix such that $P^{-1}AP = D$ then D is called a diagonal / Spectral matrix.

Note : 1. If P is orthogonal then $P^{-1} = P^T$ and we can write $P^{-1}AP = P^TAP = D$. **2.** A square matrix is diagonalizable if (a) It is a real symmetric matrix and (b) it has distinct Eigen values.

Example 14 : If $A = \begin{bmatrix} -4 & -6 \\ 3 & 5 \end{bmatrix}$ Find the nonsingular matrix ***P*** and the diagonal matrix D such that $D = P^{-1}AP$.

Solution : At First We need to find the Eigen values and Eigenvectors of ***A*** first. The characteristic equation of ***A*** is

$$\det(\lambda I - A) = \begin{vmatrix} \lambda + 4 & 6 \\ -3 & \lambda - 5 \end{vmatrix} = (\lambda + 1)(\lambda - 2) = 0 .$$

$\Rightarrow \lambda = -1$ or 2 .

By the above important result, ***A*** is diagonalizable. Then,

1. As $\lambda = 2$,

$$Ax = 2x \Leftrightarrow (2I - A)x = 0 \Leftrightarrow x = k_1\begin{bmatrix} -1 \\ 1 \end{bmatrix},$$

2. As $\lambda = -1$,

$$Ax = -x \Leftrightarrow (-I - A)x = 0 \Leftrightarrow x = k_2\begin{bmatrix} -2 \\ 1 \end{bmatrix},$$

Thus, $\begin{bmatrix} -1 \\ 1 \end{bmatrix}$ and $\begin{bmatrix} -2 \\ 1 \end{bmatrix}$ are two linearly independent Eigenvectors of ***A.***

Let $P = \begin{bmatrix} -1 & -2 \\ 1 & 1 \end{bmatrix}$. Now |P| = -1+2 = 1≠0. Therefore P is nonsingular matrix.

Now consider $P^{-1}AP$

$$P^{-1}AP = \begin{bmatrix} 1 & 2 \\ -1 & -1 \end{bmatrix}\begin{bmatrix} -4 & -6 \\ 3 & 5 \end{bmatrix}\begin{bmatrix} -1 & -2 \\ 1 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 2 & 4 \\ 1 & 1 \end{bmatrix}\begin{bmatrix} -1 & -2 \\ 1 & 1 \end{bmatrix} = \begin{bmatrix} 2 & 0 \\ 0 & -1 \end{bmatrix} = \text{D.}$$

Example 15 : Is $A = \begin{bmatrix} 5 & -3 \\ 3 & -1 \end{bmatrix}$ diagonalizable?

Solution : $|\lambda I - A| = \begin{vmatrix} \lambda - 5 & 3 \\ -3 & \lambda + 1 \end{vmatrix} = (\lambda - 2)^2 = 0 \square \lambda = 2, 2$ Since the Eigen values are same and so A is not diagonalizable.

11.6 Determinants

11.5.1 Definition : Let $A = [a_{ij}]$ be a square matrix of order n. The determinant of A, detA or A| is defined as follows:

(a) If n=2, $\det A = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$

(b) If n=3, $\det A = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$

$$= a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

By using $\begin{vmatrix} + & - & + \\ - & + & - \\ + & - & + \end{vmatrix}$.

11.5.2 Properties of Determinants :

(a) $\det(A) = \det(A^T)$

(b) If two rows (or columns) of A are equal, then $\det(A) = 0$.

(c) If a row (or column) of A consists entirely of 0, then $\det(A) = 0$

(d) If B result from the matrix A by interchanging two rows (or columns) of A, then $\det(B) = -\det(A)$.

(e) $\det(AB) = \det(A)\det(B)$.

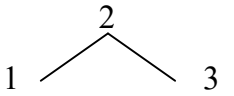
Example 16 : Solve $A = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}$, $B = \begin{bmatrix} 4 & 5 & 6 \\ 1 & 2 & 3 \\ 7 & 8 & 6 \end{bmatrix}$.

Solution : $|A| = 1(45 - 48) - 2(36 - 42) + 3(32 - 35) = -3 + 12 - 9 = 0$

$|B| = 4(12 - 24) - 5(6 - 21) + 6(8 - 14) = -48 + 75 - 36 = 75 - 84 = -9$

Now, in the next discussion, one can understand the application part of secular determinant which is taken from Hückel Theory. The following secular determinant represents a mathematical model of C_3 Molecules (3-atom chain) of Linear Conjugated Hydrocarbons.

i.e. C_3 Molecules (3-atom chain)



And its secular determinant is

$$\begin{array}{c} \\ 1 \\ 2 \\ 3 \end{array} \begin{array}{c} \begin{array}{ccc} 1 & 2 & 3 \end{array} \\ \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \end{array} = 0$$

Where the parameter α and β are constants that may be adjusted to match experimental values. If heteroatoms are presents in molecule then different α's and β's may be associated with different atoms. E is the a parameter like λ which we used in the examples of Eigen values. Each row and column may be associated with one of the atomic orbitals; thus the first row and first column contain information about the nature of orbital 1 and its interactions with the other orbitals, the second row and second column contain information about the nature of orbital 2 and its interactions with the other orbitals. Now if

$x = (\alpha - E)/\beta$ the we have

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$\Rightarrow \quad x^3 - 2x = 0$

$\Rightarrow \quad x(x^2 - 2) = 0$

$\Rightarrow \quad x = 0, \pm\sqrt{2}$

$\Rightarrow \quad x = -\sqrt{2}, \ 0, \ +\sqrt{2}$

Now $E = \alpha - x\beta$ *and so we get*

$E = \alpha - \sqrt{2}\,\beta$ - Highest Energy

$E = \alpha$

$E = \alpha + \sqrt{2}\,\beta$ - Lowest Energy

11.6 Introduction to tensors

Scalar : A physical quantity that can be completely described by a real number.

The expression of its component is independent of the choice of the coordinate system.

Example: Temperature, Mass, Density, Potential.

Vector : A physical quantity that has both direction and length. The expression of its components is dependent of the choice of the coordinate system.

Example: Displacement, Velocity, Force, Heat flow.

Tensor : A 2nd order tensor defines an operation that transforms a vector to another vector.s

In general, Scalar is a 0th order tensor; Vector is a 1st order tensor; 2nd order tensor

11.6.1 Fundamental Concept of Tensor Analysis : A 2nd order tensor is a linear operator that transforms a vector ***a*** into another vector ***b*** through a dot product.

A: $\boldsymbol{a} \rightarrow \boldsymbol{b}$ such that $\boldsymbol{b} = A\boldsymbol{a}$

Properties due to linear operations

$$A(\alpha a+b)=\alpha Aa+Ab$$

$$(A\pm B)a=Aa\pm Ba$$

11.6.2 Anatomy of a Tensor: Concepts of Dyad and Dyadic :

A *dyad* is a tensor. It transforms a vectors a and b by a mathematical product $\otimes$

i.e. Dyad $a\otimes b$ (ab)

A *dyadic* is also a tensor. It is a linear combination of dyads with scalar coefficients.

$B = k_1(a\otimes b)+k_2(c\otimes d)$

11.6.3 Properties of Dyad and Dyadic :

1. $(\mathbf{a}\otimes\mathbf{b})(\alpha\mathbf{c}+\mathbf{d})=\alpha(\mathbf{a}\otimes\mathbf{b})\mathbf{c}+(\mathbf{a}\otimes\mathbf{b})\mathbf{d}$ **2.** $(\alpha\mathbf{a}+\beta\mathbf{b})\otimes\mathbf{c}=\alpha(\mathbf{a}\otimes\mathbf{c})+\beta(\mathbf{b}\otimes\mathbf{c})$

3. $A(\mathbf{a}\otimes\mathbf{b})=(A\mathbf{a})\otimes\mathbf{b}$ 4. Positive semi-definite tensor : $a \cdot Aa \geq 0$ for any $a \neq 0$

5. Positive definite tensor : $a \cdot Aa > 0$ for any $a \neq 0$

Exercise

Q.1 Let V be a set of positive real numbers with addition and scalar multiplication defined as $x + y = xy$ and $cx = x^c$. Show that V is a vector space under these operations.

Q.2 Show that the set V of all pairs of real number of the form $(1, x)$ with the operations

defined as $(1, y) + (1 + y') = (1, y + y')$ and $k(1, y) = (1, ky)$ is a vector space.

Q.3 Show that the following set is not a subspace of R^3

$$W = \{(x, y, z) / x^2 + y^2 + z^2 \leq 1\}.$$

Q.4 Show that $W = \left\{ f / \frac{d^2 f}{dx^2} = 0 \right\}$ is a subspace of the function space.

Q.5 Show that the $w = (9, 2, 7)$ is a linear combination of the vectors $u = (1, 2, -1)$ and $v = (6, 4, 2)$ in R^2.

Q.6 Let $v_1 = (1, 0)$ and $v_2 = (0, 1)$ be two vectors in R^2. Show that every vector in R^2 is a linear combination of v_1 and v_2.

Q.7 Show that the set of vectors $\{(1, 2, 2), (2, 1, 2), (2, 2, 1)\}$ is linearly independent in R^3.

Q.8 Show that the matrices $A = \begin{bmatrix} 4 & 0 \\ -2 & -2 \end{bmatrix}$ $B = \begin{bmatrix} 1 & -1 \\ 2 & 3 \end{bmatrix} and \begin{bmatrix} 0 & 2 \\ 1 & 4 \end{bmatrix}$ are linearly independent.

Q.9 Find the Eigen value and Eigen vectors of the following matrices :

(i) $\begin{bmatrix} 3 & 1 & 4 \\ 0 & 2 & 6 \\ 0 & 0 & 5 \end{bmatrix}$ (ii) $\begin{bmatrix} 1 & 0 & -1 \\ 1 & 2 & 1 \\ 2 & 2 & 3 \end{bmatrix}$ (iii) $\begin{bmatrix} 1 & 2 & 2 \\ 0 & 2 & 1 \\ -1 & 2 & 2 \end{bmatrix}$ (iv) $\begin{bmatrix} 1 & 1 & 3 \\ 1 & 5 & 1 \\ 3 & 1 & 1 \end{bmatrix}$

(v) $\begin{bmatrix} 8 & -6 & 2 \\ -6 & 7 & -4 \\ 2 & -4 & 3 \end{bmatrix}$ (vi) $\begin{bmatrix} -5 & 2 \\ 2 & -2 \end{bmatrix}$

Q.10 Diagonalize the foolowing matrices :

(1) $\begin{bmatrix} 4 & 1 \\ 2 & 3 \end{bmatrix}$ (ii) $\begin{bmatrix} 1 & 2 \\ 5 & 4 \end{bmatrix}$ (iii) $\begin{bmatrix} 4 & 3 \\ 1 & 2 \end{bmatrix}$ (iv) $\begin{bmatrix} 1 & 6 & 1 \\ 1 & 2 & 0 \\ 0 & 0 & 3 \end{bmatrix}$

Answers

Q.9 (i) Eigen values are 3, 2, 5 and Eigen vectors are $\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 3 \\ 2 \\ 1 \end{bmatrix}$.

(ii) Eigen values are 1, 2, 3 and Eigen vectors are $\begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 2 \\ -1 \\ -2 \end{bmatrix}, \begin{bmatrix} 1 \\ 1 \\ -2 \end{bmatrix}$.

(iii) Eigen values are 1, 2, 2 and Eigen vectors are $\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 3 \\ 2 \\ 1 \end{bmatrix}$.

(iv) Eigen values are -2, 3, 6 and Eigen vectors are $\begin{bmatrix}-1\\0\\1\end{bmatrix}, \begin{bmatrix}1\\-1\\1\end{bmatrix}, \begin{bmatrix}1\\2\\1\end{bmatrix}$.

(v) Eigen values are 0, 3, 15 and Eigen vectors are $\begin{bmatrix}1\\2\\2\end{bmatrix}, \begin{bmatrix}2\\1\\-2\end{bmatrix}, \begin{bmatrix}2\\-2\\1\end{bmatrix}$.

(iv) Eigen values are 1, -6 and Eigen vectors are $\begin{bmatrix}1\\2\end{bmatrix}, \begin{bmatrix}2\\-1\end{bmatrix}$

Q.10 (i) $P = \begin{bmatrix}1 & 1\\-1 & 1\end{bmatrix}$ and $D = \begin{bmatrix}2 & 0\\0 & 5\end{bmatrix}$ (ii) $P = \begin{bmatrix}1 & 2\\-1 & 5\end{bmatrix}$ and $D = \begin{bmatrix}-1 & 0\\0 & 6\end{bmatrix}$

(iii) $P = \begin{bmatrix}1 & 1\\-3 & 1\end{bmatrix}$ and $D = \begin{bmatrix}1 & 0\\0 & 5\end{bmatrix}$ (iv) $p = \begin{bmatrix}-3 & 1 & 2\\1 & 1 & 1\\0 & -4 & 0\end{bmatrix}$ and $D = \begin{bmatrix}-1 & 0 & 0\\0 & 3 & 0\\0 & 0 & 4\end{bmatrix}$

Unit – 12: limit and continuity

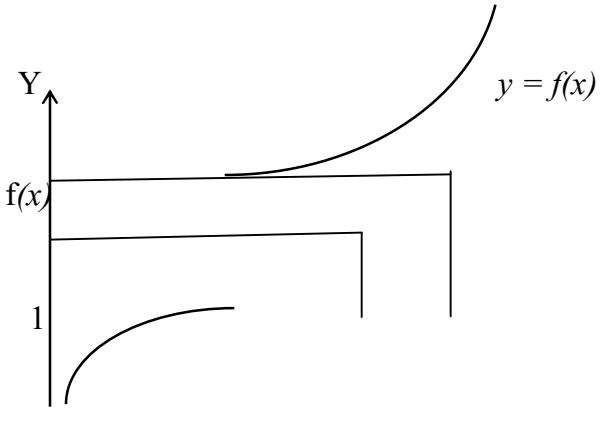
Structure of Unit:

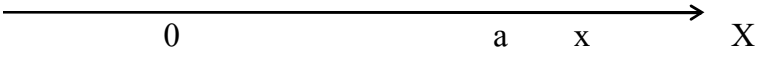
12.1 Introduction

In this chapter, we begin with the concepts of limit and continuity which are very useful to understand one of the most important notion of mathematics, namely, differentiation. Then we put our focus on differentiation and its basic rules since it plays an important role in many real world problems such as Newton's law of cooling, bending of beams, electric circuits. And at the end we discuss application of differential in thermodynamics.

12.2 Limit Continuity and Differentiability

12.2.1 Limit : Let f(x) be a function defined on R. $\lim_{x \to a} f(x) = \ell$ means that for any $\varepsilon > 0$, there exists $\delta > 0$ such that when $0 < |x - a| < \delta$, $|f(x) - \ell| < \varepsilon$.





Note : (1) $\lim_{x\to a} f(x) = \ell$ means that the difference between *f(x)* and A can be made arbitrarily small

when *x* is sufficiently close to a.

(2) If *f(x)* is a polynomial , then $\lim_{x\to a} f(x) = f(a)$.

(3) In general , $\lim_{x\to a} f(x) \neq f(a)$.

(4) *f(x)* may not defined at x = a even though $\lim_{x\to a} f(x)$ exists.

Example 1 : $\lim_{x\to 2}(x^2 + 2x + 5) = 2^2 + 2(2) + 5 = 13$,

Example 2 : Let $f(x) = \begin{cases} 3 \text{ if } x \neq 4 \\ 1 \text{ if } x = 4 \end{cases}$, then $\lim_{x\to 4} f(x) = 3$ but *f(4)* = 1 ,

and so $\lim_{x\to 4} f(x) \neq f()$.

Example 3 : Consider the function $f(x) = \begin{cases} 2x+1, & x \neq 5 \\ 4, & x = 5 \end{cases}$.

Note : $\lim_{x\to a} f(x) = l$ is equivalent to :

(i) $\lim_{x\to a} [f(x) - \ell] = 0$; (ii) $\lim_{x\to a} | f(x) - \ell | = 0$;

(iii) $\lim_{x\to a^-} f(x) = \ell = \lim_{x\to a^+} f(x)$; (iv) $\lim_{h\to 0} f(a+h) = \ell$.

Properties of Limit : Let $f(x)$ and $g(x)$ be two functions defined on an interval containing a , possibly except a . If $\lim_{x\to a} f(x) = \text{h}$ and $\lim_{x\to a} g(x) = \text{k}$, then

(a) $\lim_{x\to a}[f(x) \pm g(x)] = \text{h} \pm \text{k}$ **(b)** $\lim_{x\to a}[f(x)g(x)] = \text{hk}$ **(c)** $\lim_{x\to a} \frac{f(x)}{g(x)} = \frac{\text{h}}{\text{k}}$, (*if* $k \neq 0$)

Theorem (Sandwich Theorem for functions): Let f(x) , g(x) , h(x) be three functions defined on R. If $\lim_{x\to\infty} f(x) = \lim_{x\to\infty} h(x) = a$ and there exists a positive real number X such that when x > X , $f(x) \le g(x) \le h(x)$, then $\lim_{x\to\infty} g(x) = a$.

12.2.2 Continuous Functions :

Definition 1 : Let *f(x)* be a function defined on a region *R*, then *f(x)* is said to be **continuous** at a point

$x = a$ if and only if $\lim_{x\to a} f(x) = f(a)$.

Working Rule : A function *f(x)* is **continuous** at a point $x = a$, if and only if

(a) *f(x)* is well-defined at $x = a$, i.e. *f(a)* exists and *f(a)* is a finite value,

(b) $\lim_{x\to a} f(x)$ exists and $\lim_{x\to a} f(x) = f(a)$.

Definition 2 : A function is **discontinuous** at a point $x = a$ iff it is not continuous at that point ***a***.

Types of Discontinuity :

1. *Removable discontinuity :* If $\lim_{x\to a} f(x)$ exists but not equal to *f(a)*.
2. *Jump discontinuity :* If $\lim_{x\to a^-} f(x) \ne \lim_{x\to a^+} f(x)$
3. *Infinite discontinuity :* If $\lim_{x\to a} f(x) = \infty$ or $\lim_{x\to a} f(x) = -\infty$ i.e. limit does not exist.
4. *At least one of the one-side limit does not exist :* If $\lim_{x\to a^+} f(x)$ or $\lim_{x\to a^-} f(x)$ do not exist.

Examples 4 : Show that $f(x) = \begin{cases} 2x+1, & x \ne 2 \\ 4, & x = 2 \end{cases}$ is discontinuous at x = 2.

Solution : Since f(2) = 4 and $\lim_{x\to 2} f(x) = \lim_{x\to 2}(2x+1) = 5 \ne f(2)$, so f(x) is discontinuous at x = 2.

Example 5 : Since $\lim_{x\to 0^-} e^{\frac{1}{x}} = 0$ and $\lim_{x\to 0^+} e^{\frac{1}{x}} = \infty$, so the function $f(x) = e^{\frac{1}{x}}$ is discontinuous

at $x = 0$.

Example 6 : Show that the function f(x) = [x] is discontinuous at 2.

Solution : Here $\lim_{x\to a^-} f(x) = \lim_{x\to 2^-}(-x) = -2$ and $\lim_{x\to a^+} f(x) = \lim_{x\to 2^+}(x) = 2$ ·

Clearly, $\lim_{x\to a^-} f(x) \neq \lim_{x\to a^+} f(x)$ and hence *f(x)* is discontinuous at 2.

Example 7 : Show that the function $f(x) = \frac{1}{x}$ is discontinuous at x = 0.

Solution : Here $\lim_{x\to a} f(x) = \lim_{x\to 0}\frac{1}{x} = \infty$. Hence Proved.

Properties of Continuous Functions :

1. If *f(x)* and *g(x)* are two functions continuous at $x = a$, then so are $f(x) \pm g(x)$, $f(x)g(x)$ and

$\frac{f(x)}{g(x)}$ provided $g(a) \neq 0$.

2. Let *g(x)* be continuous at $x = a$ and *f(x)* be continuous at $x = g(a)$, then $f \mathbf{O} g$ is continuous at $x = a$.

3. If *f(x)* is continuous on [a, b], then *f(x)* is **bounded** on **[a, b]**.

Example 8 :. $f(x) = \begin{cases} \dfrac{x^3-8}{x-2}, & \text{if } x > 2 \\ x+10, & \text{if } x \le 2 \end{cases}$ **is continuous at** $x = 2$ **.**

Solution: $L.H.L.(x=2) = \lim_{x\to 2^-} f(x) = \lim_{x\to 2^-}\frac{x^3-8}{x-2} = \lim_{x\to 2^-}\frac{x^3-2^3}{x-2} = 3.2^2 = 12$

$R.H.L.(x=2) = \lim_{x\to 2^+} f(x) = x+10 = 2+10 = 12$

$f(2) = 2+10 = 12$

$\therefore L.H.L(x=2) = R.H.L.(x=2) = f(2) = 12$.

Hence function is continuous at 2.

Everywhere Continuous Function : A function is said to be continuous every where iff its domain is R (the set of real numbers) and it is continuous at every real number.

$$\lim_{x \to a} f(x) = f(a), \forall a \in R \text{ ./}$$

Note : 1. A polynomial, sine, cosine, exponential, modulus, constant functions etc. are

everywhere continuous.

2. tangent, cotangent, secant, co secant, square root, logarithmic, reciprocal functions are continuous on their domains

12.2.3 Differentiability:

A function $y = f(x)$ is said to be differentiable at a point $x = a$ in its domain D if and only if the following limit exists

$$f'(x) = \lim_{h \to 0} \frac{f(x+h) - f(x)}{h}$$

and we call $f'(x)$ as first derivative of f with respect to x and to find the derivative of any function is called ***differentiation***. It is denoted as $\frac{d}{dx}$ *or* $f'x)$.

Note : 1. A function is said to be differentiable at its domain iff it is differentiable at every point in its domain. i.e. the condition of differentiability holds at every point of its domain.

2. The above definition of differentiation is also known as *first principle.*

Basic Rules of Differentiation :

1. The Constant Rule : If y = c where c is a constant, $\frac{dy}{dx} = 0$,e.g. y = 10 then $\frac{dy}{dx} = 0$

2. The Linear Function Rule : If y = ax + b then $\frac{dy}{dx} = a$ e.g. y = 10 + 6x then $\frac{dy}{dx} = 6$ **3. The Power Function Rule :** If $y = ax^n$, where a & n are constants $\frac{dy}{dx} = nax^{n-1}$

i) y = 4x $\Rightarrow \frac{dy}{dx} = 4x^0 - 4$ ii) $y = 4x^3 \Rightarrow \frac{dy}{dx} = 12x^2$

iii) $y = 4x^{-2} \Rightarrow \frac{dy}{dx} = 4(-2)x^{-3} = -8x^{-3}$

4. The Sum-Difference Rule : If y = f(x) $\pm$ g(x) $\frac{dy}{dx} = \frac{d}{dx} f(x) \pm \frac{d}{dx} g(x)$

(i) $y = 2x^2 + 3x$ then $\frac{dy}{dx} = 4x + 3$ (ii) $y = 4x^2 - x^3 - 4x$ then $\frac{dy}{dx} = 8x - 3x^2 - 4$

5. **The Product Rule : i**f y = *u.v,* where *u* and *v* are functions of x then

$$\frac{dy}{dx} = u\frac{dv}{dx} + v\frac{du}{dx}$$

E.g. $y = (x+2)(ax^2+bx) \Rightarrow \frac{dy}{dx} = (x+2)\frac{d(ax^2+bx)}{dx} + (ax^2+bx)\frac{d(x+2)}{dx}$

$$\Rightarrow \frac{dy}{dx} = (x+2)(2ax+b) + (ax^2+bx)$$

6. The Quotient Rule : If y = *u/v,* where *u* and *v* are functions of x, then

$$\frac{dy}{dx} = \frac{v\frac{du}{dx} - u\frac{dv}{dx}}{v^2}$$

e.g. if y = (x+2)/(x+4), then $\frac{dy}{dx} = \frac{(x+4)\frac{d}{dx}(x+2) - (x+2)\frac{d}{dx}(x+4)}{(x+4)^2}$

$$\Rightarrow \frac{dy}{dx} = \frac{(x+4)-(x+2)}{(x+4)^2} = \frac{2}{(x+4)^2}$$

e.g. If y = (3x+2)/(x^2+4) then

$$\frac{dy}{dx} = \frac{(x^2+4)(3) - (3x+2)(2x)}{(x^2+4)^2}$$

$$\Rightarrow \frac{dy}{dx} = \frac{-3x^2 - 4x + 12}{(x^2+4)^2}$$

7. The Chain Rule : If y is a function of v, and v is a function of x, then y is a function

of x and $\frac{dy}{dx} = \frac{dy}{dv}.\frac{dv}{dx}$

e.g. if $y = (ax^2 + bx)^{½}$ let $v = (ax^2 + bx)$, so $y = v^{½}$ then

$$\frac{dy}{dx} = \frac{1}{2}(ax^2 + bx)^{-\frac{1}{2}}.(2ax + b)$$

8. The Inverse Function Rule : If x = f(y) then $\frac{dy}{dx} = \frac{1}{dx/dy}$

List of formulae of differentiation :

1. $\frac{d}{dx}\left[x^n\right] = nx^{n-1}$
2. $\frac{d}{dx}\left[a^x\right] = a^x \ln(a)$
3. $\frac{d}{dx}\left[e^x\right] = e^x$
4. $\frac{d}{dx}\left[\log_a x\right] = \frac{1}{x\ln(a)}$
5. $\frac{d}{dx}\left[\ln x\right] = \frac{1}{x}$
6. $\frac{d}{dx}\left[\sin x\right] = \cos x$
7. $\frac{d}{dx}\left[\cos x\right] = -\sin x$
8. $\frac{d}{dx}\left[\tan x\right] = \sec^2 x = \frac{1}{\cos^2 x}$
9. $\frac{d}{dx}\left[\cot x\right] = -\operatorname{cosec}^2 x = -\frac{1}{\sin^2 x}$
10. $\frac{d}{dx}\left[\sec x\right] = \sec x \tan x$
11. $\frac{d}{dx}\left[\operatorname{cosec} x\right] = -\operatorname{cosec} x \cot x$
12. $\frac{d}{dx}\left[\sin^{-1} x\right] = \frac{1}{\sqrt{1-x^2}}$
13. $\frac{d}{dx}\left[\cos^{-1} x\right] = \frac{-1}{\sqrt{1-x^2}}$
14. $\frac{d}{dx}\left[\tan^{-1} x\right] = \frac{1}{1+x^2}$
15. $\frac{d}{dx}\left[\cosh x\right] = \sinh x$
16. $\frac{d}{dx}\left[\sinh x\right] = \cosh x$

Example 9 : Differentiate $\sin\left(\cos\left(x^2\right)\right)$ with respect to 'x'.

Solution : Let, $y = \sin(\theta), \theta = \cos(u), u = x^2$ then,

$$\frac{dy}{dx} = \frac{dy}{d\theta} \times \frac{d\theta}{du} \times \frac{du}{dx}$$

and, $$\frac{dy}{d\theta} = \cos\theta, \frac{d\theta}{du} = -\sin u, \frac{du}{dx} = 2x$$

$$\therefore \frac{dy}{dx} = \cos\theta \times (-\sin u) \times 2x$$

$$= -\cos(\cos u) \times \sin\left(x^2\right) \times 2x$$

$$= -\cos\left(\cos x^2\right) \times \sin\left(x^2\right) \times 2x$$

$$y = \tan^{-1}\left(\frac{3x - x^3}{1 - 3x^2}\right), -\frac{1}{\sqrt{3}} < x < \frac{1}{\sqrt{3}}$$

Example 10 : Find $\frac{dy}{dx}$ if

Solution : Before differentiating an inverse trigonometric function we need to first simplify it

$$Put\ x = \tan\theta$$

$$\therefore y = \tan^{-1}\left(\frac{3x - x^3}{1-3x^2}\right) = \tan^{-1}\left(\frac{3\tan\theta - \tan^3\theta}{1-3\tan^2\theta}\right)$$

$$= \tan^{-1}(\tan 3\theta)$$

$$= 3\theta$$

$$= 3\tan^{-1}x$$

$$\therefore y = 3\tan^{-1}x \Rightarrow \frac{dy}{dx} = 3\frac{d\left(\tan^{-1}x\right)}{dx} = 3\times\frac{1}{1+x^2} = \frac{3}{1+x^2}$$

Example 11 : If $f(x) = 4\sqrt{x} - \frac{3}{\sqrt[3]{x^2}} + \frac{5}{x} - \frac{7}{x^5}$, then find $f'(x)$.

Solution : $f(x) = 4\sqrt{x} - \frac{3}{\sqrt[3]{x^2}} + \frac{5}{x} - \frac{7}{x^5} = 4x^{1/2} - 3x^{-2/3} + 5x^{-1} - 7x^{-5}$

$$\Rightarrow f'(x) = 4\left(\tfrac{1}{2}x^{-1/2}\right) - 3\left(-\tfrac{2}{3}x^{-5/3}\right) + 5\left(-1x^{-2}\right) - 7\left(-5x^{-6}\right)$$

$$\Rightarrow 2x^{-1/2} + 2x^{-5/3} - 5x^{-2} + 35x^{-6} = \frac{2}{\sqrt{x}} + \frac{2}{\sqrt[3]{x^5}} - \frac{5}{x^2} + \frac{35}{x^6}.$$

Example 12 : If $h(x) = \sin(\cos x)$, then find $h'(x)$.

Solution : $h'(x) = \cos(\cos x)\cdot(-\sin x) =$ -sin$x$ cos(cos$x$).

Example 13 : If $j(x) = \tan(2x^2 - 3x + 1)$, then find $j'(x)$.

Solution : $j'(x) = \sec^2(2x^2 - 3x + 1)\cdot(4x - 3)$

Example 14 : If $k(x) = \frac{\sin x}{1+\cos x}$, then find $k'(x)$.

Solution : $k'(x) = \frac{(1+\cos x)(\cos x) - (\sin x)(-\sin x)}{(1+\cos x)^2} = \frac{\cos x + \cos^2 x + \sin^2 x}{(1+\cos x)^2}$

$$= \frac{\cos x + 1}{(1+\cos x)^2} = \frac{1}{1+\cos x}.$$

Example 15 : If $f(x) = x^2 \sin x$, then find $f'(x)$ and $f''(x)$.

Solution : $f'(x) = x^2 \cos x + 2x \sin x$

$$f''(x) = x^2(-\sin x) + 2x\cos x + 2x\cos x + 2\sin x = -x^2 \sin x + 4x\cos x + 2\sin x$$

Example 16 : If $g(x) = \frac{2x+3}{4x-5}$, then find $g'(x)$ and $g''(x)$.

Solution :

$$g'(x) = \frac{(4x-5)(2)-(2x+3)(4)}{(4x-5)^2} = \frac{8x-10-8x-12}{(4x-5)^2} = \frac{-22}{(4x-5)^2} = -22(4x-5)^{-2}$$

$$g''(x) = 44(4x-5)^{-3}(4) = 176(4x-5)^{-3} = \frac{176}{(4x-5)^3}$$

Example 17 : If $x^2 + y^2 = 25$, then find $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$.

Solution : $\frac{d}{dx}\left(x^2 + y^2 = 25\right) \Rightarrow 2x + 2y\frac{dy}{dx} = 0 \Rightarrow \frac{dy}{dx} = \frac{-2x}{2y} = \frac{-x}{y}$

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left(\frac{dy}{dx}\right) = \frac{d}{dx}\left(\frac{-x}{y}\right) = \frac{y(-1)-(-x)\left(\frac{dy}{dx}\right)}{y^2} = \frac{-y + x\left(\frac{-x}{y}\right)}{y^2} = \frac{-y^2 - x^2}{y^3} =$$

$$\frac{-(x^2+y^2)}{y^3} = \frac{-25}{y^3}.$$

Example 18 : Find $\frac{dy}{dx}$ from the equation $x^3 + x^2y + xy^2 + y^3 = 81$

Solution: It is given that $x^3 + x^2y + xy^2 + y^3 = 81$

Differentiating both sides, we get

$$\frac{d\left(x^3+x^2y+xy^2+y^3\right)}{dx}=\frac{d(81)}{dx}$$

$$\Rightarrow 3x^2+\frac{d\left(x^2y\right)}{dx}+\frac{d\left(xy^2\right)}{dx}+\frac{d\left(y^3\right)}{dx}=0$$

$$\Rightarrow 3x^2+\frac{d\left(x^2\right)}{dx}.y+x^2.\frac{dy}{dx}+\frac{dx}{dx}.y^2+x.\frac{d\left(y^2\right)}{dx}+3y^2.\frac{dy}{dx}=0$$

$$\Rightarrow 3x^2+2xy+x^2\frac{dy}{dx}+y^2+x.2y\frac{dy}{dx}+3y^2\frac{dy}{dx}=0$$

$$\Rightarrow \frac{dy}{dx}\left(x^2+2xy+3y^2\right)=-\left(3x^2+2xy+y^2\right)$$

$$\Rightarrow \frac{dy}{dx}=-\frac{3x^2+2xy+y^2}{x^2+2xy+3y^2}$$

Differentiation of parametric functions : Parametric Function: A function of the type

$$y=f(\theta), x=g(\theta)$$

is called as parametric function.

i.e. an equation in which 'x' and 'y' depends on another variable ,here $'\theta'$, also known as parameter is called a parametric function.

In order to differentiate a parametric function of the type $y=f(\theta), x=g(\theta)$ we use following formulae:

$\frac{dy}{dx}=\frac{\frac{dy}{d\theta}}{\frac{dx}{d\theta}}$ **Note :** $\frac{dy}{dx}=\frac{\frac{dy}{d\theta}}{\frac{dx}{d\theta}}=\frac{dy}{d\theta}\times\frac{d\theta}{dx}$.

12.3 Maxima and Minima

12.3.1 Absolute Maximum / Minimum :

A function f has an ***absolute maximum*** (also called *global maximum*) at c if $f(c) \geq f(x)$ for all x in its domain, ***D***. The value $f(c)$ is called the *maximum value* of f. A function f has an ***absolute minimum*** (or *global minimum*) at c if $f(c) \leq f(x)$ for all x in

its domain. Such a value $f(c)$ is called the *minimum value* of f. The maximum and minimum values of f are called the *extreme values* of f.

12.3.2 Local Maximum / Minimum :

A function f has a ***local maximum*** (or ***relative maximum***) at c if $f(c) > f(x)$ when x near c. That is, $f(c) > f(x)$ for all x on some open interval containing c. Similarly, f has a ***local minimum*** (or *relative minimum*) at c if $f(c) < f(x)$ when x near c.

Fermat's Theorem (test for local extreme values): If f has a local maximum or minimum at c, and if $f'(c)$ exists, then $f'(c) = 0$.

Working rule to find Maxima or Minima :

Step – I Find $f'(x)$

Step – II Solve $f'(x)=0$ and find the stationary point of $x=x_0$.

Step – III Find $f''(x)$ and put the stationary point $x=a$ in it

1. $f''(x_0) < 0$, there is a local maximum at x_0.
2. $f''(x_0) > 0$, there is a local minimum at x_0.
3. $f''(x_0) = 0$, then the test is inconclusive at x_0.

Example 19 : If $f(x) = \frac{x^3}{3} + \frac{x^2}{2} - 6x - 2$. Find and classify the stationary points of f.

Solution : To find the stationary points, we solve $f'(x) = 0$:

Here, $f'(x) = x^2 + x - 6 = (x-2)(x+3)$, so that $f'(x) = 0 \Leftrightarrow x = 2$ *or* $x = -3$.

Next, we calculate $f''(x)$ and use the rule above to classify the stationary points:

$f''(x) = 2x + 1$.

$f''(2) = 5 > 0$, so that f has a local minimum at $x = 2$.

$f''(-3) = -5 < 0$, so that f has a local maximum at $x = -3$.

12.4 Exact & inexact differentials in thermodynamics

So far we have been discussing

$$du = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy,$$

total or “exact” differentials

(1)

$$du = M(x,y)dx+N(x,y)dy. \quad (2)$$

If the differential is exact, $M = \left(\frac{\partial u}{\partial x}\right)_y$ and $N = \left(\frac{\partial u}{\partial y}\right)_x$.

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial^2 u}{\partial x \partial y}\right) = \left(\frac{\partial N}{\partial x}\right)_y$$

By the identity of mixed partial derivatives, we have

(3)

Ex:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp = \frac{R}{p}dT - \frac{RT}{p^2}dp$$

Ideal gas $pV = RT$ (for 1 mole), take $V = V(T, p)$, so

(4)

Now the work done in changing the volume of a gas is

$$dW = pdV = RdT - \frac{RT}{p}dp. \quad (5)$$

Let’s calculate the total change in volume and work done in changing the system between two points A and C in *p, T* space, along paths *AC* or *ABC*.

1. Path AC :

$$\frac{dT}{dp} = \frac{T_2 - T_1}{p_2 - p_1} \equiv \frac{\Delta T}{\Delta p} \quad \text{so } dT = \frac{\Delta T}{\Delta p}dp \quad (6)$$

$$\& \ \frac{T - T_1}{p - p_1} = \frac{\Delta T}{\Delta p} \quad \Rightarrow \quad T - T_1 = \frac{\Delta T}{\Delta p}(p - p_1) \quad (7)$$

so

$$\begin{aligned} dV &= \frac{R}{p}\frac{\Delta T}{\Delta p}dp - \frac{R}{p^2}[T_1 + \frac{\Delta T}{\Delta p}(p - p_1)]dp \\ &= -\frac{R}{p^2}(T_1 - \frac{\Delta T}{\Delta p}p_1)dp \\ dW &= -\frac{R}{p}(T_1 - \frac{\Delta T}{\Delta p}p_1)dp \end{aligned} \tag{8}$$

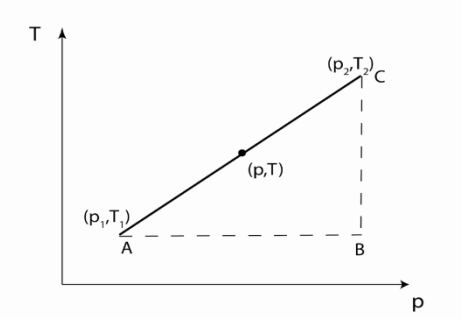


Figure 1: Path in *p, T* plane for thermodynamic process.

Now we can calculate the change in volume and the work done in the process:

$$V_2 - V_1 = \int_{AC} dV = R(T_1 - \frac{\Delta T}{\Delta p}p_1)\frac{1}{p}\Big|_{p_1}^{p_2} = R\frac{T_2p_1 - T_1p_2}{p_1p_2}$$

$$W_1 - W_2 = \int_{AC} pdV = R(T_1 - \frac{\Delta T}{\Delta p}p_1)\ln p\Big|_{p_1}^{p_2} = R\frac{T_2p_1 - T_1p_2}{p_2 - p_1}\ln\frac{p_2}{p_1}$$

2. Path ABC: Note along AB $dT = 0$, while along BC $dp = 0$.

$$V_2 - V_1 = \int_{ABC}\left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp = \int_{p_1}^{p_2}\left(\frac{\partial V}{\partial p}\right)_T dp + \int_{T_1}^{T_2}\left(\frac{\partial V}{\partial T}\right)_p dT$$

$$= \int_{p_1}^{p_2}\frac{-RT_1}{p^2}dp + \int_{T_1}^{T_2}\frac{R}{p_2}dT = R\frac{T_2p_1 - T_1p_2}{p_1p_2}$$

$$W_2 - W_1 = \int_{p_1}^{p_2} p\left(\frac{\partial V}{\partial p}\right)_T dp + \int_{T_1}^{T_2}\frac{RT}{V}\left(\frac{\partial V}{\partial T}\right)_p dT = -RT_1\ln\frac{p_2}{p_1} + R(T_2 - T_1)$$

Note the change in V is independent of the path — the volume is characteristic of a point *(p, T)* in equilibrium — but the work done in the process is not! What's the difference? In the system with *p,T* as independent variables, *dV* is an exact differential, while *dW* is not. How can you see the difference? Go back and examine the forms we had for *dV* and *dW* in (4) and (5). In the case of *dv*, we had

$$dV = Mdp + NdT, \qquad \text{with } M = \frac{R}{p} \text{ and } N = -\frac{RT}{p^2}$$

$$\frac{\partial M}{\partial p} = -\frac{R}{p^2} \qquad \frac{\partial N}{\partial T} = -\frac{R}{p^2},$$

which is indeed exact,

$$dW = M'dp + N'dT \qquad M' = R \quad ; \qquad N' = -\frac{RT}{p}$$

whereas

$$\frac{\partial M'}{\partial p} = 0 \qquad \frac{\partial N'}{\partial T} = -\frac{R}{p},$$

is not. This is a demonstration (we won't use the word proof) that for a thermodynamic process involving changes in the p — T plane, the volume of the system is a "state variable", i.e. (for 1 mole of gas) it simply depends on what p and T are; if you have specified p, T, you know the volume of the system. The change in volume between two points will therefore always be *V2 — V1* independent of which path is chosen. The work done in the same process is however not independent of the path of integration.

12.6 Exercise

Q.1 Show that the function *f(x)* given by $f(x) = \begin{cases} x\sin(1/x) & , \quad x \neq 0 \\ 0 & , \quad x = 0 \end{cases}$ is continuous at x = 0.

Q.2 Show that $f(x) = \begin{cases} 5x-4 & when \;\; 0 < x \leq 1 \\ 4x^3 - 3x & when \;\; 1 < x < 2 \end{cases}$ is continuous at x = 1.

Q.3Show that f$(x) = \begin{cases} \dfrac{1-\cos x}{x^2} & when \;\; x \neq 0 \\ 1 & when \;\; x = 0 \end{cases}$ is discontinuous at x = 0.

Q.4 Differentiate the function with respect to x

(a) $\dfrac{2^x \cot x}{\sqrt{x}}$ (b) $\dfrac{\sin x - x\cos x}{x\sin x + \cos x}$ (c) $\sin(e^{x^2})$ (d) $\log\tan\left(\dfrac{\pi}{2} + \dfrac{x}{2}\right)$

Q.5 Find all the points of local maxima and minima of the function

$f(x) = x^3 - 6x^2 + 9x - 8$

Q.6 Find the maximum and minimum value of the $f(x) = (-3/4)x^4 - 8x^3 - (45/2)x^2 + 105$

Q.7 Show that none of the function have local maxima and minima.

(a) $x^3 + x^2 + x + 1$ (b) $\log x$ (c) e^x

Unit – 13 : Integrals & Differential Calculus

Structure of Unit:

13.1 Introduction

Integral Calculus is the study of finding a function of from information about its rate of change. In chapter, we starting our discussion with basics of integration and some major techniques of solving typical integral problems. Then we focusing on function of several variables which immediate gives us the notion of partial differentiation. In which Euler's theorem and Jacobian will help us to determine functional dependence. And at last, Curve tracing/sketching is one of the most popular method to draw curves which is useful in the application of integration in finding length, area, volume etc.

13.2 Basic Rules of Integration

13.2.1 Integration :

When a function *f(x)* is known and we differentiate it to obtain its derivative *df/dx* , then the reverse process, to obtain *f(x)* again from *df/dx* is called ***integration***. Now we are put our focus on the basic techniques and method of integration which will help to improve the knowledge of integration for the author.

As we discussed above that integration is a reverse process of differentiation. Let $f(x) = x^2$ be a function then

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

i.e. $x^2 \longrightarrow$ Differentiate $\longrightarrow 2x$

Now if integration is a reverse process then we have

. $x^2 \longrightarrow$ Differentiate $\longrightarrow 2x$

$\longleftarrow$ $\longleftarrow$

Integrate

From the above discussion we got a very first result of integration

i.e. $$\int x^n dx = \frac{x^{n+1}}{n+1} + c, n \neq -1 \quad \ldots\ldots\ldots(*)$$

Here the sign $\int$ denotes integration and we call it as integration of x^n with respect to x.

Now we take a look of the functions x^2-7, x^2+9, $x^2+2.11$ etc.

All of the above functions have the same derivative $2x$, since as we knew the differentiation of a constant term is zero. But when we integrate $2x$, we get only x^2 and we can't find the constant term which is in the original function. That is why there is constant in equation (*) and in every indefinite integral. And we call it as ***constant of integration***.

Note : 1. If the $\int$ sign does not have any limit then it is known as *indefinite integral* otherwise it is said to be definite integral.

2. Integration is sometime known as antidifferentiation.

Integral Sign $\longrightarrow \int 2x^2 \, dx = \frac{2x^3}{3} + C \longleftarrow$ constant of Integration

Integrand differential Resultant

3. Equation (*) is also known as power rule of integration.

13.2.2 Integration of Some Elementary functions :

1. $\int x^n dx = \frac{x^{n+1}}{n+1} + c, n \neq -1$ **(Note:** $\int dx = x + c$ **)** **2.** $\int \frac{1}{x} dx = \log|x| + c$

3. $\int a^x dx = \frac{a^x}{\log a} + c$ **4.** $\int e^{ax} dx = \frac{e^{ax}}{a} + c$

5. $\int \sin x dx = -\cos x + c$ **6.** $\int \cos x dx = \sin x + c$

7. $\int \sin ax \ dx = -\frac{\cos ax}{a} + c$ **8.** $\int \cos ax \ dx = \frac{\sin ax}{a} + c$

9. $\int \sec^2 x \ dx = \tan x + c$ **10.** $\int \operatorname{cosec}^2 x \ \mathrm{dx} = -\cot x + \mathrm{c}$

11. $\int \sec x \tan x dx = \sec x + c$ **12.** $\int \operatorname{cosec} x \cot x dx = -\operatorname{cosec} x + c$

13. $\int \tan x dx = -\log|\cos x| + c$ **or** $\log|\sec x| + c$ **s14.** $\int \cot x dx = \log|\sin x| + c$

14. $\int \sec x dx = \log|\sec x + \tan x| + c$ or $\log\left|\tan\left(\frac{\pi}{4} + \frac{x}{2}\right)\right| + c$

15. $\int \operatorname{cosec} x dx = \log|\operatorname{cosec} x - \cot x| + c$ **or** $\log\left|\tan\frac{x}{2}\right| + c$

16. $\int \log x \ dx = x \log x - x + c$

13.2.3 Integration of functions whose resultants are inverse Trigonometric functions :

1. $\int \frac{1}{\sqrt{a^2 - x^2}} dx = \sin^{-1}\frac{x}{a} + c$ **2.** $\int \frac{dx}{a^2 + x^2} = \frac{1}{a}\tan^{-1}\frac{x}{a} + c$

3. $\int \frac{-1}{\sqrt{a^2 - x^2}} dx = \cos^{-1}\frac{x}{a} + c$ **4.** $\int \frac{-dx}{a^2 + x^2} = \frac{1}{a}\cot^{-1}\frac{x}{a} + c$

5. $\int \frac{1}{x\sqrt{x^2-a^2}}dx = \frac{1}{a}\sec^{-1}\frac{x}{a}+c$ **6.** $\int \frac{-1}{x\sqrt{x^2-a^2}}dx = \frac{1}{a}\operatorname{cosec}^{-1}\frac{x}{a}+c$

13.2.4 Some more results on Integration :

1. $\int \frac{dx}{a^2-x^2} = \frac{1}{2a}\log\left|\frac{x+a}{x-a}\right|+c$ **2.** $\int \frac{dx}{x^2-a^2} = \frac{1}{2a}\log\left|\frac{x-a}{x+a}\right|+c$

3. $\int \sqrt{a^2+x^2}dx = \frac{x}{2}\sqrt{a^2+x^2}+\frac{a^2}{2}\log(x+\sqrt{a^2+x^2})+c$

4. $\int \sqrt{a^2-x^2}dx = \frac{x}{2}\sqrt{a^2-x^2}+\frac{a^2}{2}\sin^{-1}\frac{x}{a})+c$

5. $\int \sqrt{x^2-a^2}dx = \frac{x}{2}\sqrt{x^2-a^2}+\frac{a^2}{2}\log(x+\sqrt{x^2-a^2})+c$

6. $\int \sqrt{2ax-x^2}dx = \frac{x-a}{2}\sqrt{2ax-x^2}+\frac{a^2}{2}\cos^{-1}\left(\frac{a-x}{a}\right)+c$

7. $\int \frac{f'(x)}{f(x)}dx = \log|f(x)|+c$

Definite Integral : As we discussed earlier, if we put the limit on integration as an interval (a, b) then integration is denoted as

$$\int f(x)dx = \int_a^b f(x)dx$$

Indefinite integral Definite integral

Where 'b' is called the upper limit and 'a' is called the lower limit.

Fundamental theorem of Integration :

$$\int_a^b f(x)dx = F(b)-F(a)$$

Note : All the formulae of integration listed before are applicable on definite integral also but in case of definite integral we are not adding the constant c.

4.2.4 Properties of Integration :

1. $\int_a^b cf(x)dx = c\int_a^b f(x)dx$ where c is constant

2. $\int_a^b (f(x) \pm g(x))dx = \int_a^b f(x)dx \pm \int_z^b g(x)dx$

3. $\int_a^b f(x)dx = \int_a^c f(x)dx + \int_c^b f(x)dx$

4. $\int_a^a f(x)dx = 0$ **5.** $\int_a^b f(x)dx = -\int_b^a f(x)dx$

6. $\int_a^b cdx = c(b-a)$ **7.** If $f(x) \geq 0$ on $a \leq x \leq b$ then $\int_a^b f(x)dx \geq 0$

8. If f(x) $\geq$ g(x) on $a \leq x \leq b$ then $\int_a^b f(x)dx \geq \int_a^b g(x)dx$

Example 1 : $\int x^3 dx = \frac{x^4}{4} + c, \qquad \int_0^3 5dx = [5x]_0^3 = 5\times 3 - 5\times 0 = 15.$

$$\int \frac{2}{5}x^7 dx = \frac{2}{5}\left(\frac{x^8}{8}\right) + c = \frac{x^8}{20} + c.$$

13.3 Integration by parts

In, all the formulae of integration discussed till now, only one function at a time is considered. Now the method of integration by parts by which one can integrate more than one function at a time based on differentiation's product rule.

If u(x) and v(x) are two functions of x then integration by parts is defined as

$$\int u(x).v(x)\ dx = u(x)\int v(x)dx - \int\left\{\left(\frac{d}{dx}u(x)\right)\int v(x)dx\right\}dx$$

For definite integral $\int_a^b u(x).v(x) = \{u(x)\int v(x)dx\}_a^b - \int_a^b\left\{\left(\frac{d}{dx}u(x)\right)\int v(x)dx\right\}dx$

Here, we have to be very careful while we choose u and v. Our selection should be in such a mannar that the second integral of the R.H.S. of integration by parts formula will be easier. There is a technique (trick), namely, L-I-A-T-E technique to choose u to be the function that came first in a list

L – Logarithmic fuction

I – Inverse

A – Algebraic function

T – Trigonometric function

E – Exponential function

Example 2 : Evaluate $\int x^3 \log x dx$

Solution : Let u = log$2x$ and v = x^3 then we have

$$\int x^3 \log 2x dx = \log 2x \int x^3 dx - \int \left\{ \left(\frac{d}{dx} \log 2x \right) \int x^3 dx \right\} dx$$

$$= \frac{x^4 \log 2x}{4} - \int \frac{2}{2x} . \frac{x^4}{4} dx = \frac{x^4 \log 2x}{4} - \frac{1}{4} \int x^3 dx = \frac{x^4 \log 2x}{4} - \frac{x^4}{16} + c$$

Example 4 : Evaluate $\int xe^x dx$

Solution : Let u = x and v = e^x then we have

$$\int xe^x dx = x \int e^x dx - \int \left\{ \left(\frac{d}{dx} x \right) \int e^x dx \right\} dx = xe^x - \int e^x dx = xe^x - e^x + c .$$

Example 5 : Evaluate I = $\int_0^{\pi/2} x \sin x \cos x dx$

Solution : Consider

$$\int_0^{\pi/2} x \sin x \cos x dx = \frac{1}{2} \int_0^{\pi/2} x(2 \sin x \cos x) dx = \frac{1}{2} \int_0^{\pi/2} x \sin 2x dx$$

since 2sin$x$cos$x$ = sin$2x$. Now let u = x and v = sin$2x$

$$I = \frac{1}{2}\int_0^{\pi/2} x\sin 2x\,dx = \frac{1}{2}\left\{\left[x\int \sin 2x\,dx\right]_0^{\pi/2} - \int_0^{\pi/2}\frac{(-\cos 2x)}{2}\,dx\right\}$$

$$= \frac{1}{2}\left\{\left(\frac{-x\cos 2x}{2}\right)_0^{\pi/2} + \int_0^{\pi/2}\frac{\cos 2x}{2}\,dx\right\} = \frac{1}{2}\left\{-\left(\frac{\pi}{2}\cos\pi - 0\right) + \left(\frac{\sin 2x}{4}\right)_0^{\pi/2}\right\}$$

$$= \frac{1}{2}\left\{-\frac{(-1)\pi}{4} + \frac{1}{4}(\sin\pi - \sin 0)\right\} = \frac{\pi}{8}$$ (Since cosπ = -1 and sinπ = sin0 = 0).

Generalization of Integration by parts :

$$\int u(x).v(x)\,dx = u(x)v_1(x) - u'(x)v_2(x) + u''(x)v_3(x) - u'''(x)v_4(x) + \ldots$$

where $u', u'', \ldots$ are derivatives of u with respect to x of order 1, 2,…

and $v_1, v_2, \ldots$ are integrals of v with respect to x of order 1, 2, …

Example 6 : Evaluate $\int x^4 \cos x\,dx$.

Solution : Let u = x^4 and v = cos$x$ and Since we know that

$$\int u(x).v(x)\,dx = u(x)v_1(x) - u'(x)v_2(x) + u''(x)v_3(x) - u'''(x)v_4(x) + \ldots$$

Then we have

$$\int x^4\cos x\,dx = x^4\sin x - 4x^3(-\cos x) + 12x^2(-\sin x) - 24x\cos x + 24\sin x + c$$

$$= x^4\sin x + 4x^3\cos x - 12x^2\sin x - 24x\cos x + 24\sin x + c$$

Note : 1. This method is useful and works only when a polynomial function is going to be selected as u.

2. Generally LIATE technique is useful but there are some exceptions also.

For examples : $\int x^3\sqrt{4-x^2}\,dx$ since both the functions are algebraic then LIATE rule is no more helpful here.

Now check out the next example in which, when we apply integration by par, the integral is repeating itself. Then it is likely a ***party trick integral***.

Example 7 : Evaluate I = $\int e^x \sin x dx$.

Solution : Let $u = e^x$ and $v = \sin x$, then we get

$$I = \int e^x \sin x dx = e^x \int \sin x dx - \int e^x (-\cos x) dx$$

$$\Rightarrow \cdots\cdots\cdots\cdots I = -e^x \cos x + \left\{ e^x \int \cos x dx - \int e^x \sin x dx \right\} = -e^x \cos x + e^x \sin x - I$$

$$\Rightarrow \ 2I = -e^x \cos x + e^x \sin x \Rightarrow I = \frac{-e^x \cos x + e^x \sin x}{2} + c$$

13.4 Integration by using Partial fraction

It may so happen that a given function is a rational function of two polynomials and it is difficult to integrate the function when a polynomial of denominator is complicated. To integrate such function, we expressed the given function *f(x)/g(x)* as a sum of simpler fractions, which are called ***partial fractions***

Type I: Real linear factors in denominator.

(linear factor means each factor and variable has power one)

$$\frac{f(x)}{(ax \pm b)(cx \pm d)} = \frac{A}{(ax \pm b)} + \frac{B}{(cx \pm d)}$$

Example 8: Evaluate $\int \frac{3x-4}{(x-1)(3x-5)} dx$

Solution : Write it as $\frac{3x-4}{(x-1)(3x-5)} = \frac{A}{x-1} + \frac{B}{3x-5}$

$$= \frac{A(3x-5) + B(x-1)}{(x-1)(3x-5)}$$

$$3x - 4 = A(3x-5) + B(x-1)$$

If $x = 1$: $\quad -1 = -2A \quad$ So $A = 0.5$ and

If $x = 5/3$: $\quad 1 = \frac{2}{3}B \quad$ So $B = 1.5$

therefore $\quad \frac{3x-4}{(x-1)(3x-5)} = \frac{0.5}{x-1} + \frac{1.5}{3x-5}$

We can use this form to work out the integral:

$$\int \frac{3x-4}{(x-1)(3x-5)}dx = \int\left(\frac{0.5}{x-1}+\frac{1.5}{3x-5}\right)dx$$

$$= 0.5\int \frac{1}{x-1}dx + 1.5\int \frac{1}{3x-5}dx$$

$$= 0.5\ln(x-1)+\frac{1.5}{3}\ln(3x-5)+c$$

$$= 0.5\ln(x-1)+0.5\ln(3x-5)+c$$

Example 9 : Evaluate $\int \frac{dx}{x^2+5x-14}$

Solution : We can write the given integral as $\int \frac{dx}{x^2+5x-14} = \int \frac{dx}{(x-2)(x+7)}$

Now the further solution is left for the reader which is based on Example 8, and the answer is $\int \frac{dx}{x^2+5x-14} = (1/5)\log(x+7) - (1/5)\log(x-2) + c$.

Type II : The denominator is a product of real linear factors some of which are repeated.

$\frac{f(x)}{(ax\pm b)^n} = \frac{A_1}{(ax\pm b)} + \frac{A_2}{(ax\pm b)^2} + \ldots + \frac{A_n}{(ax\pm b)^n}$ where $A_1, A_2, \ldots, A_n$ are constants.

Example 9: Evaluate $\int \frac{2x^2-2}{(x-2)^3}dx$

Solution: We can write the given function of integration as

$$\frac{2x^2-2}{(x-2)^3} = \frac{A}{(x-2)} + \frac{B}{(x-2)^2} + \frac{C}{(x-2)^3} = \frac{A(x-2)^2+(x-2)+C}{(x-2)^3} =$$

$2x^2 - 2 = Ax^2 + (-4A + B)\,x + (4A - 2B + C)$

On comparing we get

A = 2, $\quad$ - 4A + B = 0 $\square$ B = 8, $\quad$ 4A – 2B + C = -2 $\square$ C = 6

And so we have

$$\int \frac{2x^2-2}{(x-2)^3}dx = \int \frac{2dx}{(x-2)} + \int \frac{8dx}{(x-2)^2} + \int \frac{6dx}{(x-2)^3} = 2\log(x-2) - 8/(x-2) - 3/(x-2)^2 + c$$

Type III : When denominator contains irreducible quadratic factors :

If we find denominator as mentioned above then for each quadratic factor use one corresponding fraction of the form $\frac{Ax+B}{ax^2+bx+c}$, where A, B are constants.

Example 10 : Find $\int \frac{2x^2-x+4}{x^3+4x}dx$

Solution : We can write the given function of integration as

$$\frac{2x^2-x+4}{x^3+4x} = \frac{A}{x} + \frac{Bx+C}{x^2+4}$$ here x^2+4 is quadratic

$2x^2-x+4 = A(x^2+4)+(Bx+C)x$ by multiplying $x(x^2+4)$

$= (A+B)x^2+Cx+4A$

$A+B=2 \quad C=-1 \quad 4A=4$ by equating coefficients

$A=1 \quad B=1 \quad C=-1$

$$\int \frac{2x^2-x+4}{x^3+4x}dx = \int \frac{1}{x}dx + \int \frac{x-1}{x^2+4}dx = \int \frac{1}{x}dx + \int \frac{x}{x^2+4}dx - \int \frac{1}{x^2+4}dx$$

$$= \ln|x| + \frac{1}{2}\ln|x^2+4| - \frac{1}{2}\tan^{-1}\left(\frac{x}{2}\right) + C$$

13.5 Integration by Substitution

Substitution in integration is used to simplify the typical mathematical expression, which one can find difficult to solve. It is very popular method throughout mathematics. Integral which are computed by changes of variables is called U-Substitution. In this we have to change the basic variable of an integrand (like 'x') to another variable (like 'u'). This makes an integral easy to determine.

1. $I = \int f(ax+b)\ dx$ let $ax+b=u$ implies $dx = \frac{1}{a}du$ then we have

$$I = \int f(u)\ du$$

2. It is used when an integral contains some function and its derivative, when

$$I = \int f(x)\ \ f'(x)\ dx$$

Let $u = f(x)$ implies $du = f'(x)\ dx$ then we have

$$I = \int u\ du$$

This is definitely easier to integrate.

3. When we can find integral of the following type

$$I = \int f(g(x))\ \ g'(x)\ dx$$

Then let $u = g(x)$ implies $g'(x)dx = du$, then above integral become

$$I = \int f(u)\ du$$

This is easier to solve. It is known as ***chain rule.***

4. Trigonometric substitution :

(a) When Integrals of the Form $\sqrt{a^2 - x^2}$ then put $x = a\sin\theta \Rightarrow dx = a\cos\theta d\theta$

(b) when Integrals of the Form $\sqrt{a^2 + x^2}$ then put $x = a\tan\theta \Rightarrow dx = a\sec^2\theta d\theta$

(c) when Integrals of the Form $\sqrt{x^2 - a^2}$ then put

$x = a\sec\theta \Rightarrow dx = 2\sec\theta\tan\theta d\theta$

Working rule for Substitution Method :

Step – 1 : Choose u.

Step – 2 : Calculate du as $du = \frac{du}{dx}dx$

Step – 3 : Substitute u. Arrange to have du in your integral also. (All x and dx must be replaced!)

Step – 4 : Solve the new integral.

Step – 5 : Substitute back in to get x again.

Step – 6 : In case of definite integral we have to change the limits also.

Example 11 : Evaluate $I = \int (3x+2)^3 dx$

Solution : let $3x+2 = u$ implies $3dx = du$ *or* $dx = \frac{1}{3}du$ then we have

$$I = \frac{1}{3}\int u^3 du \quad = \frac{1}{3}(\frac{u^4}{4}) + C \; = \frac{u^4}{12} \; + C = \frac{(3x+2)^4}{12} + C \quad \text{(Answer).}$$

Example 12 : Evaluate $I = \int \cos(5x-1)\ dx$

Solution : let $5x-1 = u$ implies $5dx = du$ *or* $dx = \frac{1}{5}du$ then we have

$$I = \frac{1}{5}\int \cos u \ du \quad = \frac{1}{5}\sin u \; + C \; = \frac{1}{5}\sin(5x-1) + C \ \text{(Answer).}$$

Example 13 : Evaluate $I = \int x \ \sin x^2 dx$

Solution : let $x^2 = u$ implies $2xdx = du$ *or* $xdx = \frac{1}{2}du$ then we have

$$I = \frac{1}{2}\int \sin u \ du \quad = \frac{1}{2}(-\cos u) + C = -\frac{1}{2}\cos x^2 + C \ \text{(Answer)}$$

Example 14 : Evaluate $I = \int_0^1 x^2 (x^3+1)^4 dx$

Solution : $x^3 + 1 = u$ *imples* $3x^2 dx = du$ *or* $x^2 dx = \frac{du}{3}$

Also from $x^3+1 = u$ gives us u = 1 when x = 0 and u = 2 when x = 1 then we have

$$I = \frac{1}{3}\int_1^2 u^4 du \quad = \frac{u^5}{15} + C \quad = \frac{(x^3+1)^5}{15} + C$$

Example 15 : Find $\int \sqrt{4-x^2}\ dx$.

Solution : Let $x = 2\sin\theta$ where $-\pi/2 \le \theta \le \pi/2$. Then $\sqrt{4-x^2} = 2\cos\theta$ and $dx = 2\cos\theta\ d\theta$. Therefore

$$\int \sqrt{4-x^2}\ dx = \int (2\cos\theta)(2\cos\theta\ d\theta) = 4\int \cos^2\theta\ d\theta = 4\int \frac{1+\cos\theta}{2} d\theta$$

$$= 4\left[\frac{1}{2}\theta + \frac{1}{2}\sin\theta\cos\theta\right] + C = 2\theta + 2\sin\theta\cos\theta + C$$

$$= 2\sin^{-1}\left(\frac{x}{2}\right) + 2\left(\frac{x}{2}\right)\left(\frac{\sqrt{4-x^2}}{2}\right) + C =$$

$$= 2\sin^{-1}\left(\frac{x}{2}\right) + \frac{x\sqrt{4-x^2}}{2} + \text{C}.$$

13.6 Reduction Formulae

Reduction formulae are a technique of integration in which one can use integration by parts. Reduction formulae enable us to deal with the solution of integrals which are not immediately solvable. Reduction formula means a relation between the integral and its simpler form. In this topic we evaluate the integrals of any powers of sine, cosine and other trigonometric function.

1. $\int \sin^n x\ dx = -\frac{1}{n}\sin^{n-1} x\cos x + \frac{n-1}{n}\int \sin^{n-2} x\ dx$
2. $\int \cos^n x\ dx = \frac{1}{n}\cos^{n-1} x\sin x + \frac{n-1}{n}\int \cos^{n-2} x\ dx$
3. $\int \tan^n x\ dx = \frac{1}{n-1}\tan^{n-1} x - \int \tan^{n-2} x\ dx$
4. $\int \cot^n x\ dx = -\frac{1}{n-1}\cot^{n-1} x - \int \cot^{n-2} x\ dx$
5. $\int \sec^n x\ dx = \frac{1}{n-1}\sec^{n-2} x\tan x + \frac{n-1}{n-1}\int \sec^{n-2} x\ dx$
6. $\int \operatorname{cosec}^n x\ dx = -\frac{1}{n-1}\operatorname{cosec}^{n-2} x\cot x + \frac{n-1}{n-1}\int \operatorname{cosec}^{n-2} x\ dx$
7. $\int \sin^m x\cos^n x\, dx = -\frac{1}{m+n}\sin^{m-1} x\cos^{n+1} x + \frac{m-1}{m+n}\int \sin^{m-2} x\cos^n x\ dx$

   (here m, n>0)

Example 16 : Find $\int \cos^3 x \, dx$.

Solution : Use the reduction formula: $\int \cos^3 x \, dx = \frac{1}{3}\cos^2 x \sin x + \frac{2}{3}\int \cos x \, dx$

$$= \frac{1}{3}\cos^2 x \sin x + \frac{2}{3}\sin x + C = \frac{1}{3}\sin x(1-\sin^2 x) + \frac{2}{3}\sin x + C$$

$$= \sin x - \frac{1}{3}\sin^3 x + C .$$

Example 17 : Find $\int \sec^3 x dx$.

Solution : $\int \sec^3 x \, dx = \frac{\sec x \tan x}{2} + \frac{1}{2}\int \sec x \, dx = \frac{1}{2}\sec x \tan x + \frac{1}{2}\ln\left|\sec x + \tan x\right| + C$.

Example 18 : Find $\int \sin^3 x \cos^2 x dx$.

Solution : Here m = 3 and n = 2, therefore we have

$$\int \sin^3 x \cos^2 x dx = -\frac{\cos^3 x \sin^2 x}{5} + \frac{2}{5}\int \sin x \cos^2 dx$$

$$= -\frac{\cos^3 x \sin^2 x}{5} - \frac{2}{5}\int t^2 di = -\frac{\cos^3 x \sin^2 x}{5} - \frac{2}{15}t^3 + c = -\frac{\cos^3 x \sin^2 x}{5} - \frac{2}{15}\cos^3 x + c$$

Let cos x = t imply -sin$x$ dx = dt then we have

13.7 Function of Several Variables

The function f denoted by $z = f(x, y)$ where z is dependent variable and $f(x, y)$ are independent variables, then z is called function of two variables.

Example 18 : z = ax + by is a function of two variables.

Example 19 : Every surface in a space is a function of two variables.

Example 20 : V = xyz the volume is a function of three variables.

13.7.1Limit : A function *f(x, y)* is said to have a limit L as the point (x, y) approaches (a, b) And is denoted as $\lim_{(x,y)\to(a,b)} f(x,y) = L$

Note : The limit of a function *f(x, y)* of two variables is said to exists only when the same value is obtained for the limit along any path in the *(x, y)* – plane from (*x, y*) to *(a, b).*

13.7.2 Properties of Limits : if $\lim_{(x,y)\to(a,b)} f(x,y) = L$ and $\lim_{(x,y)\to(a,b)} g(x,y) = M$ then

1. $\lim_{(x,y)\to(a,b)} f \pm g = L \pm M$ 2. $\lim_{(x,y)\to(a,b)} f.g = L.M$
2. $\lim_{(x,y)\to(a,b)} f / g = L / M$

13.7.3 Continuity: A function *f(x, y)* is said to be continuous at a point (*a,b*) if

(1) *f(x, y)* must be well defined.

(2) $\lim_{(x,y)\to(a,b)} f(x,y) = exists$

(3) $\lim_{(x,y)\to(a,b)} f(x,y) = value\ \ of\ \ a\ \ function\ \ (a,b)$

Example 21 : Evaluate $\lim_{(x,y)\to(0,0)} (x^2 + y^2)$

Solution : $\lim_{\substack{x\to 0\\ y\to 0}} (x^2 + y^2) = \lim_{y\to 0} y^2 = 0$

And $\lim_{\substack{y\to 0\\ x\to 0}} (x^2 + y^2) = \lim_{x\to 0} x^2 = 0$

Since, the value of the limit along any path is same, hence limit exists and is zero.

Example 22 : If *f(x, y)*= $\frac{y^2 - x^2}{x^2 + y^2}$, show that limit does not exists at (0, 0).

Solution : Consider $\lim_{\substack{y\to 0\\ x\to 0}} \frac{y^2 - x^2}{x^2 + y^2} = \lim_{x\to 0} \frac{-x^2}{x^2} = -1$

$$\lim_{\substack{x\to 0\\ y\to 0}} \frac{y^2 - x^2}{x^2 + y^2} = \lim_{y\to 0} \frac{y^2}{y^2} = 1$$

Since the limits along two different path are not same therefore limit does not exixsts.

Example 23 : Discuss the continuity of $f(x, y) = \begin{cases} x \Big/ \sqrt{x^2 + y^2} & (x, y) \neq (0,0) \\ 2 & (x, y) = (0,0) \end{cases}$

Solution : [I]. $\lim\limits_{\substack{x\to 0\\ y\to 0}} \frac{x}{\sqrt{x^2 + y^2}} = 0$ [II]. $\lim\limits_{\substack{y\to 0\\ x\to 0}} \frac{x}{\sqrt{x^2 + y^2}} = \lim\limits_{x\to 0} \frac{x}{\sqrt{x^2}} = 1$

Since limits along different path is different therefore function is not continuous.

Example 24 : Discuss the continuity of $f(x, y) = \begin{cases} \frac{x^3 - y^3}{x^2 + y^2} & (x, y) \neq (0,0) \\ 0 & (x, y) = (0,0) \end{cases}$

Solution : [I]. $\lim\limits_{\substack{x\to 0\\ y\to 0}} \frac{x^3 - y^3}{x^2 + y^2} = \lim\limits_{y\to 0} (-y) = 0$

[II]. $\lim\limits_{\substack{y\to 0\\ x\to 0}} \frac{x^3 - y^3}{x^2 + y^2} = \lim\limits_{x\to 0} x = 1$

[III]. Also $f(0, 0) = 0$

Therefore function is continuous at $(0, 0)$.

13.8 Partial Differentiation

The partial derivative of a function of two or more variables is the ordinary derivative of the function with respect to only one of the variables (or "partials"), considering the others as constants. All the rules of ordinary differentiation are also applicable in partial differentiation with only one difference that while differentiating (partially) with respect to one independent variable, all other independent variables are temporary treated as constants.

Consider a function *u* of three independent variables *x, y, z* i.e. *u = f(x, y, z)*

Then the partial derivative of *u* with respect to *x, y, z* are denoted as $\frac{\partial u}{\partial x}$, $\frac{\partial u}{\partial y}$ *and* . $\frac{\partial u}{\partial z}$

And we call it as (del u/del x) etc. these partial derivative are also denoted as f_x, f_y, f_z.

Second order partial derivative of *u* with respect to *x* is defined as

$\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial x}\right) = \frac{\partial^2 u}{\partial x^2} = f_{xx}$ Similarly we can define $\frac{\partial^2 u}{\partial y^2} = f_{yy}$ and $\frac{\partial^2 u}{\partial z^2} = f_{zz}$ And in similar manner we can define partial derivative of any order.

Standard Notation : If *z = f(x, y)* then

$$\frac{\partial z}{\partial x} = p, \quad \frac{\partial z}{\partial y} = q \quad \frac{\partial^2 z}{\partial x^2} = r \quad \frac{\partial^2 z}{\partial y^2} = t \quad \frac{\partial^2 z}{\partial x \partial y} = s$$

And if *f(x, y)* is continuous function then $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$.

Example 25 : Let $f(x, y) = x^2 + 3xy + y - 1$. Find the values of $\frac{\partial f}{\partial x}$ and $\frac{\partial f}{\partial y}$ at the point (4, -5).

Solution : To find c, we treat *y* as a constant and differentiate with respect to *x*.

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}\left(x^2 + 3xy + y - 1\right) = 2x + 3y$$

The value of $\frac{\partial f}{\partial x}$ at (4, -5) is 2(4) + 3(-5) = -7.

To find $\frac{\partial f}{\partial y}$, we treat *x* as a constant and differentiate with respect to *y*:

$$\frac{\partial f}{\partial y} = \frac{\partial}{\partial x}\left(x^2 + 3xy + y - 1\right) = 3x + 1.$$

The value of $\frac{\partial f}{\partial y}$ at (4, -5) is 3(4) + 1 = 13.

Example 26 : Find $\frac{\partial^2 u}{\partial x \partial y}$ if $u = e^{x^2 + y^2}$

Solution : $\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right) = \frac{\partial}{\partial x}\left(2y e^{x^2+y^2}\right) = 2y.2x e^{x^2+y^2} = 4xy e^{x^2+y^2}$

Example 27 : If $u = e^{a\theta}\cos(a\log r)$ then show that $\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} + \frac{1}{r^2}\frac{\partial^2 u}{\partial \theta^2} = 0$

Solution : $\frac{\partial u}{\partial r} = e^{a\theta}(-\sin(a\log r))\frac{a}{r} \Rightarrow \frac{\partial u}{\partial r} = \frac{-ae^{a\theta}\sin(\log r)}{r}$

Continuing the same we get $\frac{\partial^2 u}{\partial r^2} = \frac{-ae^{a\theta}}{r^2}\left[a\cos(\log r) - \sin(a\log r)\right]$

Now $\frac{\partial u}{\partial \theta} = ae^{a\theta}\cos(a\log r) \Rightarrow \frac{\partial^2 u}{\partial \theta^2} = a^2 e^{a\theta}\cos(a\log r) \Rightarrow \frac{\partial^2 u}{\partial \theta^2} = a^2 u$

On putting all the values of partial derivatives in $\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} + \frac{1}{r^2}\frac{\partial^2 u}{\partial \theta^2}$ we get 0.

13.8.1 Chain Rule : Let $u = f(x, y)$ be a function of x & y and x, y are also themselves functions of single independents variable t, then this case is known as function of function and the differentiation of with respect to t is defined as :

$$\frac{df}{dt} = \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial y}\frac{dy}{dt}$$

If f is function of three variable x, y, and z then

$$\frac{df}{dt} = \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial y}\frac{dy}{dt} + \frac{\partial f}{\partial z}\frac{dz}{dt}$$

This type of derivative is also known as ***total derivative***.

Example 28 : Find $\frac{\partial u}{\partial t}$ as a total derivative where $u = x^2 + y^2 + z^2$ and $x = e^{3t}$, $y = e^{2t}$ $\sin t$ and $z = e^{2t}\cos 3t$.

Solution : Since we know that $\frac{du}{dt} = \frac{\partial u}{\partial x}\frac{dx}{dt} + \frac{\partial u}{\partial y}\frac{dy}{dt} + \frac{\partial u}{\partial z}\frac{dz}{dt}$ here

$$\frac{\partial u}{\partial x} = 2x,\ \frac{\partial u}{\partial y} = 2y,\ \frac{\partial u}{\partial z} = 2z \quad \text{and} \quad \frac{\partial x}{\partial t} = 3e^{3t},\ \frac{\partial y}{\partial t} = e^{2t}(2\sin t + \cos t)$$

$$\frac{\partial z}{\partial t} = e^{2t}(2\cos 3t - 3\sin 3t)$$

$$\frac{du}{dt} = 2x(3e^{3t}) + 2ye^{2t}(2\sin t + \cos t) + 2ze^{2t}(2\cos 3t - 3\sin 3t)$$

$$\Rightarrow \frac{du}{dt} = 6e^{3t}e^{3t} + 2(\mathrm{e}^{2t}\sin t)e^{2t}(2\sin t + \cos t) + 2(e^{2t}\cos 3t)e^{2t}(2\cos 3t - 3\sin 3t)$$

$$\Rightarrow \frac{du}{dt} = 6e^{6t} + \mathrm{e}^{4t}\left\{(4\sin^2 t + 2\sin t\cos t) + (4\cos^2 3t - 6\sin 3t\cos 3t)\right\}$$

$$\Rightarrow \frac{du}{dt} = 6e^{6t} + \mathrm{e}^{4t}\left\{(4\sin^2 t + \sin 2t) + (4\cos^2 3t - \sin 6t)\right\}$$

13.8.2 Homogeneous functions : A polynomial in x and y is said to be homogeneous if all its terms are of same degree. A function *f(x, y)* is said to be homogeneous of degree n if for any positive number t

$$f(tx, ty) = t^n f(x, y).$$

Also a function *f(x, y)* is said to be homogenous of degree if it can be expressed as one of the form $x^n\phi\left(\frac{y}{x}\right)$ *or* $y^n\varphi\left(\frac{x}{y}\right)$

Example 29 : 1. $4x^2 + 6xy + (17/5)y^2$ is a homogeneous function of degree 2.

2. $\frac{\sqrt{x}+\sqrt{y}}{x+y}$ is a homogeneous function of degree -1/2.

3. $\sin(y/x) + \tan^{-1}(x/y)$ is a homogeneous function of degree 0 since we can write it as $x^0 \sin(y/x) + y^0 \tan^{-1}(x/y)$.

4. $x^4y + x^3$ is not a homogeneous function.

13.8.3 Euler's Theorem :

If f is a homogeneous function of x and y of degree n, then

$$x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} = nf$$

For three variables $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = nf$

Corollary 1 : If f is a homogeneous function of x and y of degree n, then

$$x^2\frac{\partial^2 f}{\partial x^2}+2xy\frac{\partial^2 f}{\partial x\partial y}+y^2\frac{\partial^2 f}{\partial y^2}=n(n-1)f$$

Corollary 2 : If z is a homogeneous function of x and y of degree n, and if $z = f(u)$ then

(a) $x\frac{\partial u}{\partial x}+y\frac{\partial u}{\partial y}=n\frac{f(u)}{f'(u)}$

(b) $x^2\frac{\partial^2 u}{\partial x^2}+2xy\frac{\partial^2 u}{\partial x\partial y}+y^2\frac{\partial^2 u}{\partial y^2}=g(u)(g'(u)-1))$ *where* $g(u)=n\frac{f(u)}{f'(u)}$

Example 30 : Verify Euler's theorem for $f = (2x + 3y)^{1/3}$

Solution : Clearly, f is homogeneous function of degree 1/3 therefore by Euler's theorem

c

Verification : $\frac{\partial f}{\partial x} = (1/3)\ (2x + 3y)^{-2/3}.2$ and $\frac{\partial f}{\partial y} = (1/3)\ (2x + 3y)^{-2/3}.3$

Now consider

$$x\frac{\partial f}{\partial x}+y\frac{\partial f}{\partial y}=(1/3)\ (2x + 3y)^{-2/3}(2x + 3y) = (1/3)\ (2x + 3y)^{1/3}$$

Hence the results.

Example 31 : If $u = f(y/x) + (x^2 + y^2)^{1/2}$ then find the value of $x\frac{\partial u}{\partial x}+y\frac{\partial u}{\partial y}$.

Solution : Let $u = v + w$

Here $v = x^0 f(y/x)$ is a homogeneous function of degree 0, therefore

$$x\frac{\partial v}{\partial x}+y\frac{\partial v}{\partial y}=0$$

And w is a homogeneous function of degree one and so $x\frac{\partial w}{\partial x}+y\frac{\partial w}{\partial y}=\sqrt{x^2+y^2}$

Thus finally we have $x\frac{\partial(v+w)}{\partial x}+y\frac{\partial(v+w)}{\partial y}=x\frac{\partial u}{\partial x}+y\frac{\partial u}{\partial y}=0+\sqrt{x^2+y^2}=\sqrt{x^2+y^2}$.

Example 32 : If $u = \log \frac{x^2 + y^2}{x + y}$ then prove that $x\frac{\partial u}{\partial x} + y\frac{\partial u}{\partial y} = 1$.

Solution : Let *f(u)* = $e^u = \frac{x^2 + y^2}{x + y}$. Clearly, *f* is a homogeneous function of degree one, then by Euler's theorem

$$x\frac{\partial u}{\partial x} + y\frac{\partial u}{\partial y} = n\frac{f(u)}{f'(u)} = 1\frac{e^u}{e^u} = 1$$ Hence proved.

Example 33 : If $u = \sin^{-1}\frac{\sqrt{x} + \sqrt{y}}{x^2 + y^2}$ then find $x^2\frac{\partial^2 u}{\partial x^2} + 2xy\frac{\partial^2 u}{\partial x \partial y} + y^2\frac{\partial^2 u}{\partial y^2}$.

Solution : Let *f(u)* = sin*u* = $\frac{\sqrt{x} + \sqrt{y}}{x^2 + y^2}$. Clearly, *f* is a homogeneous function of degree -3/2, then by Euler's theorem

$$x\frac{\partial u}{\partial x} + y\frac{\partial u}{\partial y} = n\frac{f(u)}{f'(u)} = -\frac{3}{2}\frac{\sin u}{\cos u} = -\frac{3}{2}\tan u \; (g(u))$$

Also we know that

$$x^2\frac{\partial^2 u}{\partial x^2} + 2xy\frac{\partial^2 u}{\partial x \partial y} + y^2\frac{\partial^2 u}{\partial y^2} = g(u)(g'(u) - 1))$$

$$x^2\frac{\partial^2 u}{\partial x^2} + 2xy\frac{\partial^2 u}{\partial x \partial y} + y^2\frac{\partial^2 u}{\partial y^2} = -\frac{3}{2}\tan u(-\frac{3}{2}\sec^2 u - 1) = \frac{3}{4}\tan u(3\sec^2 u + 2).$$

13.8.4 Jacobian : Jacobian is a functional determinant which is very useful in transformation of variables like Cartesian to polar, spherical cylindrical in multiple integral. The Jacobian of u and v with respect to x and y is denoted by $J\left(\frac{u,v}{x,y}\right)$ *or* $\frac{\partial(u,v)}{\partial(x,y)}$ and defined as

$$J\left(\frac{u,v}{x,y}\right) = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

Similarily we can define jacobian for three variables

$$J\left(\frac{u,v,w}{x,y,z}\right)=\begin{vmatrix}\partial u/\partial x & \partial u/\partial y & \partial u/\partial z\\ \partial v/\partial x & \partial v/\partial y & \partial v/\partial z\\ \partial w/\partial x & \partial w/\partial y & \partial w/\partial z\end{vmatrix}.$$

Properties : 1. If $J=\frac{\partial(u,v)}{\partial(x,y)}$ and $J^{*}=\frac{\partial(x,y)}{\partial(u,v)}$ then $JJ^{*}=1$

2. $J\left(\frac{u,v}{x,y}\right)=J\left(\frac{u,v}{r,s}\right)+J\left(\frac{r,s}{x,y}\right)$

Example 34: If $x = r\cos\theta$ and $y = r\sin\theta$ then find $J\left(\frac{x,y}{r,\theta}\right)$

Solution : by the definition of Jacobian, we have

$$J\left(\frac{x,y}{r,\theta}\right)=\begin{vmatrix}\frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta}\\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta}\end{vmatrix}=\begin{vmatrix}\cos\theta & -r\sin\theta\\ \sin\theta & r\cos\theta\end{vmatrix}$$

$$= r(\cos^2\theta + \sin^2\theta) = r$$

$$\text{therefore } J\left(\frac{x,y}{r,\theta}\right)= r$$

Similarly for spherical coordinates $x = r\sin\theta\cos\varphi$, $y = r\sin\theta\sin\varphi$ and $z = r\cos\theta$

$$J\left(\frac{x,y,z}{r,\theta,\phi}\right)=r^2\sin\theta$$

Note : In multiple integral **1.** $\iint dxdy=\iint|J|\,drd\theta=\iint rdrd\theta$

2. $\iiint dxdydz=\iiint|J|\,drd\theta d\phi=\iiint r^2\sin\theta drd\theta d\phi$

13.9 CURVE TRACING/ CURVE SKETCHING

13.9.1 Curve Tracing for Cartesian Form {y = f(x) or x = f(y)}

(a) Symmetry

1. If the equation of curve contains even powers of y then curve is symmetric

about X axis.

2. If the equation of curve contains even powers of x then curve is symmetric about Y axis.
3. If the equation of curve contains even powers of x and y both then curve is symmetric about both the axes.
4. If equation of curve remains unchanged by replacing y = x, then curve is symmetric about the line y = x or symmetric in opposite quadrants.

(b) Origin

If L.H.S. = R.H.S. while putting (x, y) = (0, 0) in the equation of the curve, then we say that curve is passing through origin.

(c) Tangent at origin

Tangents initially tell the shape of the curve at the point. For finding tangents at origin, equate the lowest degree term of the equation of the curve to zero, then

1. If the tangents are real and distinct then origin is a node.
2. If the tangents are real and equal then origin is cusp.
3. If the tangents are imaginary then origin is

Above points are all double pints, if we will get only one tangent then origin is a simple point.

Cusp Node Conjugate point

(d) Point of Intersection

For finding points of intersection we put x = 0 & y = 0 and then we find the values of y and x respectively.

It may so happen that sometime curve is passes through origin but it is a simple point in that case we shift the origin at the intersection points to know the shape of the curve at these points. To do this, let (h, k) be one of the intersection point, then we replace x by x+h and y by y+k in the given equation of the curve and then we try to find origin.

(e) Asymptotes

Asymptotes are the straight line which intersect the curve at infinity. For finding asymptotes we equate the coefficient of the highest degree term of each x and y to zero. Asymptotes are represents by straight lin in the graph of the given curve.

(f) Region

If possible express the given equation of the curve as y = f(x) or x = f(y). Then we see the behavior of the dependent variable with respect to the independent variable . it will help us to understand the boundary of the given curve.

(g) Convex and Concave nature of the curve

If in the interval (here interval represents the boundary of the intersection poins)

(i) $d^2y/dx^2 > 0$, then the curve is concave upward of convex downward.

(ii) $d^2y/dx^2 < 0$, then the curve is concave downward of convex upward.

We check this only if all the intersection points or origin are simple points.

Example 35 : Sketch the curve $y^2(2a - x) = x^3$ (a > 0).

Solution : (a) Since all the powers of y are even and so curve is symmetric about X-axis.

(b) On Putting (0, 0) in the equation we get LHS = RHS, means curve is passing through origin.

(c) On comparing the lowest degree term to zero we get

$2ay^2 = 0 \square y^2 = 0 \square \cdot y = 0, 0 \cdot \cdot$ tangents are real and equal and so shape of the curev at origin is like a cusp.

(d) there are no intersection points other then (0, 0).

(f) The coefficients of highest power y is (2a – x) which gives us an asymptotes x = 2a parallel to Y-axis.

(g) Region : the given curve can be written as $y = \sqrt{\frac{x^3}{(2a - x)}}$

Clearly, as x $\rightarrow$0 $\square$ ▪ y$\rightarrow$0, x>2a ▪ ▪ y$\rightarrow$ imaginary value

x<0 ▪ y$\rightarrow$ imaginary value

means curve is not exits for 0 > x > 2a.

Example 36 : Sketch the curve $9ay^2 = x(x - 3a)^2$ a > 0.

Solution : (a) Since all the powers of y are even and so curve is symmetric about X-axis.

(b) On Putting (0, 0) in the equation we get LHS = RHS, means curve is passing through origin.

(c) On comparing the lowest degree term to zero we get

$9a^2x = 0$ ▪ x =0 (0, 0) is a simple point

(d) there are no intersection points other then (3a, 0). To shift the origin at this point replace x by x+3a and y bu y+0 i.e. y by y, we get

$$9ay^2 = (sx+3a)x^2$$

by equating the lowest degree term to zero we get y = ± x/, it means that (3a, 0) is a node.

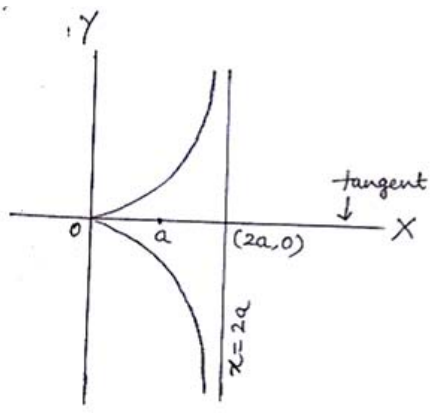
(f) No asymptotes.

(g) Region : the given curve can be written as $y = \sqrt{x}\sqrt{\frac{(x - 3a)^2}{9a}}$

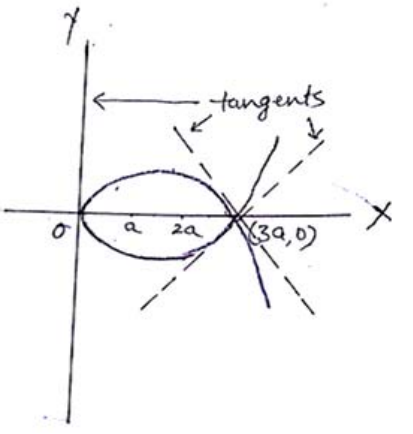
Clearly, as x $\rightarrow$0 ▪ ▪ y$\rightarrow$0, x< 0 ▪ ▪ y$\rightarrow$ imaginary value

$x \to 0 \square y \to 0$

means curve is not exits for $x<0$.



Example 35



Example 36

13.9.2 Curve Tracing for Polar Form ($x= r\cos\theta$ & $y=r\sin\theta$) :

(a) Symmetry

(i) If the equation of the curve remains unchanged by replacing θ by $-\theta$, then the curve is symmetric about initial line.

(ii) If the equation of the curve remains unchanged by replacing r by $-r$, then the curve is symmetric about the pole.

(iii) If the equation of the curve remains unchanged by replacing θ by $\pi-\theta$, t then the curve is symmetric about the line $\pi 2$ or Y.axis..

(b) Tangents

To find tangents at a pole put in the given equation, solve it and find values of θ which represents the tangent at a pole.

(c) Pairs of (r, θ)

In this step we find the different values of r for different values of θ. and then plot this ppints in the plan to find the approximate shap of the curve.

Example 37 : Sketch the curve $r = a(1 + \cos\theta)$ $a > 0$.

Solution : (a) The given curve is symmetric about the initial line since cos(-θ) = $\cos\theta$.

(b) For finding tangents we put r = 0 which gives us $\cos\theta$ = -1which imply

$\theta = \pm\pi$.

(c) now we have the following pairs

θ :	0	$\pi/4$	$\pi/3$	$\pi/2$	$2\pi/3$	$3\pi/4$	π
r :	$2a$	$1.7a$	$1.5a$	a	$0.7a$	$0.3a$	0

For plotting the curve we assume a = 1, then curve is looks like

Example 38 : Sketch the curve $r^2 = a^2 \cos 2\theta$.

Solution : (a) The given curve is symmetric about the initial line, pole and the line θ =

$\pi/2$ since equation remains unchanged by replacing r by –r and θ by $-\theta$.

(b) For finding tangents we put r = 0 which gives us $\cos\theta$ = -1which imply

$\theta = \pi/4, 3\pi/4, 5\pi/4, \ldots$.Also we know that cosine curve is negative in

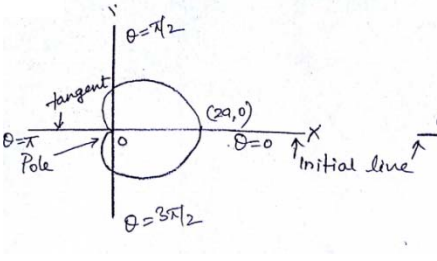
$\pi/2 < \theta < 3\pi/2$

(c) now we have the following pairs

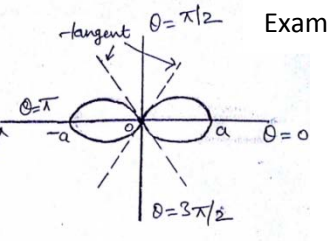
θ :	0	$\pi/4$	$3\pi/4$	π	$5\pi/4$	$7\pi/4$	2π
θ :	a	0	0	$-a$	0	0	a

For plotting the curve we assume a = 1, then curve is looks like

Example 37



Example 38



Exercise

Q.1 Evaluate the following integral with respect to x :

(a) $x^{5/4}$ (b) $1/x^{3/2}$ (c) $((1-\cos 2x)/2)^{1/2}$ (d) $(\cos 2x + 2\sin^2 x)/\sin^2 x$

Q.2 Evaluate : (a) $\int (3\sin x - 2\cos x + 4\sec^2 x - 5\cos ec^2 x)dx$

(b) $\int \sin 4x \cos 3x dx$ (c) If $\int_0^1 (3x^2 + 2x + k)dx = 0$ then find k.

(d) $\int \sin^3 x \cos x dx$

Q.3 Solve by integration by parts : (a) $\int \frac{\log x}{x^2} dx$ (b) $\int x \sin^{-1} x dx$

Q.4 Evaluate $\int \sqrt{4x^2 + 9} dx$

Q.5 Solve by partial fraction :

(a) $\int \frac{x-1}{(x+1)(x-2)} dx$ (b) $\int \frac{x^2 - 1}{(x-1)^2 (x+3)} dx$ (c) $\int \frac{8}{(x+2)\ (x^2 + 4)} dx$

Q.6 Solve by reduction formula :

(a) $\int \sin^5 x dx$ (b) $\int \sec^5 x dx$ (c) $\int_0^{\pi/3} \cos^6 x dx$

Q.7 Find the first order partial derivatives of $f(x, y, z) = z \sin^{-1}(y/x)$

Q.8 Verify $u_{xx} = u_{yy}$ for (a) $u = \log(2x+3y)$ (b) $u = \tan^{-1}(y/x)$

Q.9 If $w = x^2y + y^2z + z^2x$ then show that $w_x + w_y + w_z = (x + y + z)^2$

Q.10 Find $\frac{\partial^3 w}{\partial x \partial y \partial z}$ if $w = e^{xyz}$

Q.11 Find du/dt when $u = \sin(x/y)$ and $x = e^t$, $y = t^2$

Q.12 Determine the degree of the following homogeneous functions :

(a) $(x^2 - xy)^{1/2}$ (b) $(x^3 - y^3)/(x + y)$ (c) $\frac{x^2(x^2 - y^2)^{1/3}}{(x^2 + y^2)^{2/3}}$

Q.13 Verify Euler's theorem for $\cos^{-1}(x/y)$.

Q.14 (a) If $u = \frac{x^2 y^2}{x + y}$ then show that $x u_x + y u_y = 3u \log u$

(b) If $u = \sin^{-1}\sqrt{x^2 + y^2}$ then Find $x^2 u_{xx} + 2xy\, ux_y + y^2 u_{yy}$

(c) If $u = \tan^{-1}\left(\frac{x^3 + y^3}{2x + 3y}\right)$ then show that

$$x^2 u_{xx} + 2xy\, ux_y + y^2 u_{yy} = \sin 4u - \sin 2u$$

Q.15 If (a) u = x siny and v = y sinx and (b) $u = e^x \text{siny}$ & v = x + log(siny) the Find

$$J\left(\frac{u, v}{x, y}\right)$$

Q.16 Prove that $JJ^* = 1$ where $u = x + ((y^2)/x)$ and $v = y^2/x$.

Q.17 Trace the following curves (a) $27ay^2 = 4(x - 2a)^3$ (b) $a^2 x^2 = y^3 (2a - y)$

(c) $(x^2 - a^2)(y^2 - b^2) = a^2 b^2$ (d) $r = a \sin\theta$ (d) $r = a \cos 2\theta$

Answers

Q.1 (a) $(4/9)\, x^{9/4} + c$ (b) $(-2)/x^{1/2} + c$ (c) $\sin x + c$ (d) $-\cot x + c$

Q.2 (a) $-3\cos x - 2\sin x + 4\tan x + 5\cot x + c$

(b) $\frac{1}{2}\left\{\frac{-\cos 7x}{7} - \cos x\right\} + c$ (c) k = -2 (d) $\frac{\sin^4 x}{4} + c$

Q.3 (a) $\frac{1}{2}(1 + \log x) + c$ (b) $(1/2)x^2 \sin^{-1} x + (1/4)x\sqrt{1 - x^2} - (1/4)\sin^{-1} x + c$

Q.4 $\frac{x}{2}\sqrt{4x^2 + 9} + \frac{9}{2}\log|2x + \sqrt{4x^2 + 9}| + c$

Q.5 (a) $(2/3)\log|x + 1| + (1/3)\log|x - 2| + c$

(b) $\frac{3}{8}\log(x - 1) - \frac{1}{2(x - 1)} - \frac{5}{8}\log(x + 3) + c$

(c) $\log(x + 2) - (1/2)\log(x^2 + 4) + \tan^{-1}\frac{x}{2} + c$

Q.6 (a) $-(1/5)\cos x \sin^4 x - (4/15)\cos x \sin^2 x + (2/3)\cos x + c$

(b) $(1/4)\tan x \sec^3 x + (3/8)\tan x \sec x + (3/8)\log(\sec x + \tan x) + c$

(c) $\frac{3\sqrt{3}}{8} + \frac{5\pi}{48}$

Q.7 $f_x = \dfrac{-yz}{\sqrt{x^4 - x^2y^2}}$, $f_y = \dfrac{xz}{x\sqrt{x^2 - y^2}}$, $f_z = \sin^{-1}(y/x)$

Q.10 $e^{xyz}(x^2 y^2 z^2 + 3xyz + 1)$

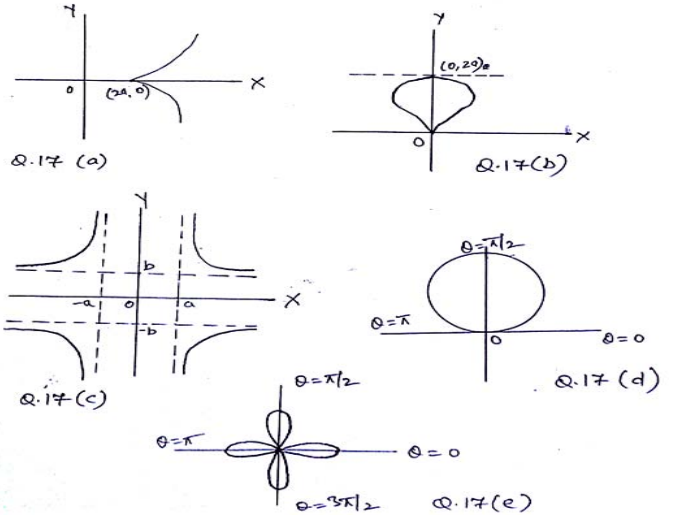
Q.11 $du/dt = \dfrac{t-2}{t^3} e^t \cos\left(\dfrac{e^t}{t^2}\right)$

Q.12 (a) -1/2 (b) 0 (c) not a homogeneous function

Q.14 (b) $x^2 u_{xx} + 2xy\, ux_y + y^2 u_{yy} = \tan^3 u$

Q.15 (a) sinx siny – xy cosx cosy (b) 0

Q.17



Unit -14 : Differential Equations and Fourier Series

Structure of Unit:

14.1 Objective

Differential equations are of prime importance because of its applications in chemical field. Motion of fluid through Porous media, heat transfer through spherical or cylindrical shells, decay of radioactive elements. Study of concentration of sugar in blood, Newton's law of cooling are some of the examples.

14.2 Introduction

When we are studying Differential & Integral calculus, the concept of Differential equation has been introduced. Ordinary Differential equation can be defined as an equation involving derivatives with respect to a independent variable.

As we know that integration of every function is not easily possible. Different method are used to integrate particular type of functions. Similarly the solution of every DE is not easily possible. Here various methods will be used to solve particular type of DE.

14.3 Solution of Differential equations of first order & first degree

(a) Variable Separable Form (V.S. Form)

Many first order differential equations can be reduced to the form $\frac{dy}{dx}=\frac{f(x)}{g(y)}$ $\left(or\frac{dy}{dx}=\frac{g(y)}{f(x)}\right)$, can be written as $g(y)dy=f(x)dx$ $\left(or\frac{dy}{g(y)}=\frac{dx}{f(x)}\right)$ which can be integrate

i.e. $\therefore \int g(y)dy=\int f(x)dx+c$ $\left(or\int\frac{dy}{g(y)}=\int\frac{dx}{f(x)}+c\right)$

Where C is arbitrary constant.

(b) Homogeneous Differential Equations :

Consider a differential equation in the form $M(x,y)dx+N(x,y)dy=0$ $\left(or\frac{dy}{dx}=\frac{M(x,y)}{N(x,y)}\right)$

It is said to be Homogeneous if $M(x,y)\&N(x,y)$ are Homogeneous functions in $x\&y$ are of same degree. These equations are reducible to V.S. form by changing the dependent variable from y to u by substitution $y=vx\Rightarrow\frac{dy}{dx}=v+x\frac{dv}{dx}$

(c) Exact Differential Equations :

Consider a DE of the form

$$M(x,y)dx+N(x,y)dy=0$$

If there exists a function $u(x,y)$ such that $Mdx+Ndy=du$ then DE is called exact Differential Equation.

Condition that $Mdx+Ndy=0$ is exact is

$\frac{\partial M}{\partial y}=\frac{\partial N}{\partial x}$ then it's solution.

$$\int Mdx+\int\left(N-\frac{\partial}{\partial y}\int Mdx\right)dy=C$$

Or $$\int Ndy+\int\left(M-\frac{\partial}{\partial x}\int Ndy\right)dx=C$$

(d) Linear Differential Equation :

A differential equation is said to be linear if the dependent variable & it's derivatives appears in first degree only. First order linear differential equation is of the form

$$\frac{dy}{dx} + Py = Q \qquad \ldots(1)$$

where P & Q are functions of x or constant.

Or $$\frac{dx}{dy} + P_1 x = Q_1 \qquad \ldots(2)$$

Where $P_1 \& Q_1$ are functions of y only or constant it's solution

First Find I.F. it is

$$I.F. = e^{\int P dx} \quad \text{for equation (1)}$$

& $$I.F = e^{\int P_1 dy} \quad \text{for equation (2)}$$

& solution is

$$y.(I.F.) = \int Q.(I.F.)dx + C \quad \text{(for (1))}$$

$$x(I.F.) = \int Q_1(I.F.)dy + C \quad \text{(for (2))}$$

Self Assessment Questions

Q.1 Write the condition for equation $Mdx + Ndy = 0$ to be exact.

Ans. $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$

Q.2 Write solution of $\frac{dy}{dx} + Py = Q$.

Ans. $y.(I.F.) = \int Q.(I.F.)dx + C$

Illustrative Examples

Example 1 : *Solve* $\frac{dy}{dx} = e^{x-y} + 3x^2 e^{-y}$

Sol. : Multiply by e^y,

$$e^y \frac{dy}{dx} = e^x + 3x^2$$

$$e^y dy = \left(e^x + 3x^2\right) dx$$

G.S. $e^y = e^x + x^3 + C$ is the G.S.

Example 2 : *Solve* $y\left(x\cos\frac{y}{x} + y\sin\frac{y}{x}\right) - \left(y\sin\frac{y}{x} - x\cos\frac{y}{x}\right) x\frac{dy}{dx} = 0$

Sol. : We divided by

$$\frac{y}{x}\left(\cos\frac{y}{x} + \frac{y}{x}\sin\frac{y}{x}\right) - \left(\frac{y}{x}\sin\frac{y}{x} - \cos\frac{y}{x}\right)\frac{dy}{dx} = 0$$

Or $$\frac{dy}{dx} = \frac{\frac{y}{x}\left(\cos\frac{y}{x} + \frac{y}{x}\sin\frac{y}{x}\right)}{\left(\frac{y}{x}\sin\frac{y}{x} - \cos\frac{y}{x}\right)}$$

Put $\frac{y}{x} = v$ or $y = xv$ or $\frac{dy}{dx} = x\frac{dv}{dx} + v$

$\therefore$ $x\frac{dv}{dx} + v = \frac{v\left(\cos v + v\sin v\right)}{\left(v\sin v - \cos v\right)}$ or $x\frac{dv}{dx} = \frac{v\left(\cos v + v\sin v\right)}{v\sin v - \cos v} - v$

or $x\frac{dv}{dx} = \frac{2v\cos v}{v\sin v - \cos v}$ or $\left(\frac{v\sin v - \cos v}{v\cos v}\right)dv = \frac{2}{x}dx$ (V.S. Form)

G.S. $2\int\frac{1}{x}dx + \int\frac{\cos v - \sin v}{v\cos v}\,dv = \log C$

$\therefore$ $2\log x + \log\left(v\cos v\right) = \log C$

or $\log\left(x^2 v\cos v\right) = \log C$ or $x^2\frac{y}{x}\cos\frac{y}{x} = C$

$xy\cos\frac{y}{x} = C$ is the G.S.

Example 3 : *Solve* $\left(y^2.e^{xy^2} + 4x^3\right)dx + \left(2xy\,e^{xy^2} - 3y^2\right)dy = 0$

Sol. : Here $M = y^2 e^{xy^2} + 4x^3$; $\dfrac{\partial M}{\partial y} = 2ye^{xy^2} + y^2 e^{xy^2}(2xy)$

And $N = 2xy\,e^{xy^2} - 3y^2$; $\dfrac{\partial N}{\partial x} = 2ye^{xy^2} + 2xy\,e^{xy^2}(y)$

$\therefore$ $\dfrac{\partial M}{\partial y} = \dfrac{\partial N}{\partial x}$ $\therefore$ Given differential equation is exact. G.S. is,

G.S. $y^2 \int e^{xy^2} dx + 4\int x^3 dx - 3\int y^3 dy = C$

$$y^2 \frac{e^{xy^2}}{y^2} + x^4 - y^3 = C$$

$$e^{xy^2} + x^4 - y^3 = C$$

Example 4 : *Solve* $\left(1+y^2\right) = \left(x - e^{-\tan^{-1} y}\right)\dfrac{dy}{dx} = 0$

Sol. : It can be written as $\left(1+y^2\right)\dfrac{dx}{dy} + x = e^{-\tan^{-1} y}$.

$\dfrac{dx}{dy} + P_1 y = Q_1$ Which is linear in x.

I.F. $= e^{\int \frac{1}{1+y^2} dy} = e^{\tan^{-1} y}$

G.S. is, $x.e^{\tan^{-1} y} = \int \dfrac{e^{-\tan^{-1} y}}{1+y^2} \times e^{\tan^{-1} y} dy + C = \int \dfrac{dy}{1+y^2} + C$

$$xe^{\tan^{-1} y} = \tan^{-1} y + C$$

Example 5 : *Solve* $\cos x \dfrac{dy}{dx} + y \sin x = \sqrt{y \sec x}$

Sol. : Given $\cos x \dfrac{dy}{dx} + y \sin x = \sqrt{y \sec x}$ (Bernoulli's differential equation), divide by $\sqrt{y}\cos x$

$y^{-1/2}\dfrac{dy}{dx} + y^{1/2}\tan x = \sec^{3/2} x$ Put $y^{1/2} = u$ $\therefore$ $y^{-1/2}\dfrac{dy}{dx} = 2.\dfrac{du}{dx}$

$2\dfrac{du}{dx} + u.\tan x - \sec^{3/2} x$ or $\dfrac{du}{dx} + \left(\dfrac{1}{2}\tan x\right)u = \dfrac{1}{2}\sec^{3/2} x$

$$P = \frac{1}{2}\tan x\,,\ Q = \frac{1}{2}\sec^{3/2} x\,;\ \int P dx = \frac{1}{2}\int \tan x dx = \frac{1}{2}\log\sec x = \log\sqrt{\sec x}$$

$\therefore$ $\quad I.F. = \sqrt{\sec x}$

$\therefore$ $\quad$ G.S. is $u\sqrt{\sec x} = \int \frac{1}{2}\sec^{3/2} x\sqrt{\sec x}\ dx + C$

$$u\sqrt{\sec x} = \frac{1}{2}\int \sec^2 x\, dx + C = \frac{1}{2}\tan x + C$$

$$\sqrt{y\sec x} = \frac{1}{2}\tan x + C \text{ is the required G.S.}$$

Example 6 : *In a chemical reaction in which two substances A and B initially of amount a and b respectively are concerned, the velocity of transformation* $\frac{dx}{dt}$ *at any time* t *is known to be equal to the product* $(a-x)(b-x)$ *of the amounts of the two substances then remaining untransformed. Find* t *in terms of* x *if* $a = 0.7$, $b = 0.5$ *and* $x = 0.3$ *when* $t = 300$ *seconds.*

Sol. : We have $\frac{dx}{dt} = (a-x)(b-x) = \left(\frac{7}{10} - x\right)\left(\frac{1}{2} - x\right)$

$$\frac{dx}{\left(\frac{7}{10} - x\right)\left(\frac{1}{2} - x\right)} = dt \qquad \text{or} \qquad 5\left[\frac{dx}{\frac{1}{2} - x} - \frac{dx}{\frac{7}{10} - x}\right] = dt$$

Integrating, $\quad 5\left[\log\left(\frac{7}{10} - x\right) - \log\left(\frac{1}{2} - x\right)\right] = t + c$

But $\quad x = \frac{3}{10} \quad$ when $\quad t = 300$.

$$5\left(\log\frac{2}{5} - \log\frac{1}{5}\right) = 300 + c \Rightarrow c = 5\log 2 - 300$$

$\therefore$ $\quad t = 5\left[\log\left(\frac{7}{10} - x\right) - \log\left(\frac{1}{2} - x\right)\right] - 5\log 2 + 300$

$$t = 5\left[\log\left(\frac{7}{10} - x\right) - \log\left(\frac{1}{2} - x\right)\log 2\right] + 300$$

Example 7 : *When investigating the stress in the material of a thick cylinder subjected to internal pressure, the following relations are found to exist;* $p + r\frac{dp}{dr} = q$ *and* $p + q = 2a$, *where* p *and* q *are the radial stress and the circumferential stress respectively and* r *is the radius. Express* p *as a function of* r.

Sol. : We have to eliminate q between the given equations.

$\therefore \quad q = 2a - p \quad \therefore \quad p + r\frac{dp}{dr} = 2a - p$

i.e. $r\frac{dp}{dr} + 2p - 2a = 0$ or $\int \frac{dp}{p-a} + 2\int \frac{dr}{r} = 0$

$\log(p-a) + 2\log r = \log c \Rightarrow (p-a)r^2 = c$

$p = \frac{c}{r^2} + a$

Example 8 : *For a thick cylinder under internal pressure, if 'p' is the compressive stress and 'f' the tensile stress at a distance 'r' from the axis of the cylinder, the differential equation is* $r\frac{dp}{dr} + p + f = 0$. *Assuming* $f + ap = b$, $p = 0$. *When* $r = r_2$ *and* $p = p_1$, *when* $r = r_1$, *show that* $\left(\frac{r_1}{r_2}\right)^{a-1} = \left(\frac{1-a}{b}\right)p_1 + 1$.

Sol. : $r\frac{dp}{dr} + p + f = 0$ and $f = b - ap$

$r\frac{dp}{dr} + (p - ap + b) = 0$

$\frac{dp}{b-(a-1)p} + \frac{dr}{r} = 0$ (by using V.S. Form)

But $p = 0$ when $r = r_2$; $p = p_1$ when $r = r_1$ and multiplying by $(a-1)$ throughout, we have

$(a-1)\int_{r_2}^{r_2} \frac{dr}{r} = \int_{r_2}^{r_2} \frac{-(a-1)dp}{b-(a-1)p}$

$\log\left(\frac{r_1}{r_2}\right)^{a-1} = \log\left(\frac{b-(a-1)p_1}{b}\right)$

$$\left(\frac{r_1}{r_2}\right)^{a-1} = 1-\left(\frac{a-1}{b}\right)p_1 = 1+\left(\frac{1-a}{b}\right)p_1$$

Example 9 : *Under certain condition it is observed that the rate at which a solid substance dissolves varies directly as the product of the amount of undissolved solid present in the solvent and the difference between the saturation concentration and the instantaneous concentration of the substance. If 20 lb of solute is dumped into a tank containing 120 lb of solvent and at the end of 12 min the concentration is observed to be 1 part in 30, find the amount of solute in solution at any time t, if the saturation concentration is 1 part of solute in 3 parts of solvent.*

Sol. : If Q is the amount of the material in solution at time t, then 20-Q is the amount of undissolved material present at that time and Q/120 is the corresponding concentration. Hence according to the given law,

$$\frac{dQ}{dt} = k(20-Q)\left(\frac{1}{3}-\frac{Q}{120}\right) = \frac{k}{120}(20-Q)(4-Q)$$

$$\frac{dQ}{(20-Q)(40-Q)} = \frac{k}{120}kt$$

$\therefore$ $$\frac{1}{20}\left(\frac{1}{20-Q}-\frac{1}{40-Q}\right)dQ = \frac{k}{120}dt\,.$$

Integrating, we have $$-ln(20-Q)+ln(40-Q) = \frac{k}{6}t+c\,. \qquad \ldots(1)$$

To determine the integration constant c, we observe that $Q=0$ when $t=0$. Hence

$$-ln\,20+ln\,40 = c \quad \text{or} \quad c = ln\,2$$

and (1) can be written as $$ln\frac{40-Q}{2(20-Q)} = \frac{k}{6}t \qquad \ldots(2)$$

To find the physical constant k we use the fact that when $t=12$, the concentration $Q/120 = \frac{1}{130}$ or $Q=4$. Substitution of these values given $ln\frac{36}{32} = 2k$ or $k = \frac{1}{2}\,ln\frac{9}{8} = 0.05889$.

$$\frac{40-Q}{40-2Q} = e^{0.0098t}$$

$$\Rightarrow \qquad Q = \frac{40 - 40\ e^{0.0098t}}{1 - 2e^{0.0098t}} = \frac{40\left(1 - e^{-0.0098t}\right)}{2 - e^{-0.0098t}}$$

Example 10 : *A certain chemical dissolves in water at a rate proportional to the product of theamount undissolved and the difference between the concentration in a saturated solution and the concentration in the actual solution. In 100 grams of a saturated solution it is known that 50 grams of the substance are dissolved. If when 30 grams of the chemical are agitated with 100 grams of water, 10 grams are dissolved in 2 hours. how much will be dissolved in 5 hours?*

Sol : Let x denote the number of grams of the chemical dissolved after t hours. At this time, the concentration of the actual solution is $\frac{30-x}{100}$ and that of the saturated solution is $\frac{50}{100}$.

Then $\frac{dx}{dt} = kx\left(\frac{50}{100} - \frac{30-x}{100}\right) = kx\left(\frac{x+20}{100}\right)$ or

$\frac{dx}{x} - \frac{dx}{x+20} = \frac{k}{5}dt$.

Integrating between $t = 0$, $x = 30$ and $t = 2$, $x = 30 - 10 = 20$.

$$\int_{30}^{20} \frac{dx}{x} - \int_{30}^{20} \frac{dx}{x+20} = \frac{k}{5}\int_{0}^{2} dt, \quad \text{and} \quad k = \frac{5}{2}\,ln\,\frac{5}{6} = \frac{k}{6} = -0.46.$$

Integrating between $t = 0$, $x = 30$ and $t = 5$, $x = x$,

$$\int_{30}^{x} \frac{dx}{x} - \int_{30}^{x} \frac{dx}{x+20} = \frac{k}{5}\int_{0}^{0} dt\ ,ln\,\frac{5x}{3(x+20)} = k - 0.46\ \frac{x}{x+20} = \frac{3}{5}\ e^{-0.46} = 0.38$$

And. This the amount dissolved after 5 hours in 30 - 12 = 18 grams.

Example 11 : *A tank contains 10,000 litres of brine in which 200 kg of salt are dissolved. Fresh water runs into the tank at the rate of 100 litres per minute, and the mixture kept uniform by stirring, runs out at the same rate. How long will it be before only 20 kg of salt is left in the tank?*

Sol. : Let Q be the total amount of salt at any time t.

Then $\frac{dQ}{dt}$ = Rate at which salt is entering - Rate at which salt is leaving the tank

$\frac{dQ}{dt} = 0 - 100\,C$, where is the concentration at time t

$C = \frac{\text{Amount of salt present at time t}}{\text{Volume of liquid at time t}} = \frac{Q}{10{,}000}$

$\frac{dQ}{dt} = -\frac{Q}{100} \quad \therefore \quad \frac{dQ}{Q} = -\frac{1}{100}dt$

$\log Q = -\frac{t}{100} + A \qquad \because \quad t = 0\,,\ Q = 200\,kg$

$\log Q = -\frac{t}{100} + \log 200\,,\ Q = 20\ kg$

$\log 20 = -\frac{t}{100} + \log 200\, t = 100 \log 10$

$t = 230$ minutes approximately

Exercise

Solve following Differential Equation. (1 to 8)

Q.1 $y\frac{dy}{dx} = \sqrt{1 + x^2 + y^2 + x^2y^2}$ Ans.

$\sqrt{1+y^2} = \frac{x}{2}\sqrt{1+x^2} + \frac{1}{2}\log\left(x + \sqrt{1+x^2}\right) + C$

Q.2 $\frac{dy}{dx} = \frac{x(2\log x + 1)}{\sin y + y\cos y}$ Ans. $x^2 \log x = y \sin y + C$

Q.3 $x^3\frac{dy}{dy} = y^3 + y^2\sqrt{y^2 - x^2}$ Ans. $y + \sqrt{y^2 - x^2} = C\,x\,y$

Q.4 $y e^{x/y}dx = \left(x e^{x/y} + y^2\right)dy$ Ans. $e^{x/y} - y = C$

Q.5 $\left(\frac{y^2}{(y-x)^2} - \frac{1}{x}\right)dx + \left(\frac{1}{y} - \frac{x^2}{(x-y)^2}\right)dy = 0$ Ans. $\frac{y^2}{y-x} + \log\frac{y}{x} = C$

Q.6 $\frac{dy}{dx} = \frac{1 + y^2 + 3x^2y}{1 - 2xy - x^3}$ Ans. $x(1+y^2) + x^2y - y = C$

Q.7 $x^2\left(x^2-1\right)\dfrac{dy}{dx}+x\left(x^2+1\right)y=x^2-1$ Ans. $\dfrac{y\left(x^2-1\right)}{x}-\log x-\dfrac{1}{2x^2}=C$

Q.8 $ye^y=\left(y^3+2xe^y\right)\dfrac{dy}{dx}$ Ans. $\dfrac{x}{y^2}+e^{-y}=C$

Q.9 A tank contains 1000 litres of brine in which 20 kg of salt is dissolved. Brine containing 0.1 kg per litre of salt runs into the tank at the rate of 40 litres per minute and mixture, assumed to be kept uniform by stirring, runs out at the rate of 30 litres per minute. Assuming that tank is sufficiently large to avoid overflow, find the amount of salt in the tank as a function of time. When will the concentration of the salt in the tank reach 0.05 kg per litre? How much salt will be in the tank after 30 minutes?

Hint : $\dfrac{dQ}{dt}=4-30C$, $C=\dfrac{Q}{1000+10t}$

Use $t=0$, $Q=20\Rightarrow$ $Q=100+t-80\times(100)^3(100+t)^{-3}$

Use $C=0.05$, $t=12.47$ minutes, $t=30$, $Q=93.59$ kg

Q.10 Under certain conditions it is observed that the rate at which a solid substance dissolves varies directly as the product of the amount of undissolved solid present in the solvent and the difference between saturation concentration and the instantaneous concentration of the substance. If 20 kg of solute is dumped into the tank containing 500 litres of solvent and at the end of 10 minutes the concentration observed is one part in fifty, find the solute in solution at any time *t*, if the saturation concentration is 1 part of solute in 10 parts of solvent.

Hint: $C=\dfrac{Q}{500}$, $\dfrac{dQ}{dt}=k(20-Q)\left(\dfrac{1}{10}-\dfrac{Q}{500}\right)$

Use $t=0$, $Q=0$. To find k, $t=10$, $Q=\dfrac{1}{50}(500)=10$

$k=0.752$, $Q=20\dfrac{1-e^{-0.045t}}{1-0.4e^{-0.045t}}$

Q.11 A tank contains 5000 litres of fresh water. Salt water which contains 100 gm of salt per litre from into it at the rate of 10 litres per minute and the mixture kept

uniform by stirring runs out at the same rate. When will the tank contain 200000 gm of salt?

How long will it take for the quantity of salt in the tank to increase from 150000 gm to 250000 gm?

Ans. 168.23 Minutes

Q.12 A tank initially contains 50 gallons of fresh water. Brine, containing 2 pounds per gallon of salt, flows into the tank at the rate of 2 gallons per minute and the mixture kept uniform by stirring, runs out at the same rate. How long will it take for the quantity of salt in the tank to increase from 40 to 80 pounds?

Ans. 27 Min. 28 sec.

Q.13 The temperature of a body decreases at a rate $k\theta$, where θ° is the amount the body is hotter than the surrounding air. the body is heated by a source which makes the body's temperature increase at a rate "at" where 't' is the time and 'a' is a constant. If this source is applied at $t = 0$, and the body is then at the temperature of the surrounding air, show that $\theta = \frac{a}{k}\left(t - \frac{1}{k} + \frac{1}{k}\, e^{-kt}\right)$.

Q.14 In a certain culture of bacteria, the rate of increase is proportional to the number present. if it is found that the number doubles in 4 hours, how many may be expected at the end of 12 hours?

Ans. 8 times

Q.15 A long hollow pipe has an inner diameter of 10 cm and outer diameter of 20 cm. The inner surface is kept at 200°C and the outer surface at 50°C. The thermal conductivity is 0.12. How much heat is lost per minute from a portion of the pipe 20 metres long? Find the temperature at a distance $x = 7.5$ cm from the centre of the pipe.

Ans. 113°C

14.4 Fourier Series

Consider a periodic function $f(x)$ defined in the interval $c \le x \le c + 2L$.

Fourier series, the series must be of the form

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos\frac{n\pi}{L}x + b_n \sin\frac{n\pi}{L}x \right)$$

Where,

$$\left.\begin{aligned} a_0 &= \frac{1}{L}\int_c^{c+2L} f(x)dx \\ a_n &= \frac{1}{L}\int_c^{c+2L} f(x)\cos\frac{n\pi}{L}xdx \\ b_n &= \frac{1}{L}\int_c^{c+2L} f(x)\sin\frac{n\pi}{L}xdx \end{aligned}\right\} \text{ (to remember)}$$

Cor. 1 : If $c = 0$, then result gives

$$a_0 = \frac{1}{L}\int_0^{2L} f(x)dx$$

$$a_n = \frac{1}{L}\int_0^{2L} f(x)\cos\frac{n\pi x}{L}dx$$

$$b_n = \frac{1}{L}\int_0^{2L} f(x)\sin\frac{n\pi x}{L}dx$$

Cor. 2 : If $c = -L$, then result gives

$$a_0 = \frac{1}{L}\int_{-L}^{L} f(x)dx$$

$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\frac{n\pi x}{L}dx$$

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\frac{n\pi x}{L}dx$$

Even and Odd Functions in the Interval $-L \le x \le L$,

Even Function : If $f(x)$ is an even function in $-L \le x \le L$, then the Fourier coefficients a_0, a_n and b_n given by (15) are reduced as follows :

$$a_0 = \frac{1}{L}\int_{-L}^{L} f(x)\,dx = \frac{2}{L}\int_0^{L} f(x)\,dx \qquad [\, f(x) \text{ is even function}]$$

$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\frac{n\pi x}{L}dx = \frac{2}{L}\int_{0}^{L} f(x)\cos\frac{n\pi x}{L}dx$$

[Product $f(x)\cos\frac{n\pi x}{L}$ is even]

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\frac{n\pi x}{L}dx = 0$$

[Product $f(x)\sin\frac{n\pi x}{L}$ is odd]

Thus for even function $f(x)$ in $-L \le x \le L$, the Fourier coefficients are given by

$$a_0 = \frac{2}{L}\int_{0}^{L} f(x)\,dx$$

$$a_n = \frac{2}{L}\int_{0}^{L} f(x)\cos\frac{n\pi x}{L}dx$$

$$b_n = 0$$

Odd Function : If f(x) is an odd function in $-L \le x \le L$, then the Fourier coefficients , and given by (15) are reduced as follows :

$$a_0 = \frac{1}{L}\int_{-L}^{L} f(x)dx = 0$$

[$f(x)$ is odd function]

$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\frac{n\pi x}{L}dx = 0$$

[Product $f(x)\cos\frac{n\pi x}{L}$ is odd]

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\frac{n\pi x}{L}dx = \frac{2}{L}\int_{0}^{L} f(x)\sin\frac{n\pi x}{L}dx$$ [Product $f(x)\sin\frac{n\pi x}{L}$ is even]

Thus for odd function in $-L \le x \le L$, the Fourier coefficients are given by

$$a_0 = 0, \qquad a_n = 0$$

$$b_n = \frac{2}{L}\int_0^L f(x)\sin\frac{n\pi x}{L}dx$$

Self Assessment Questions

Q.1 Write formuia for a_0, a_n, b_n in Fourier series expansion of a periodic function $f(x)$ defined in the interval $c \le x \le c+2L$.

Ans.

$$\left.\begin{aligned} a_0 &= \frac{1}{L}\int_c^{c+2L} f(x)dx \\ a_n &= \frac{1}{L}\int_c^{c+2L} f(x)\cos\frac{n\pi}{L}xdx \\ b_n &= \frac{1}{L}\int_c^{c+2L} f(x)\sin\frac{n\pi}{L}xdx \end{aligned}\right\}$$

Q.2 If f(x) is an odd function in $-L \le x \le L$, then write the Fourier coefficients.

Ans. $a_0 = 0$

$a_n = 0$

$$b_n = \frac{2}{L}\int_0^L f(x)\sin\frac{n\pi x}{L}dx$$

Illustrative Examples

Example 1 : *What is the Fourier expansion of the periodic function whose definition in one period is*

$$f(x) = \begin{cases} -\pi & 0 < x < \pi \\ x - \pi & \pi < x < 2\pi \end{cases}$$

State the value of the series at and hence show that

$$\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} = \frac{\pi^2}{8}$$

Sol. : There Interval $(0, 2\pi)$ so $L = \pi$

Let $\quad f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} (a_n \cos n x + b_n \sin n x)$

Where $a_0 = \frac{1}{\pi} \int_0^{2\pi} f(x)\, dx = \frac{1}{\pi}\left[\int_0^{\pi} (-\pi) dx + \int_0^{2\pi} (x - \pi) dx\right]$

$$= \frac{1}{\pi}\left[-\pi(x)_0^{\pi} + \left\{\frac{(x-\pi)^2}{1}\right\}_{\pi}^{2\pi}\right] = \frac{1}{\pi}\left[-\pi^2 + \left\{\frac{\pi^2}{2} - 0\right\}\right] = \frac{1}{\pi}\left[-\frac{\pi^2}{2}\right]$$

$$= -\frac{\pi}{2}$$

$$a_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \cos n x \; dx$$

$$= \frac{1}{\pi}\left[\int_0^{\pi} (-\pi) \cos n x \, dx + \int_{\pi}^{2\pi} (x - \pi) \cos n x \, dx\right]$$

$$= \frac{1}{\pi}\left[(-\pi)\left\{\frac{\sin nx}{n}\right\}_0^{\pi} + \left\{(x-\pi)\left(\frac{\sin nx}{n}\right) - (1)\left(\frac{-\cos nx}{n^2}\right)\right\}_{\pi}^{2\pi}\right]$$

$$= \frac{1}{\pi}\left[0 \left\{\left(0 + \frac{1}{n^2}\right) - \left(0 + \frac{\cos n\pi}{n^2}\right)\right\}\right] = \frac{1}{\pi}\left[\frac{1 - \cos n\pi}{n^2}\right]$$

$$= \frac{1}{\pi n^2}\left[1 - (-1)^n\right] \qquad \left[\because \cos n\pi = (-1)^n\right]$$

$$= \begin{cases} 0, & \text{if n is even} \\ \frac{2}{\pi n^2} & \text{if n is odd} \end{cases}$$

Thus $\quad a_1 = \frac{2}{\pi 1^2}, \qquad a_3 = \frac{2}{\pi 3^2}, \qquad a_5 = \frac{2}{\pi 5^2}$,..etc.

$$b_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \sin n x \, dx = \frac{1}{\pi}\left[\int_0^{\pi} (-\pi) \sin n x \, dx + \int_{\pi}^{2\pi} (x - \pi) \sin n x \, dx\right]$$

$$= \frac{1}{\pi}\left[(-\pi)\left\{-\frac{\cos nx}{n}\right\}_0^{\pi} + \left\{(x-\pi)\left(-\frac{\cos nx}{n}\right)(-1)\left(-\frac{\sin nx}{n^2}\right)\right\}_{\pi}^{2\pi}\right]$$

$$= \frac{1}{\pi}\left[\frac{\pi}{n}(\cos n\pi - 1) + \left\{\frac{-\pi}{n}(\cos 2n\pi) + 0\right\}\right]$$

$$= \frac{1}{n}[\cos n\pi - 2] = -\frac{1}{n}\left[2 - (-1)^n\right]$$

Thus $b_1 = -3, \qquad b_2 = -\frac{1}{2}, \qquad b_3 = -\frac{3}{3} = -1, \ldots$ etc.

Hence the required Fourier series is

$$f(x) = -\frac{\pi}{4} + \frac{2}{\pi}\left[\frac{1}{1^2}\cos x + \frac{1}{3^2}\cos 3x + \frac{1}{5^2}\cos 5x + \ldots\right]$$

$$+\left[3\sin x - \frac{1}{2}\sin 2x - \sin 3x \ldots\right]$$

$$= -\frac{\pi}{4} + \frac{2}{\pi}\sum_{n=0}^{\infty}\frac{\cos(2n+1)x}{(2n+1)} - \sum_{n=1}^{\infty}\frac{\left[2-(-1)^n\right]\sin nx}{n}$$

Since $f(x)$ is discontinuous at $x = \pi$, therefore, the value of $f(x)$ at $x = \pi$, the point of discontinuity is calculated by rule

$$f(\pi) = \frac{f(\pi - 0) + f(\pi + 0)}{2} = \frac{\text{L.H.L} + \text{R.H.L}}{2}$$

Where $\quad \text{L.H.L} = f(\pi - 0) = \lim_{h \to 0} f(\pi - h) = -\pi$

and $\quad \text{R.H.L} = f(\pi + 0) = \lim_{h \to 0} f(\pi + h) = \lim_{h \to 0}(\pi + h - \pi) = 0$

$\therefore \quad f(\pi) = \frac{-\pi + 0}{2} = -\frac{\pi}{2}$

Thus from (5), on putting $x = \pi$, we have

$$-\frac{\pi}{2} = -\frac{\pi}{4} = \frac{2}{\pi}\sum_{n=0}^{\infty}\frac{\cos(2n+1)\pi}{(2n+1)}$$

$\therefore \quad \sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} = \frac{\pi^2}{8}$

Example 2 : *Find the Fourier series expansion of the function*

$f(x) = 2x - x^2$, $0 \le x \le 3$ *and period is 3.*

Also graph the function.

Sol. : Here period $2L = 3 \quad \therefore L = \frac{3}{2}$

Let $$2x - x^2 = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos\frac{n\pi}{L}x + b_n \sin\frac{n\pi}{L}x\right) \qquad \ldots(1)$$

Where $a_0 = \frac{1}{L}\int_0^{2L} f(x)dx = \frac{2}{3}\int_0^3 (2x - x^2)dx$

$\left(\because L = \frac{3}{2}\right)$

$$= \frac{2}{3}\left[x^2 - \frac{x^3}{3}\right]_0^3 = \frac{2}{3}\left[9 - \frac{27}{3}\right]$$

$$= 0 \qquad \ldots(2)$$

$$a_n = \frac{1}{L}\int_0^{2L} f(x)\cos\frac{n\pi x}{L}dx = \frac{2}{3}\int_0^3 (2x - x^2)\cos\frac{2n\pi x}{3}dx$$

$\left(\because L = \frac{3}{2}\right)$

$$= \frac{2}{3}\left[(2x - x^2)\left(\frac{3}{2n\pi}\sin\frac{2n\pi x}{3}\right)\right] - (2 - 2x)\left(-\frac{9}{4n^2\pi^2}\cos\frac{2n\pi x}{3}\right)$$

$$+ (-2)\left(-\frac{27}{8n^3\pi^3}\sin\frac{2n\pi x}{3}\right)_0^3$$

$$= \frac{2}{3}\left[\left\{0 - \frac{9}{n^2\pi^2}\cos 2n\pi + 0\right\} - \left\{0 - \frac{9}{2n^2\pi^2} + 0\right\}\right]$$

$$(\because \cos 0 = \cos 2n\pi = 1)$$

$$= \frac{2}{3}\cdot\frac{9}{n^2\pi^2}\left[-1 - \frac{1}{2}\right] = -\frac{9}{n^2\pi^2} \qquad \ldots(3)$$

$$b_n = \frac{1}{L}\int_0^{2L} f(x)\sin\frac{n\pi x}{L}dx = \frac{2}{3}\int_0^3 (2x - x^2)\sin\frac{2n\pi x}{3}dx$$

$\left(\because L = \frac{3}{2}\right)$

$$= \frac{2}{3}\left[(2x - x^2)\left(-\frac{3}{2n\pi}\cos\frac{2n\pi x}{3}\right) - (x - 2x)\left(-\frac{9}{4n^2\pi^2}\sin\frac{2n\pi x}{3}\right)\right.$$
$$\left. + (-2)\left(\frac{27}{8n^3\pi^3}\cos\frac{2n\pi x}{3}\right)\right]_0^3$$

$$= \frac{2}{3}\left[\left\{\frac{9}{2n\pi} - 0 - \frac{27}{4n^3\pi^3}\right\} - \left\{0 + 0 - \frac{27}{4n^3\pi^3}\right\}\right] = \frac{2}{3}\left(\frac{9}{2n\pi}\right)$$
$$= \frac{3}{n\pi}$$

Substituting the values of a_0, a_n and b_n from (2), (3) and (4) in (1), we get

$$2x - x^2 = 0 + \sum_{n=1}^{\infty}\left(-\frac{9}{n^2\pi^2}\cos\frac{2n\pi x}{3} + \frac{3}{n\pi}\sin\frac{2n\pi x}{3}\right)$$
$$= \frac{-9}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\cos\frac{2n\pi x}{3} + \frac{3}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\frac{2n\pi x}{3}$$

Example 3 : *Find Fourier series to represent the function* $f(x) = x$ *in the interval* $-\pi < x < \pi$ *and* $f(x + 2\pi) = f(x)$.

Sol. : Here $f(-x) = -x = -f(x)$. Therefore $f(x)$ isan odd function of x in $-\pi < x < \pi$. Hence $a_0 = a_n = 0$ and Fourier series for odd function is

$$x = \sum_{n=1}^{\infty} b_n \sin n x$$

Where
$$b_n = \frac{2}{\pi}\int_0^{\pi} f(x)\sin n x\, dx = \frac{2}{\pi}\int_0^{\pi} x \sin x\, dx$$
$$= \frac{2}{\pi}\left[x\left(-\frac{\cos nx}{n}\right) - (1)\left(-\frac{\sin nx}{n^2}\right)\right]_0^{\pi} = -\frac{2\cos n\pi}{n} \quad \ldots(2)$$

$\therefore$
$$b_1 = \frac{2}{1}, \qquad b_2 = \frac{2}{2}, \qquad b_3 = \frac{2}{3}, \qquad b_4 = -\frac{2}{4} \quad \ldots(3)$$

Hence the required Fourier series is

$$x = 2\left(\sin x - \frac{1}{2}\sin 2x + \frac{1}{3}\sin 3x - \frac{1}{4}\sin 4x + \ldots\right) \qquad \ldots(4)$$

14.5 Practical Harmonic Analysis

So far we have discussed the problem of expanding the periodic function $y = f(x)$, defined within its range, as Fourier series

$$y = f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx) \qquad \ldots(1)$$

By evaluating exactly the integrals (known as Fourier coefficients a_0, a_n and b_n).

$$a_0 = \frac{1}{\pi} \int_0^{2\pi} f(x)\, dx$$

$$a_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \cos nx\, dx \qquad \ldots(2)$$

$$b_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \sin nx\, dx$$

However, in many engineering and scientific problems, the function which is to be analysed into harmonic is often given not by formula (explicit function of an independent variable) but by an irregular graph or experimentally a set of discrete values of the function in tabular form. In such cases, we cannot evaluate the integrals in (2) for Fourier coefficients but we can determine approximate values of the first few terms of Fourier expansion by method of approximate integrations.

The term $(a_1 \cos x + b_1 \sin x)$ is called **fundamental** or **firstharmonic**, the term $(a_2 \cos 2x + b_2 \sin 2x)$ the **second harmonic**, $(a_3 \cos 3x + b_3 \sin 3x)$ the **third harmonic** and so on. In majority of the practical problems, often the first three or four harmonics are required. We shall now discuss the method of finding approximate values of first few harmonics.

Let (x_i, y_i), $i = 0, 1, 2, 3, \ldots m-1$ be the given set of values where x_i are equispaced. Let $y = f(x)$ be periodic function of period 2π defined in the range $(0, 2\pi)$ and $x_i = x_o + \frac{2\pi i}{m}$ (i.e. each subinterval is of the length $\frac{2\pi}{m}$). The coefficients a_0, and a_n, $b_n (n = 1, 2, 3, \ldots)$ in the Fourier series are then determined by applying the definition of definite integral as limite of $\Sigma\, y\, dx$ for y, $y \cos nx$, $y \sin nx$.

$$\frac{1}{\pi} \int_0^{2\pi} y\, dx = \frac{1}{\pi} \times \frac{2\pi}{m} \sum_{i=0}^{m-1} y_i$$

$$= 2 \times \frac{1}{m} \sum_{1=0}^{m-1} y_i$$

$$= 2 \times \text{ (mean value of } y = f(x) \text{ between 0 and } 2\pi \quad \ldots(3)$$

$$= \frac{1}{\pi} \int_0^{2\pi} y \cos nx \, dx = \frac{1}{\pi} \times \frac{2\pi}{m} \sum_{i=0}^{m-1} y_i \cos nx_i$$

$$= 2 \times \frac{1}{m} \sum_{i=0}^{m-1} y_i \cos nx_i$$

$$= 2 \times \text{ [mean value of } y \cos nx \text{ between 0 and } 2\pi \quad \ldots(4)$$

$$= \frac{1}{\pi} \int_0^{2\pi} y \sin nx \, dx = \frac{1}{\pi} \times \frac{2\pi}{m} \sum_{i=0}^{m-1} y_i \sin nx_i$$

$$= 2 \times \frac{1}{m} \sum_{i=0}^{m-1} y_i \sin nx_i$$

$$= 2 \times \text{[mean value of } y \sin nx \text{ between 0 and } 2\pi \text{]} \quad \ldots(5)$$

Remark 1 : There are numerous other methods of finding the values of Fourier coefficients a_0, a_n, b_n which constitute the field of harmonic analysis.

Remark 2 : It may be noted that the number of ordinates used should not be less than twice the number of highest harmonic to be found.

Illustrative Examples

Example 1 : *Using tabulated values of x (in digrees) and y given in the table, obtain a Fourier series upto third harmonic to represent the relation between x and y.*

x^0	0	30	60	90	120	150	180	210	240	270	300	330
y	298	356	373	337	254	155	80	51	60	93	147	221

Sol. : Let the Fourier series upto the third harmonic representing y in $(0, 2\pi)$ be

$$y = \frac{a_0}{2} + (a_1 \cos x + b_1 \sin x) + (a_2 \cos 2x + b_2 \sin 2x) + (a_2 \cos 3x + b_3 \sin 3x) + \ldots\ldots$$

(31)

To evaluate the coefficients, the values of x, y, $\sin x$, $\cos x$, $\sin 2x$, $\cos 2x$, $\sin 3x$, $\cos 3x$ are tabulated as follows :

x^0	y	sin x	cos x	sin 2x	cos 2x	sin 3x	cos 3x
0	298	0	1	0	1	0	1
30	356	0.50	0.87	0.87	0.50	1	0
60	373	0.87	0.50	0.87	-0.50	0	-1
90	337	1	0	0	-1	-1	0
120	254	0.87	-0.50	-0.87	0.50	0	1
150	155	0.50	-0.87	-0.87	0.50	1	0
180	80	0	-1	0	1	0	-1
210	51	-0.50	-0.87	0.87	0.50	-1	0
240	60	-0.87	-0.50	0.87	-0.50	0	1
270	93	-1	0	0	-1	1	0
300	147	-0.87	0.50	-0.87	-0.50	0	-1
330	221	-0.50	0.87	-0.87	0.50	-1	0

Using the values in the table, we have

$$a_0 = 2 \times \frac{\Sigma y}{12} = -\frac{1}{6}\left[298 + 356 + 373 + 337 + 254 + 155 + 80 + 51 + 60 + 93 + 147 + 221\right]$$

$$= \frac{1}{6}\left[2425\right] = 404.17$$

$$a_1 = 2 \times \frac{\Sigma y \cos x}{12} = \frac{1}{6}\left[(298)(1) + (356)(0.87) + (373)(0.50)\right.$$

$$\left. + (337)(0) + (254)(-0.50) + (155)(-0.87) + (80)(-1)\right.$$

$$+(51)(-0.87)+(60)(0)+(93)(0)$$
$$+(147)(0.50)+(221)(0.87)]$$

$$\approx 107.048$$

$$b_1 = 2\times\frac{\Sigma\ y\sin x}{12} = \frac{1}{6}\ [(298)(0)+(356)(0.50)+(373)(0.87)$$
$$+(337)(1)+(254)(0.87)+(155)(0.50)+(80)(0)+(51)(-0.50)$$
$$+(60)(-1)+(93)(-1)+(147)(0.587)+(221)(-0.50)]$$

$$\approx 121.203$$

$$a_2 = 2\times\frac{\Sigma\ y\cos 2x}{12} = \frac{1}{6}\ [(298)(1)+(356)(0.50)+(373)(-0.50)$$
$$+(337)(-1)+(254)(-0.54)+(155)(-0.50)$$
$$+(80)(1)+(51)(0.50)+(60)(-1)+(93)(-1)$$
$$+(147)(-0.50)+(221)(0.50)]$$

$$\approx -13$$

$$b_2 = 2\times\frac{\Sigma\ y\sin 2x}{12} = \frac{1}{6}\ [(298)(0)+(356)(0.87)+(373)(0.87)$$
$$+(337)(0)+(254)(-0.87)+(155)(-0.87)$$
$$+(80)(0)+(51)(0.87)$$
$$+(60)(0)+(93)(0)+(1470)(-0.87)+(221)(-0.87)]$$

$$\approx 9.093$$

$$a_3 = 2\times\frac{\Sigma\ y\cos 3x}{12} = \frac{1}{6}\ [(298)(1)+(356)(0)+(373)(-1)$$
$$+(337)(0)+(254)(1)+(155)(0)+(80)(-1)+(51)(0)$$
$$+(60)(0)+(93)(0)+(147)(-1)+(221)(0)]$$

$$\approx 2.0$$

$$b_3 = 2\times\frac{\Sigma\ y\sin 3x}{12} = \frac{1}{6}\ [(298)(0)+(356)(1)+(373)(0)$$
$$+(337)(-1)+(254)(0)+(155)(1)+(80)(0)+(51)(-1)$$
$$+(60)(1)+(93)(1)+(147)(0)+(221)(-1)]$$

≈ -1

Thus $y = 202 + (107\cos x + 121\sin x) + (-13\cos 2x + 9\sin 2x) + (2\cos 3x - 1\sin 3x)$

Example 2 : *Obtain the constant term and the coefficient of the first sine and cosine terms in the Fourier expansion of y as given in the following table. Also obtain amplitude of the first harmonic.*

x	0	1	2	3	4	5	6
y	9	18	24	28	26	20	0

Sol. : Here number of subintervals $m = 6$ and period $2L = 6$ or $L = 3$.

Let the Fourier series to represent y in (0, 6) upto first harmonic (n =1) is

$$y = \frac{a_0}{2} + \left(a_1 \cos \frac{\pi x}{3} + b_2 \sin \frac{\pi x}{3} \right)$$

The values of x, y, $\sin \frac{\pi x}{3}$, $\cos \frac{\pi x}{3}$ are tabulated as below :

θ	**x**	**y**	$\sin \frac{\pi x}{3}$	$\cos \frac{\pi x}{3}$	$y \sin \frac{\pi x}{3}$	$y\cos \frac{\pi x}{3}$
0	0	9	0	1	0	9
$\frac{\pi}{3}$	1	18	$\sqrt{3}/2$	$1/2$	$9\sqrt{3}$	9
$\frac{2\pi}{3}$	2	24	$\sqrt{3}/2$	$-1/2$	$12\sqrt{3}$	-12
$\frac{3\pi}{3}$	3	28	0	-1	0	-28
$\frac{4\pi}{3}$	4	26	$-\sqrt{3}/2$	$-1/2$	$-13\sqrt{3}$	-13
$\frac{5\pi}{3}$	5	20	$-\sqrt{3}/2$	$1/2$	$-10\sqrt{3}$	10

Here $\Sigma y = 125$, $\Sigma y \sin\frac{\pi x}{3} = -2\sqrt{3}$, $\Sigma y \cos\frac{\pi x}{3} = -25$

$$a_0 = 2\times\frac{\Sigma y}{6} = 2\times\frac{125}{6} = \frac{1}{3}\left[125\right] = 41.66$$

$$a_1 = 2\times\frac{\Sigma y\cos\frac{\pi x}{3}}{6} = 2\times\frac{-25}{6} = \frac{1}{3}\left[-25\right] = -8.33$$

$$b_1 = 2\times\frac{\Sigma y\sin\frac{\pi x}{3}}{6} = 2\times\frac{-2\sqrt{53}}{3} = -1.15$$

Amplitude of the first harmonic $= \sqrt{a_1^2 + b_1^2} = \sqrt{(-8.33)^2 + (-1.1547)^2} = 8.4126$

The Fourier series of y(x) is

$$y = \frac{41.66}{2} + (-8.33)\cos\frac{\pi x}{3} + (-1.15)\sin\frac{\pi x}{3}$$

Remark : The interval $(0, 2\pi)$ is divided into 6 sub-intervals of size $2\pi/6 = \pi/3 = 60^\circ$. The above results can also be obtained by using notation θ for $\frac{\pi x}{3}$

.

Exercise

Expend following function by Fourier Series

1. $x\sin x$, $-\pi \le x \le \pi$ Ans. $\left(x\sin x = 1 - \frac{1}{2}\cos x - \frac{2\cos 2x}{1.3}...\right)$

2. $x - x^2$, $-1 \le x \le 1$

Ans. $-\frac{1}{3} + \frac{4}{\pi^2}\left(\frac{\cos\pi x}{12} - \frac{\cos 2\pi x}{22} + ...\right) + 2/\pi\left(\sin\pi x - \frac{1}{2}\sin 2\pi x\right)$

3. $\pi - x$, $0 \le x \le 2\pi$ Ans. $\pi - xc = 2\left[\sin x + \frac{\sin 2x}{2} + ...\right]$

4. $f(x) = \begin{Bmatrix} x & 0 < x < \pi \\ 2\pi - x & \pi < x < 2\pi \end{Bmatrix}$ Ans. $f(x) = \frac{\pi}{2} - \frac{4}{\pi}\left(\cos x + \frac{1}{3^2}\cos 3x...\right)$

5. $f(x) = \begin{Bmatrix} x & 0 < x < 1 \\ 0 & 1 < x < 2 \end{Bmatrix}$

Ans. $\frac{1}{4}-\frac{2}{\pi^2}\left(\cos\pi x+\frac{\cos 3\pi x}{3^2}+....\right)+\frac{1}{\pi}\left(\sin\pi x\frac{1}{2}\sin 2\pi x...\right)$

6. The following table gives values of y at various value of x find Fourier series expansions of y.

x	0	$\pi/6$	$2\pi/6$	$3\pi/6$	$4\pi/6$	$5\pi/6$
y	0	9.2	14.4	17.8	17.3	11.7

Ans. $y=(11.733-(7.733\cos 2x+1.566\sin 2x)-(2.833\cos 4x+0.116\sin 4x)...)$

7. The following table gives the variation of Periodic current over a period.

t (sec.)	0	$T/6$	$2T/6$	$3T/6$	$4T/6$	$5T/6$	T
A (amp.)	1.98	1.30	1.05	1.30	-0.88	-0.25	1.98

Show by practical analysis that there is direct current part of 0.75 amp. In variable current & amplitude of first harmonic is 1.072.

14.6 Solution of Second Order Differential Equation

Important Definition and Theorem

(1) Power Series : A series of form

$$f(xa)=a_1+a_1x+a_2x^2+a_3x^3+...$$

$\Rightarrow$ $f(x)=\sum_{r=0}^{\infty}a_rx^r$ is called power series.

(2) Regular Function : A function $f(x)$ is called regular at $x=0$. If it can be expressed as a power series of the form

$$f(x)=\sum_{r=0}^{\infty}a_rx^r$$

(3) Ordinary Point : Consider a linear differential equation with variable coefficients

$$P_0\frac{d^2y}{dx^2}+P_1\frac{dy}{dx}+P_2y=0 \qquad \ldots(1)$$

Where P_0, P_1 and P_2 all are functions of x. A point $x=0$ is called ordinary point of equation (1) if $P_0(x)\neq 0$ at $x=0$.

(4) **Singular Point :** If $P_0(x)=0$, at $x=0$, then $x=0$ is called singular point of the differential equation (1) or when $\frac{P_1(x)}{P_0(x)}$ and $\frac{P_2(x)}{P_0(x)}$ both are infinite at $x=0$, then $x=0$ is called singular point of the differential equation.

(5) **Regular singular point :** A point $x=0$ is called a regular singular point of the differential equation if $P_0(x)=0$ at $x=0$. Also $x\frac{P_1(x)}{P_0(x)}$ and $x^2\frac{P_2(x)}{P_0(x)}$ tend to a finite value at $x=0$ i.e.

$$\lim_{x\to 0} x\frac{P_1(x)}{P_0(x)} = \text{finite value}$$

and

$$\lim_{x\to 0} x^2\frac{P_2(x)}{P_0(x)} = \text{finite value}$$

(6) **Irregular singular point :** A point which is not regular singular point of the differential equation is called irregular singular point.

(7) **Theorem :** If $x=0$ is an ordinary point of the differential equation (1), then the solution of (1) can be expressed as a series of the form.

$$y=\sum_{r=0}^{\infty} a_r x^r$$

(8) **Theorem :** If $x=0$ is a regular singular point of the differential equation (1), then the solution of (1) can be expressed as a series form

$$y=\sum_{r=0}^{\infty} a_r x^{m+sr}$$

Where m is called the index of the series solution.

(9) **Theorem :** If $x=0$ is an irregular singular point of the differential equation (1), then the solution of (1) can not be expressed as a series form.

Solution of a Differential Equation when $x=0$ is an Ordinary Point

If $x = 0$ is an ordinary point of the given differential equation, then for the solution of differential equation we follow following steps :

Step – I : Assume a solution in the form

$$y = \sum_{r=0}^{\infty} a_r x^r$$

Step – II : Find $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$

Step – III : Substitute the value of y, $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ in the given differential equation.

Step – IV : Equate to zero the coefficient of various power of x. It gives the recurrence relation.

Step – V : Find the value of all coefficients $a_2, a_3, a_4, \ldots$ in terms of a_0 and a_1.

Step – VI : Substitute these values in the assumed solution to get the required solution.

Illustrative Examples

Example 1 : Solve in series the equation $\left(2 - x^2\right)\frac{d^2y}{dx^2} + 2x\frac{dy}{dx} = 2y = 0$.

Solution : Comparing given differential equation with $P_0\frac{d^2y}{dx^2} + P_1\frac{dy}{dx} = P_2 y = 0$, we get

$$P_0 = \left(2 - x^2\right),\ P_1 = 2x \text{ and } P_2 = -2.$$

At $x = 0$, $P_0 = (0) = 2 \neq 0$,

$\therefore$ $x = 0$ is an ordinary point. …(1)

So, let the solution be $y = \sum_{r=0}^{\infty} a_r x^r$

$\Rightarrow$ $$\frac{dy}{dx} = \sum_{r=0}^{\infty} r a_r\, x^{r-1} \quad \ldots(2)$$

and $$\frac{d^2y}{dx^2} = \sum_{r=0}^{\infty} r(r-1) a_r\, x^{r-2} \quad \ldots(3)$$

Putting the values of y . $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ in the given equation, we get

$$\left(2-x^2\right)\sum_{r=0}^{\infty} r(r-1)a_r\, x^{r-2} + 2x\sum_{r=0}^{\infty} r a_r\, x^{r-1} - 2\sum_{r=0}^{\infty} a_r\, x^r = 0$$

$$\Rightarrow \quad 2\sum_{r=0}^{\infty} r(r-1)a_r\, x^{r-2} + \sum_{r=0}^{\infty}\left[-r(r-1)+2r-2\right]a_r x^r = 0$$

$$\Rightarrow \quad 2\sum_{r=0}^{\infty} r(r-1)a_r\, x^{r-2} + \sum_{r=0}^{\infty}\left[-r+r+2r+2r-2\right]a_r x^r = 0$$

$$\Rightarrow \quad 2\sum_{r=0}^{\infty} r(r-1)a_r\, x^{r-2} - \sum_{r=0}^{\infty}\left[r^2-3r+2\right]a_r x^r = 0$$

$$\Rightarrow \quad 2\sum_{r=0}^{\infty} r(r-1)a_r\, x^{r-2} - \sum_{r=0}^{\infty}(r-1)(r-2)a_r x^r = 0$$

Now equation to zero, coefficients of the smallest power of x i.e. x^{r-2}, we get

$$2r(r-1)a_r(r-3)(r-4)a_{r-2} = 0$$

$$\Rightarrow \quad a_r = \frac{(r-3)(r-4)}{2r(r-1)}a_{r-2} \qquad \ldots(4)$$

This is called recurrence relation.

Putting $r = 2, 3, 4, 5,...$ in equation (4), we get

$$r = 2;\ a_2 = \frac{(2-3)(2-4)}{2.2(2-1)}a_0 = \frac{a_0}{2}$$

$$r = 3;\ a_0 = 3$$

$$r = 4;\ a_4 = \frac{(4-3)(4-4)}{2.4(4-1)}a_2 = 0$$

$$r = 5;\ a_5 = \frac{(5-3)(5-4)}{2.5(5-1)}a_3 = 0$$

$$r = 6;\ a_6 = \frac{(6-3)(6-4)}{2.6(6-1)}a_4 = 0$$

Putting the value of $a_2, a_3, a_4,...$ in (1), we get

$$y = a_0 + a_1x + a_2x^2$$

$$\Rightarrow \qquad y = a_0 + a_1 x + \frac{a_0}{2} x^2$$

Example 2 : Solve in series the equation $\left(1-x^2\right)\frac{d^2y}{dx^2} + 2x\frac{dy}{dx} + y = 0$.

Solution : Given differential equation is

$$\left(1-x^2\right)\frac{d^2y}{dx^2} + 2x\frac{dy}{dx} + y = 0 \qquad \ldots(1)$$

Comparing given differential equation with $P_0\frac{d^2y}{dx^2} + P_1\frac{dy}{dx} + P_2 y = 0$, we get

$P_0 = 1-x^2$; $P_1 = 2x$ and $P_2 = 1$

Here $P_0(0) = 1 \neq 0$

Thus, $x = 0$ is an ordinary point.

So, let the solution be

$$y = \sum_{r=0}^{\infty} a_r x^r \qquad \ldots(2)$$

$$\Rightarrow \qquad \frac{dy}{dx} = \sum_{r=0}^{\infty} r a_r x^{r-1} \qquad \ldots(3)$$

and $$\frac{d^2y}{dx^2} = \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} \qquad \ldots(4)$$

Putting the values of y, $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ in the given equation, we get

$$\left(1-x^2\right)\sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} + 2x\sum_{r=0}^{\infty} r a_r x^{r-1} + \sum_{r=0}^{\infty} a_r x^r = 0$$

$$\Rightarrow \qquad \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} + \sum_{r=0}^{\infty} \left[-r(r-1) + 2r + 1\right] a_r x^r = 0$$

$$\Rightarrow \qquad \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} + \sum_{r=0}^{\infty} \left[-r^2 + 3r + 1\right] a_r x^r = 0$$

$$\Rightarrow \qquad \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} - \sum_{r=0}^{\infty} \left[r^2 - 3r - 1\right] a_r x^r = 0$$

Now equating to zero, the coefficient of the smallest power of x i.e. x^{r-2}, we get

$$r(r-1)a_r - \left[(r-2)^2 - 4(r-2) - 1\right]a_{r-2} = 0$$

$$\Rightarrow \qquad a_r = \frac{(r-2)^2 - 3(r-2) - 1}{r(r-1)} a_{r-2} \qquad \ldots(5)$$

This is called recurrence relation. Putting $r = 2, 3, 4, 5, \ldots$ in (5), we get

$$r = 2; \quad a_2 = \frac{1}{2} a_0$$

$$r = 3; \quad a_3 = \frac{1-3-1}{6} a_1 = -\frac{1}{2} a_1$$

$$r = 4; \quad a_4 = \frac{4-6-1}{12} a_2 = -\frac{1}{4} a_2 = \frac{1}{8} a_0$$

$$r = 5; \quad a_5 = \frac{9-9-1}{20} a_3 = -\frac{1}{20} a_3 = \frac{1}{40} a_1$$

Putting the values of $a_2, a_3, a_4, \ldots$ in (2), we get

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5 + \ldots$$

$$\Rightarrow \qquad y = a_0 \left(1 - \frac{1}{2} x^2 + \frac{1}{8} x^4 + \ldots\right) + a_1 \left(x - \frac{x^2}{2} + \frac{x^5}{40} + \ldots\right)$$

Example 3 : Solve in series the equation $\left(1 - x^2\right) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + 2y = 0$.

Solution : Given differential equation is

$$\left(1 - x^2\right) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + 2y = 0 \qquad \ldots(1)$$

Comparing given differential equation with $P_0 \frac{d^2 y}{dx^2} + P_1 \frac{dy}{dx} + P_2 y = 0$, we get

$$P_0 = 1 - x^2; \qquad P_1(x) = -2x \qquad \text{and} \qquad P_2(x) = 2$$

Here $P_0(0) = 1 \neq 0$

Thus $x = 0$, is an ordinary point.

So let the solution be

$$y = \sum_{r=0}^{\infty} a_r x^r \qquad \ldots(2)$$

$$\Rightarrow \qquad \frac{dy}{dx} = \sum_{r=0}^{\infty} r a_r x^{r-1} \qquad \ldots(3)$$

and $$\frac{d^2y}{dx^2} = \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} \qquad \ldots(4)$$

Putting the values of y, $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ in the given equation (1), we get

$$(1-x^2)\sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} - 2x \sum_{r=0}^{\infty} r a_r x^{r-1} + 2 \sum_{r=0}^{\infty} a_r x^r = 0$$

$$\Rightarrow \qquad \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} - \sum_{r=0}^{\infty} [r(r-1) + 2r - 2] a_r x^r = 0$$

$$\Rightarrow \qquad \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} - \sum_{r=0}^{\infty} (r^2 + r - 2) a_r x^r = 0$$

$$\Rightarrow \qquad \sum_{r=0}^{\infty} r(r-1) a_r x^{r-2} - \sum_{r=0}^{\infty} (r-1)(r-2) a_r x^r = 0$$

Now equating to zero, the coefficient of the smallest power of x i.e. x^{r-2}, we get

$$r(r-1)a_r - r(r-3)a_{r-2} = 0$$

$$\Rightarrow \qquad a_r = \frac{r(r-3)}{r(r-1)} a_{r-2}$$

$$\Rightarrow \qquad a_r = \frac{(r-3)}{(r-1)} a_{r-2} \qquad \ldots(5)$$

Putting $r = 2, 3, 4, 5, \ldots$ in equation (5), we get

$r = 2$; $a_2 = -a_0$

$r = 3$; $a_3 = 0$

$r = 4$; $a_4 = \frac{1}{3} a^2 = -\frac{1}{3} a_0$

$r = 5$; $a_5 = 0$ and so on.

Putting the values of $a_2, a_3, a_4, \ldots$ in (2), we get

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + \ldots$$

$$\Rightarrow \qquad y = a_0 \left(1 - x^2 - \frac{1}{3} x^4 - \ldots\right) + a_1 x$$

Example 4 : Solve in series the equation (Legendre Equation)

$$(1-x^2)\frac{d^2y}{dx^2}-2x\frac{dy}{dx}+n(n+1)=0$$

Solution : Given differential equation is

$$(1-x^2)\frac{d^2y}{dx^2}-2x\frac{dy}{dx}+n(n+1)=0 \qquad \ldots(1)$$

Comparing given differential equation with $P_0\frac{d^2y}{dx^2}+P_1\frac{dy}{dx}+P_2y=0$, we get

$P_0=1-x^2$; $P_1(x)=-2x$; and $P_2(x)=n(n+1)$

Here $P_0(0)=1\neq 0$

Thus $x=0$, is an ordinary point.

So, let the solution be

$$y=\sum_{r=0}^{\infty}a_r x^r \qquad \ldots(2)$$

$$\Rightarrow \quad \frac{dy}{dx}=\sum_{r=0}^{\infty}ra_r x^{r-1} \qquad \ldots(3)$$

and $$\frac{d^2y}{dx^2}=\sum_{r=0}^{\infty}r(r-1)a_r x^{r-2} \qquad \ldots(4)$$

Putting the values of y, $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ in the given equation (1), we get

$$(1-x^2)\sum_{r=0}^{\infty}r(r-1)a_r x^{r-2}-2x\sum_{r=0}^{\infty}ra_r x^{r-1}+n(n+1)\sum_{r=0}^{\infty}a_r x^r=0$$

$$\Rightarrow \quad \sum_{r=0}^{\infty}r(r-1)a_r x^{r-2}-\sum_{r=0}^{\infty}[r(r-1)+2r-n(n+1)]a_r x^r=0$$

$$\Rightarrow \quad \sum_{r=0}^{\infty}r(r-1)a_r x^{r-2}-\sum_{r=0}^{\infty}[r^2+r-n(n+1)]a_r x^r=0$$

$$\Rightarrow \quad \sum_{r=0}^{\infty}r(r-1)a_r x^{r-2}-\sum_{r=0}^{\infty}(r-n)(r+n+1)a_r x^r=0$$

Now equating to zero, the coefficient of the smallest power of x i.e. x^{r-2}, we get

$$r(r-1)a_r-(r-2-n)(r+n-1)a_{r-2}=0$$

$$\Rightarrow a_r = \frac{(r-2-n)(r+n-1)}{r(r-1)} a_{r-2} \qquad \ldots(5)$$

Putting $r = 2, 3, 4, 5, \ldots$ in (5), we get

$$r = 2 \; ; \; a_2 = -\frac{n(n+1)}{2} a_0$$

$$r = 3 \; ; \; a_3 = \frac{(1-n)(n+2)}{6} a_1 = \frac{-(n-1)(n+2)}{6} a_1$$

$$r = 4 \; ; \; a_4 = \frac{-(n-2)(n+3)}{12} a_2$$

or $$a_4 = \frac{n(n-2)(n+1)(n+3)}{24} a_0$$

$$r = 5 \; ; \; a_5 = \frac{-(n-3)(n+4)}{20} a_3 = \frac{(n-3)(n-1)(n+2)(n+4)}{120} a_1 \text{ and so on.}$$

Putting the values of $a_2, a_3, a_4, \ldots$ in (2), we get

$$y = a_0\left(1 - \frac{n(n+1)}{2}x^2 + \frac{n(n-2)(n+1)(n+3)}{24}x^4 - \ldots\right)$$

$$+ a_1\left(x - \frac{(n-1)(n+2)}{6}x^3 + \frac{(n-3)(n-1)(n+2)(n+4)}{120}x^5 - \ldots\right)$$

Exercise

Solve in series the equations

1. $\left(1+x^2\right)\frac{d^2y}{dx^2} + x\frac{dy}{dx} - y = 0$

2. $\frac{d^2y}{dx^2} + xy = 0$

3. $\frac{d^2y}{dx^2} + x^2y = 0$

4. $\frac{d^2y}{dx^2} + x\frac{dy}{dx} + y = 0$

5. $\left(2+x^2\right)\frac{d^2y}{dx^2} + x\frac{dy}{dx} + (1+x)y = 0$

Answers

1. $y = a_0\left(1+\frac{x^2}{2}-\frac{x^4}{8}+\frac{x^6}{16}-\ldots\right)+a_1 x$

2. $y = a_0\left(1-\frac{x^2}{3!}+\frac{4x^6}{6!}-\ldots\right)+a_1\left(x-\frac{2x^4}{4!}+\frac{10x^7}{7!}-\ldots\right)$

3. $y = a_0\left(1-\frac{x^4}{3.4}+\frac{x^8}{3.4.7.8}-\ldots\right)+a_1\left(x-\frac{x^5}{4.5}+\frac{x^7}{4.5.8.9}-\ldots\right)$

4. $y = a_0\left(1-\frac{x^2}{2}+\frac{x^4}{8}-\ldots\right)+a_1\left(x-\frac{x^3}{3}+\frac{x^5}{15}-\ldots\right)$

5. $y = a_0\left(1-\frac{x^2}{4}+\frac{x^3}{12}-\ldots\right)+a_1\left(x-\frac{x}{6}-\frac{x^4}{24}-\ldots\right)$

14.7 Summary

Various methods of solution of first order DE & there usages in Chemical Science are discussed. Expending a function by fourier series & practical harmonic analysis are discussed. Solution of differential equations of Second order (involving legendre equations etc.) by power series method are discussed.

14.8 Glossary

- Differential equation: A differential equation is any equation which contains derivatives, either ordinary derivatives or partial derivatives.
- Homogeneous: Having all terms of the same degree
- Exact: Characterized by strict adherence to standards or rules
- Linear: Involving measurement in one dimension only
- Periodic function: A periodic function is a function that repeats its values in regular intervals or periods series.
- Interval: The set containing all real numbers or points between two given numbers or points
- Even Function: A function is "even" when f(x) = f(-x) for all x.

- Odd Function: A function is "odd" when f(-x)= -f(x) for all x.

14.9 References

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Unit -15 Permutation and Probability Permutations and combinations, probability and probability theorems, average, probability curves

Unit Structure

15.0 Objectives

In this unit we briefly discuss Probability theory. After studying this unit, students are able to solve and understand problems pertaining to probability.

15.1 Introduction

To have an understanding in combinations and permutations we must first have a basic understanding in probability.

A probability is a numerical measure of the likelihood of the event. Probability is established on a scale from 0 to 1. A rare even has a probability close to 0; a very common event has a probability close to 1.

In order to solve and understand problems pertaining to probability you must know some vocabulary:

- An experiment, such as rolling a die or tossing a coin, is a set of trials designed to study a physical occurrence.
- An outcome is any result of a particular experiment. For example, the possible outcomes for flipping a coin are heads or tails.
- A sample space is a list of all the possible outcomes of an experiment.
- An event is a subset of the sample space. For example, getting heads is an event.

The probability of an event, *E*, is represented by *P(E)*. To calculate the probability of an event, you must find the total number of outcomes, and the favorable number of outcomes.

The general equation of the probability of an event is:

$$P(E) = \frac{\text{Number of Favorable Outcomes}}{\text{Total Number of Outcomes}}$$

Example What is the probability of drawing a spade from a pack of 52 well-shuffled playing cards?

Sol. The probability of drawing a spade from a pack of 52 well-shuffled playing cards is; Event (E) = ‘ a spade drawn ’ , the number of outcomes corresponding to E = 13 (spades) and the total number of outcomes = 52 (cards)

$$13/52=1/4=.25$$

Note that When there is no possibility for an event to occur, the probability of the event happening is 0. For example in a bag of red and blue marbles the probability of picking an orange one is 0. Similarly, when the event is certain to occur, the probability of that event is 1.

Example Suppose we have a jar with 4 red marbles and 6 blue marbles, and we want to find the probability of drawing a red marble at random. In this case we know that all outcomes are equally likely: any individual marble has the same chance of being drawn. What's the probability of drawing a red marble?

Number of red marbles / Total marbles in Jar = 4/10

Sol. Since 4/10 reduces to 2/5, the probability of drawing a red marble expressed as a decimal is 0.4 ; as a percent, 4/10 = 40%. The probability of picking a blue marble is 6/10, which reduces to 3/5. As a decimal this is 0.6.

Fundamental Counting Principles: There are two principles of counting that will enable you to find the number of outcomes without listing and counting each one.

1. **The Multiplication Principle**: If there are n_1 ways to choose a first item, n_2 ways to choose a second item, n_3 ways to choose a third item, and so on, the the total number of ways to choose all the items is given by the product $n_1 \times n_2 \times n_3 \times \ldots$

Example: The Shoe store sells 9 different styles of running shoes, each available in 2 colors. How many combinations of color and style are there?

Choose : style and color = choices

$$\underline{9} \times \underline{2} = 18$$

2. **The Addition Principle:** If one outcome can occur in *r* ways, and a second mutually exclusive outcome, can occur in *s* ways, then there are a total of (r + s) possible outcomes.

Example: You can order one item from a list of 5 hamburgers and 3 pizzas. How many choices do you have?

Choose: burger or pizza = choices

5 + 3 = 8

15.2 Priori' Probability and Posteriori Probability

Mathematical of Classical or 'A Priori' Probability

According to 'Jacob Bernaulli', 'if a random experiment results N exhaustive, mutually exclusive and equally likely outcomes, out of which m are favourable to the happening of an event E, then the probability of happening of the event E, denoted by $P(E)$ is given by

$$P(E) = \frac{\text{Total number of favourable cases}}{\text{Exhaustive number of cases}}$$

$$P(E) = \frac{m}{N}$$

Statistical or Empirical or Posteriori Probability

According to von Mises, 'if an experiment is performed repeatedly under essentially homogeneous and identical conditions, then the limiting value of the ratio of the number of times the event happens to the number of trials, as the number of trials becomes indefinitely large, is called the probability of happening of the event'. It being assumed that the limit is unique and finite.

Symbolically, if in N trials, an event E happens m times, then the probability P of happening of E, denoted by $P(E)$ and written as

$$P(E) = \lim_{n \to \infty} \left(\frac{m}{N}\right)$$

Axioms of Probability: Let S be a sample space and set P be a real valued function defined on the subsets of S. Then, P is called a probability function and the probability of happening of E is given by $P(E)$, if the following three axioms hold well.

Axiom $P(E)$ is a real number i.e., $P(E) \geq 0$ for every event E in S or $0 \leq P(E) \leq 1$.

Proof Let E be the event of S, then $E \subset S$

Let $n(E) = m$ and $n(S) = N$

Now, we have from $E \subset S$, then $0 \leq n(E) \leq n(S)$

$$= 0 \leq m \leq N$$

$$= \frac{0}{N} \leq \frac{m}{N} \leq \frac{N}{N}$$

$$= 0 \leq P(E) \leq 1$$

Hence, the probability of happening of an event lies between 0 and 1.

Axiom The probability of a certain event is unity

i.e., $$P(S) = 1$$

Proof Let E be an event of S and E' be its compliment let $n(E) = m$ and $n(E') = N - m, n(S) = N$

$$\therefore \quad P(E) = \frac{m}{N} \text{ and } P(E') = \frac{N-m}{N} = 1 - \frac{m}{N}$$

Since, E and E' are mutually exclusive events.

So, $$P(E) + P(E') = \frac{m}{N} + 1 - \frac{m}{N}$$

$$= P(E \cup E') = 1$$

$$P(S) = 1$$

Hence, probability of a certain event is unity.

Axiom If $E_1, E_2, \ldots\ldots\ldots\ldots, E_3$ are any finite or infinite sequence of disjoint events of S, then

$$P\left(\bigcup_{i=1}^{k} E_i\right) = \sum_{i=1}^{k} P(E_i)$$

or

$$P\left(\bigcup_{i=1}^{\infty} E_i\right) = \sum_{i=1}^{\infty} P(E_i)$$

Proof Let exhaustive number of cases = $n(S) = N$ and favourable case to the event $E_i = m_i, i = 1, 2, 3, \ldots\ldots, k$ and E_i is mutually exhaustive events.

So, the favourable case to the event either $E_1 \, or \, E_2 \, or \, E_3 \, or \, \ldots \ldots . or \, E_k = m_1 + m_2 + m_3 + \cdots \ldots . + m_k \;\; So \, P(E_1 \, or \, E_2 \, or \, E_3 \, or \, \ldots \ldots or \, E_k)$

$$= \frac{m_1 + m_2 + m_3 + \cdots \ldots + m_k}{N}$$

$$= P\,(E_1 \cup \; E_2 \cup \; E_3 \cup \ldots . \cup E_k)$$

$$= \frac{m_1}{N} + \frac{m_2}{N} + \frac{m_3}{N} + \cdots . + \frac{m_k}{N}$$

$$= P\,(E_1 \cup \; E_2 \cup \; E_3 \cup \ldots . \cup E_k)$$

$$= P(E_1) + \; P(E_2) + \; P(E_3) + \cdots . . + P(E_k)$$

$$= P\left(\bigcup_{i=1}^{k} E_i\right) = \sum_{i=1}^{k} P\,(E_i)$$

$$P\left(\bigcup_{i=1}^{\infty} E_i\right) = \sum_{i=1}^{\infty} P\,(E_i)$$

Theorem The probability of an impossible event is zero i.e., $P(\phi) = 0$.

Proof Since, we know that an impossible event contains no sample point thus, the certain event S and the impossible event ϕ are mutually exclusive.

Hence, from $(S \; \cup \; \phi) = S$

$$= P(S \cup \; \phi) = \; PS$$

$$\because S \, and \, \phi \, are \, mutually \, exclusive$$

So, $$P(S) \; + \; P(\phi) \; = \; P(S)$$

$$p\,(\phi) = 0$$

Hence, the probability of an impossible event is zero.

Theorem If $\overline{A}$ is the complimentary event of A, then

$$P(\overline{A}\,) \; = \; 1 \; - \; P(A)$$

Proof

Since, A and $\overline{A}$ are complimentary events, then they disjoint events.

So, $$A \; \cup \; \overline{A} \; = S$$

$$= n(A \; \cup \; \overline{A}\,) = n\,(S)$$

$$= \frac{n(A \; \cup \; \overline{A}\,)}{n(S)} = \frac{n(S)}{n\,(S)}$$

$$P(A \cup \bar{A}) = 1$$

$$P(A) + P(\bar{A}) = 1$$

$$(\because A \text{ and } \bar{A} \text{ are mutually disjoints\_})$$

$$P(\bar{A}) = 1 - P(A)$$

Theorem For any two events $A \text{ and } B$

(a) $P(A \cap \bar{B}) = P(A) - P(A \cap B)$
(b) $P(\bar{A} \cap B) = P(B) - P(A \cap B)$

Theorem If B is the subset of A, then

(a) $P(B)P(A \cap \bar{B}) = P(A) -$
(b) $P(B) \leq P(A)$

Theorem For any two events $A \text{ and } B$

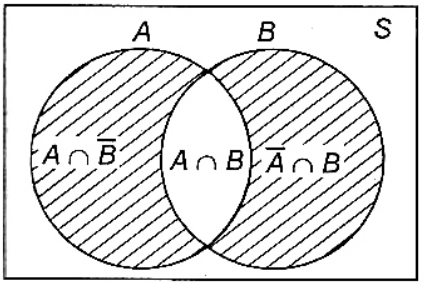
$$P(A \cap \bar{B}) \cup P(\bar{A} \cap B) = P(A) + P(B) - 2P(A \cap B)$$

Theorem (Addition law of probabilities)

If $A \text{ and } B$ are any two events which are the subsets of the sample space S and are not mutually exclusive, then we have

$$P(A \cup B) = P(A) + P(B) - P(A \cap B)$$

Proof Let total exclusive number of cases of a random experiment $= n(S)$



And favourable number of cases for the event $A \cup B = n(A \cup B)$

$$= P(A \cup B) = \frac{n(A \cup B)}{n(S)}$$

Now, from Venn diagram

$$n(A \cup B) = n(A \cap \bar{B}) + n(A \cap B) + n(\bar{A} \cap B)$$

$$= n(A) - n(A \cap B) + n(A \cap B) + n(B) - n(A \cap B)$$

$$= n(A) + n(B) - n(A \cap B)$$

$$= \frac{n(A \cup B)}{n(S)} = \frac{n(A)}{n(S)} + \frac{n(B)}{n(S)} - \frac{n(A \cap B)}{n(S)}$$

$$= P(A \cup B) = P(A) + P(B) - P(A \cap B)$$

Note * If A and B are mutually exclusive events, then

$$A \cap B = \phi$$

$$= P(A \cap B) = 0$$

Hence, from Eq. (ii) $P(A \cup B) = P(A) + P(B)$

* If $A_1, A_2, \ldots\ldots, A_n$ are n mutually exclusive events, then

$$P(A_1 \cup A_2 \cup A_3 \cup \ldots\ldots \cup A_n) = P(A_1) + P(A_2) + \ldots\ldots + P(A_n)$$

15.3 Conditional Probability

If there are two events A_1 and A_2, then the happening of an event A_2 with the condition that A_1 has already happened is denoted by $\frac{A_2}{A_1}$ and the probability of happening of the event A_2, when the event A_1 has already happened is called the conditional 1 probability and is written as $P\left(\frac{A_2}{A_1}\right)$ and is read as 'probability of A_2, given that A_1 has already happened'.

Multiplicative Theorem of Probability

Statement For two events A_1 and A_2, we have

$$P(A_1 \cap A_2) = P(A_1).P\left(\frac{A_2}{A_1}\right), P(A_1) \neq 0$$

$$P(A_1 \cap A_2) = P(A_2).P\left(\frac{A_1}{A_2}\right), P(A_2) \neq 0$$

where, $P\left(\frac{A_2}{A_1}\right)$represents the conditional probability of happening of $A_2$when the event A_1 has already happened and the $P\left(\frac{A_1}{A_2}\right)$ is the conditional probability of happening of $A_1$when the event A_2 has already occurred.

Proof Let exhaustive number of cases to a random experiment $= n(S)$

Favourable cases to the event $A_1 = n(A_1)$

Favourable cases to the event $A_2 = n(A_2)$

Favourable cases to the event $(A_1 \cap A_2) = n(A_1 \cap A_2)$

$$\therefore \qquad P(A_1) = \frac{n(A_1)}{n(S)}$$

$$P(A_2) = \frac{n(A_2)}{n(S)}$$

$$P(A_1 \cap A_2) = \frac{n(A_1 \cap A_2)}{n(S)}$$

$$P\left(\frac{A_1}{A_2}\right) = \frac{n(A_1 \cap A_2)}{n(A_2)}$$

$$P\left(\frac{A_2}{A_1}\right) = \frac{n(A_1 \cap A_2)}{n(A_1)}$$

Now

$$P(A_1 \cap A_2) = \frac{n(A_1 \cap A_2)}{n(S)}$$

$$= \frac{n(A_1)}{n(S)} = \frac{n(A_1 \cap A_2)}{n(A_1)}$$

$$= P(A_1).P\left(\frac{A_2}{A_1}\right)$$

$$P(A_1 \cap A_2) = P(A_1).P\left(\frac{A_2}{A_2}\right)$$

$$[P(A_1) \neq 0]$$

$$P(A_1 \cap A_2) = \frac{n(A_1 \cap A_2)}{n(S)}$$

$$= \frac{n(A_2)}{n(S)} \cdot \frac{n(A_1 \cap A_2)}{n(A_2)}$$

$$= P(A_2).P\left(\frac{A_1}{A_2}\right)$$

$$P(A_1 \cap A_2) = P(A_2).P\left(\frac{A_1}{A_1}\right) \quad [P(A_2) \neq 0]$$

Note If the events A_1 and A_2 are independent, then

$$P\left(\frac{A_1}{A_2}\right) = P(A_1), P(A_2) \neq 0$$

$$and \qquad P\left(\frac{A_2}{A_1}\right) = P(A_2), P(A_1) \neq 0$$

$$\therefore \quad P(A_1 \cap A_2) = P(A_1).P(A_2) \neq 0$$

Hence, for independent events $A_1$and A_2 the probability of their simultaneous happening is the product of their respective probabilities. This rule is known as 'multiplicative rule of probability'.

If $A_1, A_2, \ldots, A_n$ are n independent events.

Then $P(A_1 \cap A_2 \cap A_3 \cap \ldots \cap A_n)$

$$= P(A_1).P(A_2) \ldots . P(A_n)$$

Theorem If A and B are independent events, then that

(a) $A \; and \; \bar{B}$ are also independent.

(b) $\bar{A} \; and \; B$ are also independent.

(c) $\bar{A} \; and \; \bar{B}$ are also independent.

Proof ∵ A and B are independent events.

Then, $(A \cap B) = P(A).P(B)$

(a) From $P(A \cap \bar{B}) = P(A) - P(A \cap B)$

$$= P(A) - P(A).P(B)$$
$$= P(A)[1 - P(B)]$$
$$P(A \cap \bar{B}) = P(A).P(\bar{B})$$

Hence, if $A \; and \; B$ are independent events and $A \; and \; \bar{B}$ are also independent.

(b) From $P(\bar{A} \cap B) = P(B) - P(A \cap B)$

$$= P(B) - P(A).P(B)$$

$$= P(B)[1 - P(A)]$$
$$P(\bar{A} \cap \bar{B}) = P(B).P(\bar{A})$$

Hence, $A\ and\ B$ is also independent.

(c) From $P(\bar{A} \cap \bar{B}) = P(\overline{A \cup B})$

$$= 1 - P(A \cup B)$$
$$= 1 - [P(A) + P(B) - P(A \cap B)]$$
$$= 1 - [P(A) + P(B) - P(A).P(B)$$
$$= [1 - P(A)] - P(B)[1 - P(A)]$$
$$= [1 - P(A)][1 - P(B)]$$
$$P(\bar{A} \cap \bar{B}) = P(A\bar{A}).P(\bar{B})$$

Hence $\bar{A}\ and \bar{B}$ are also independent.

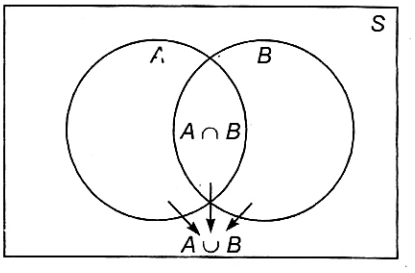
Theorem For any two events $A\ and\ B$, prove that

$$P(A \cap B) \leq P(A) \leq P(A \cup B) \leq P(A) + P(B)$$

Proof

From Venn diagram, we have

$$n(A \cap B) \leq n(A)$$
$$= \frac{n(A \cap B)}{n(S)} \leq \frac{n(A)}{n(S)}$$
$$= P(A \cap B) \leq P(A)$$



Again from Venn diagram,

$$n(A) \leq n(A \cup B)$$
$$\frac{n(A)}{n(S)} \leq \frac{n(A \cup B)}{n(S)}$$
$$P(A) \leq P(A \cup B)$$

Now, from addition law of probability

$$P(A \cup B) = P(A) + P(B) - P(A \cap B)$$

$$P(A \cup B)P(A) + P(B)$$

$$[if\ P(A \cap B) \geq 0]$$

$$P(A \cap B) \leq P(A) \leq P(A \cup B) \leq P(A) + P(B)$$

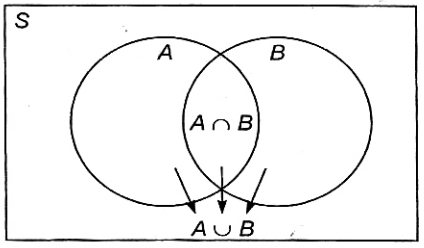
Theorem If $A\ and\ B$ are two events and $P(B)\ \neq\ 1$, then show that

$$P\left(\frac{A}{B}\right) = \frac{PA(-P(A \cap B}{1 - P(B)}$$

Proof We know,

$$P(A \cap \bar{B}) = P(A) - P(A \cap B)$$

and $$P(\bar{B}) = 1 - P(B)$$



Now, $$P\left(\frac{A}{B}\right) = \frac{P(A \cap \bar{B})}{P(\bar{B})} = \frac{P(A) - P(A \cap B)}{1 - P(B)}$$

$$P\left(\frac{A}{B}\right) = \frac{P(A) - P(A \cap B)}{1 - P(B)}$$

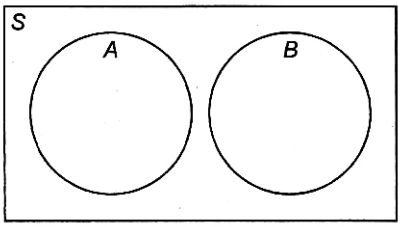
Theorem If A and B are mutually exclusive events and $P(A \cup B) \neq 0$ then show that

$$P\left(\frac{A}{A \cup B}\right) = \frac{P(A)}{P(A) + P(B)}$$

Proof Given, $A\ and\ B$ are mutually exclusive events i.e., $A \cap B = \phi$

$$P(A \cap B) = P(\phi)$$

$$P(A \cap B) = 0$$



Now, $P\left(\frac{A}{A\cup B}\right) = \frac{P[A\cap(A\cup B)]}{P(A\cup B)}$

$$= \frac{P[(A \cap B) \cup (A \cap B)]}{P(A \cup B)}$$

$$= \frac{P[A \cup \phi]}{P(A \cup B)}$$

$$= \frac{P(A)}{P(A \cup B)}$$

$$= \frac{P(A)}{P(A) + P(B) - P(A \cap B)}$$

$$= \frac{P(A)}{P(A) + P(B) - 0}$$

$$= P\left(\frac{A}{A \cup B}\right) = \frac{P(A)}{P(A) + P(B)}$$

Pairwise Independent Events

A set of events $A_1, A_2, \ldots, A_n$ are said to be pairwise independent, if

$$P(A_1 \cap A_1) = P(A_i)P(A_j)\forall_i \neq j$$

Theorem For any two events $A \; and \; B$ such than $P(A) > 0$

$$P(A) = P(B).P(A/B) + P(\bar{B}).P(A/\bar{B})$$

Proof As we have already proved

$$P(A \cap B) = P(B).P(A/B)$$

$$P(A \cap \bar{B}) = P(\bar{B}).P(A/\bar{B})$$

We have,

$$A = (A \cap \bar{B}) \cup (A \cap B)$$

$$P(A) = P(A \cap \bar{B}) \cup (A \cap B)$$

$$= P(A \cap \bar{B}) + P(A \cap B)$$

$$= P(\bar{B}).P(A/\bar{B}) + P(B).P(A/B)$$

Mutually Independent Events

If we have three events $A, B \text{ and } C$ such that

$$P(A \cap B) = P(A)P(B)$$
$$P(B \cap C) = P(B)P(C)$$
$$P(C \cap A) = P(C)P(A)$$

And $$P(A \cap B \cap C) = P(A)P(B)P(C)$$

Then $A, B \text{ and } C$ are called mutually independent events.

Theorem If $A, B \text{ and } C$ are mutually independent events than $A \cup B \text{ and } C$ are also independent.

Theorem $A, B \text{ and } C$ are random events in a simple space and if $A, B \text{ and } C$ are pairwise independent and A is independent of $(B \cup C)$, then $A, B \text{ and } C$ are mutually independent.

Theorem If an event A is independent of the events $B, B \cap C \text{ and } B \cup C$, then it is also independent of C.

Example $A \text{ and } B$ are two independent events. The probability that both $A \text{ and } B$ occur is $\frac{1}{6}$ and the probability that neither of them occurs is$\frac{1}{3}$. Then find the probability of the occurrence of A.

Sol. Given,$P(A \, n \cap \, B) \, = \, \frac{1}{6} \, = \, P(A) \, P(B)$, where $A \text{ and } B$ are independent. $P(\bar{A} \cap \bar{B}) = \frac{1}{3} = P(\bar{A})P(\bar{B})$

We know that

$$P(A \cup B) = 1 - P(\bar{A} \cap \bar{B})$$
$$P(A) + P(B) - P(A \cap B) = 1 - P(\bar{A} \cap \bar{B})$$
$$P(A) + P(B) = P(A \cap B) + 1 - P(\bar{A} - \bar{B})$$
$$P(A) + P(B) = \frac{1}{6} + 1 - \frac{1}{3} = \frac{1 + 6 - 2}{6}$$

$$Thus \quad P(A) + P(B) = \frac{5}{6}$$

Now, $[P(A) - P(B)]^2 = [P(A) + P(B)]^2 - 4P(A)P(B)$

$$= \left(\frac{5}{6}\right)^2 - 4 \times \frac{1}{6}$$

$$= \frac{25}{26} - \frac{4}{6} = \frac{1}{36}$$

$$P(A) - P(B) = \pm\frac{1}{6}$$

$$2P(A) = \frac{5}{6} \pm \frac{1}{6}$$

$$P(A) = \frac{1}{2} \; or \frac{1}{3}$$

Bayes' Theorem

Statement If $E_1, E_2, \ldots, E_n$ are n mutually disjoint events with $P(E_i) \neq 0$ where, $i = 1, 2, 3, \ldots, n$ then for any arbitrary event A which is a subset of $\bigcup_{i=1}^{n} E_i$ such that $P(A) > 0$, we have

$$P\left(\frac{E_i}{A}\right) = \frac{\mathrm{P(E_i).\,P\left(\frac{A}{E_i}\right)}}{\sum_{i=1}^{n} \mathrm{P(E_i)\,.\,P\left(\frac{A}{E_i}\right)}} \qquad (\mathrm{i} = 1, 2, \ldots, \mathrm{n})$$

Proof Given A is subset of $\bigcup_{i=1}^{n} E_i$.

i.e. $A \subset \bigcup_{i=1}^{n} E_i$

$$A = A \cap \bigcup_{i=1}^{n} E_i$$

$$A = A \cap (E_1 \cup E_2 \cup \ldots \cup E_n)$$

$$A = (A \cap E_1) \cup (A \cap E_2) \cup \ldots\ldots \cup (A \cap E_n)$$

Since, $E_1, E_2, \ldots, E_n$ are mutually disjoint events.

$\therefore (A \cap E_1) \cup (A \cap E_2), \ldots\ldots, (A \cap E_n)$ are also mutually disjoint events.

$\therefore P(A) = P(A \cap E_1) + P(A \cap E_2) + \cdots . + P(A \cap E_n)$

$$= P(E_1).\mathrm{P}\left(\frac{\mathrm{A}}{E_1}\right) + \mathrm{P}(E_2) + P\left(\frac{A}{E_2}\right) + \cdots + \mathrm{P}(E_n)\left(\frac{\mathrm{A}}{E_n}\right)$$

$$P(A) = \sum_{i=1}^{n} P(E_i).P\left(\frac{A}{E_i}\right)$$

For any particular event E_i the conditional probability is given by

$$P\left(\frac{E_i}{A}\right) = \frac{\mathrm{P}(E_i \cap \mathrm{A})}{\mathrm{P}(\mathrm{A})}$$

$$= \frac{P(E_i).P\left(\frac{A}{E_i}\right)}{\sum_{i=1}^{n} p(E_i)P\left(\frac{A}{E_i}\right)}$$

Hence, $P\left(\frac{E_i}{A}\right) = \frac{P(E_i).P\left(\frac{A}{E_i}\right)}{\sum_{i=1}^{n} p(E_i)P\left(\frac{A}{E_i}\right)}$

Random Variable:

A random variable is function from sample space to set of real numbers which relate each sample point to a real number.

e.g., In throwing a die, if s denotes the number obtained, then x is a random variable which can take any one of the values 1, 2, 3, 4m 5 and 6 each with equal probability $\frac{1}{6}$.

Discrete Random Variable

A random variable which can assume only a finite or countably infinite set of real values is called a discrete random variable.

Or

A real valued function defined on a discrete sample space is called a discrete random variable. e.g., In throwing two dice, if X is a random variable denoting the sum of the numbers on both the dice, then X can take any one of the values 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12.

Probability Mass Function

If X is a discrete random variable with distinct values ($x_1, x_2, \ldots, x_n$), then the function $P(X)$ defined as

$$P(X) = \begin{cases} p(x = x_i) = pi & , \quad for\ x = x_i \ \ (i = 1,2, \ldots, n) \\ 0 & , \quad for\ x \neq x_i \end{cases}$$

is called the probability mass function of the random variable X, if it satisfies the following conditions :

(a) $P(x) \geq 0$

(b) $\sum_x P(x) = 1$

Discrete Probability Distribution

The set of ordered pairs $\{x_i, P(x_i)\}$ where, $i = 1, 2, \ldots, n$ is called the probability distribution of the random variable x.

e.g., In throwing a die, if X denotes the number obtained, then the probability distribution of a random variable X is given by

X	1	2	3	4	5	6
P(x)	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$

Probability Density Function

A continuous function $f(x)$ is called a probability density function of a continuous random variable X, if it satisfies the following conditions :

(a) $f\ (x) \geq 0$

(b) $\int_{-\infty}^{\infty} f\ (x)\ dx\ = 1$

(c) $P(E)\ =\ \int_E\ f\ (x)\ dx$ is well defined for any event E.

Distribution Function or Cumulative Distribution Function

If X be a random variable, then the function

$$F(x) = P(X \leq x) \qquad -\infty < x < \infty$$

As called the distribution function of the random variable X. It is also called the cumulative distribution function of the random variable X.

Discrete Distribution Function

If X is a discrete random variable with probability function $P(x)$, then the discrete distribution function is defined as

$$F(x) = P[X \leq x] = \sum_{x \leq x_i} P(x_i)$$

Continuous Distribution Function

If X be the continuous random variable with probability density function $f(x)$, then the distribution function of the random variable X is defined as

$$F(x) = P[X \leq x] = \int_{-\infty}^{\infty} f(x)dx$$

Properties of Distribution Function

1. The distribution function of the random variable X lies between 0 and 1.
   i.e., $0 \leq F(x) \leq 1$
2. If $F(x)$ is a distribution function of the random variable X and if $a < b$, then $P[a \leq x \leq b] = F(b) - F(a)$
3. If $f(x)$ is a distribution function of the random variable X and it is non-decreasing function of X, then if $b \geq a$. Then, $F(b) \geq F(a)$.
4. If $F(x)$ is a distribution function of the random variable X, then $F(-\infty) = 0$ and $F(\infty) = 1$.

Example Let $f(x)$ be the continuous probability density function of a random variable X, the probability that $a \leq x \leq b$ is.

Sol. Total probability for an event $= \int_{-\infty}^{\infty} f\,(x)\,dx$

So, $P[a < x \leq b] = \int_{-\infty}^{\infty} f\,(x)\,dx$

15.4 Mathematical Expectation

The average value of the random phenomenon is known as its expected value or mathematical expectation.

Mathematical Expectation of a Discrete Random Variable

The expected value of a discrete random variable is a weighted average of all possible values of the random variable, where the weights are the probabilities associated with the corresponding values. If x be a random variable assuming the values $x_1, x_2, \ldots\ldots, x_n$ with probabilities $P(x_1), P(x_2), \ldots\ldots, P(x_n)$; then the mathematical expectation of the random variable x is defined as

$$E(x) = x_1\,P(x_1) + x_2\,P(x_2) + \cdots . + x_n\,P(x_n) = \sum_{i=1}^{n} x_i\,P(x_i)$$

Here, (a) $P(x_i) \geq 0\ \forall_i$

(b) $\sum_{i=1}^{n} P(x_i) = 1$

(c) $\sum_{i=1}^{n} P(x_i)$ is finite and absolutely convergent.

Mathematical Expectation of a Continuous Random Variable

The expected value of a continuous random variable x with probability density function $f(x)$ is defined as

$$E(x) = \int_{-\infty}^{\infty} x\,f(x)\,dx$$

Here, (a) $f(x) \geq 0$

(b) $\int_{-\infty}^{\infty} f\,(x)\,dx = 1$

(c) $\int_{-\infty}^{\infty} x\,f(x)\,dx$ is finite and absolutely convergent.

Properties of Expectation

1. $E(C) = C, C$ is a constant.
2. $E(Cx) = CE(x), C$ is a constant.
3. $E(ax + b) = aE(x) + b, a \text{ and } b$ are constants.
4. $E(x + y) = E(x) + E(y)$
5. $E(x - y) = E(x) - E(y)$

Moments

If the function $g(X)$ is equal to X^r and if we take its expectation, then we get the rth moment about the origin of the random variable X. The rth moment about origin is denoted by μ'_r.

i.e., $\mu'_r = E[g(X) = X^r]$

$= \sum_{i=1}^{n} x_i^r \ f(x_i),$ (if X is discrete)

$= \int_{-\infty}^{\infty} x^r f(x)\, dx,$ (if X is continuous)

Putting $r = 1$, we get

$\mu'_1 = E(X) = \sum_{i=1}^{n} x_i f(x_i)$ (if X is discrete)

$= \int_{-\infty}^{\infty} x f(x)\, dx$ (if X is continuous)

It is to be noted that $\mu = \mu'_1 = E(X)$ is the first moment about origin called the mean of the distribution of X. The mean or expected value of a random variable X is of special importance in statistics as it describes, where the probability distribution is centered.

If $g(X) = (X - \mu)^r$, then its expection gives the rth moment about mean of the random variable X, denoted by μ_r i.e.

$$\mu_r = (X - \mu)^r$$

$= \sum_{i=1}^{n} (x_i - \mu)^r f(x_i)$ (if X is discrete)

$= \int_{-\infty}^{\infty} (x - \mu)^r f(x)\, dx$ (if X is continuous)

Note that $\mu_0 = 1$ and $\mu_1 = 0$ for any random variable.

Variance

The second central moment denoted by $\mu_2$is called the variance of the random variable x and is defined

$$V(x) = \sigma^2 = \mu_2 = E[X - E(X)]^2$$

The positive square root of variance is called the standard deviation.

Properties

1. $V(x) = EX^2 - [E(X)]^2$
2. If x is a random variable, then $V(a) = 0, a =$ constant.
3. $V(aX) = a^2 V(x)$
4. $V(aX + b) = a^2 V(X), a \; and \; b$ are constants.

Covariance

The measures of the simultaneous variation between the random variable $X \; and \; Y$ is called the covariance and written as $Coy\ (X, Y).$

If $X \; and \; Y$ are two random variables with respective expected values $E(X) \; and \; E(Y)$, then

$$Cov\ (X, Y) = E(XY) - E(X)\ E(Y)$$

The Covariance of two independent variables is equal zero.

15.5 Binomial Probability Distribution

A random variable x is said to have a binomial distribution, if it assumes only non-negative valu and its probability mass function is given by

$$P(x) = \begin{cases} nC_x p^x q^{n-x} & , \; x = 0,1,2, \ldots, n \\ 0 & . \; otherwise \end{cases}$$

Here, $n \; and \; p$ are the parameters of this distribution. The notation $x \sim B(n, p)$ is used to denote that x follows binomial distribution with parameters $n \; and \; p$.

Note The frequency function of binomial distribution is given by

$$f(x) = N.P(x) = {}^{N}C_x P^x q^{n-x} \qquad (x = 0,1,2,\ldots,n)$$

Physical Conditions for Binomial Distribution

There are following physical conditions :

1. The number of trials are finite.
2. The trials are independent of each other.
3. Each trial results in two exhaustive and mutually disjoint outcomes known as success and failure.
4. The probability of success (p) is constant for each trial.

Mean of Binomial Distribution

If $x \sim B\ (n, p)$ then

$$P(x) = {}^{n}C_x P^x q^{n-x} \qquad (x = 1, 2, \ldots, n)$$

Mean $= E(x)$

$$= \sum_x x\ P\ (x)$$

$$\sum_{x=0}^{n} x\ {}^{n}C_x P^x q^{n-x}$$

$$\sum_{x=0}^{n} x \cdot \frac{n!}{x!\,(n-x)!} p^x q^{n-x}$$

$$= np \sum_{x=1}^{n} {}^{n-1}C_{x-1} P^{x-1} q^{n-x}$$

$$= np \sum_{x=1}^{n} P(x-1) \qquad [\because P(x-1) - 1]$$

$$= np$$

Variance of Binomial Distribution

Variance, $V(x) = E(x^2) + [E(x)]^2$

$$= n\ (n-1)p^2 + np - (np)^2$$

$$= np\ (1-p) [\because q = 1 - p]$$

$$-np2$$

Example The mean and variance of a binomial distribution are 4 and $\frac{4}{3}$ respectively. Then, the value of $p(x \geq 1)$

Sol. ∵ Mean = 4

$$np = 4$$

And variance $= \frac{4}{3}$

$$npq = \frac{4}{3}$$

Dividing above Eqs.

$$\frac{npq}{np} = \frac{4/3}{4}$$

$$q = \frac{1}{3}$$

So, $p = 1 - q = 1 - \frac{1}{3} = \frac{2}{3}$

$$p = \frac{2}{3}$$

On putting the value of p,

$$n \times \frac{2}{3} = 4$$

$$n = 6$$

Now, for $P(x \geq 1) = 1 - P(x < 1)$

$$= 1 - P(x = 0)$$

$$= 1 - {}^{6}C_0 \left(\frac{2}{3}\right)^0 \left(\frac{1}{3}\right)^6$$

$$= 1 - \left(\frac{1}{3}\right)^6 = \frac{728}{729} = 0.9986$$

Example It is known that screws produced by a certain company will be defective with probability 0.01 independent of each other. The company sells the screws in

packages of 10 and offers a replacement guarantee that at most 1 of the 10 screws is defective. What proportion of packages sold must the company replace?

Sol. If X is the number of defective screws in a package then, X is a binomial variable with parameters (10, 0.01). Hence, the probability that a package will have to be replaced is

$$P(x \geq 2) = 1 - P(x \leq 1)$$
$$= 1 - [P(x = 0) + P(x = 1)]$$
$$= 1 - [{}^{10}C_0(0.01)^0(0.99)^{10} + {}^{10}C_1(0.01)^1(0.99)^9]$$
$$= 1 - 0.996 = 0.004$$

Hence, only 0.4% of packages will have to be replaced.

Example A box contains 10 screws, 3 of which are defective. Two screws are drawn at random with replacement. Find the probability that none of the two screws is defective.

Sol. Sol. The problem is to be solved by binomial distribution.

∵ Although population is finite.

Sampling is done with replacement and so probability does not change from trial to trial.

∵ $$n = 2, x = 0 \; and \; p = \frac{3}{10}$$

$$q = 1 - \frac{3}{10} = \frac{7}{10}$$

So, $$P(x = 0) = {}^2C_0 \left(\frac{3}{10}\right)^0 \left(\frac{7}{10}\right)^2$$
$$= 0.49 - 49\%$$

Example A fair coin is tossed independently four times. Find the probability of the event 'the number of times heads, show up is more than the number of times tails show up.

Sol. The coin is tossed 4 times.

So, P(Number of heads > Number of tails)

= P(Exactly 4 heads) + P(Exactly 3 heads)

$$^4C_4\left(\frac{1}{2}\right)^4\left(\frac{1}{2}\right)^0 + {}^4C_3\left(\frac{1}{2}\right)^3\left(\frac{1}{2}\right)^1$$
$$= \frac{1}{16} + \frac{4}{16} = \frac{5}{16}$$

15.6 Poisson Distribution

In the year 1837, a French mathematician 'S.D. Poisson' (1781-1840) discovered this distribution. This is a limiting case of the binomial distribution under the following conditions :

1. The number of trials are indefinitely large i.e., $n \to \infty$
2. The constant probability of success for each trial is indefinitely small i.e., $p \to 0$
3. np = λ, a finite quantity, thus $p = \frac{\lambda}{n}, q = 1 - \frac{\lambda}{n},$ where, X is positive real number.

Definition A random variable x is said to have a Poisson distribution if it assumes only

non-negative values and its probability mass function is given by

$$P(x) = \begin{cases} \frac{e^{-\lambda}\lambda^x}{x!} & , x = 0,1,2, \dots \infty \\ 0 & , otherwise \end{cases}$$

Here, λ is known as the parameter of the distribution. The notation $x \sim P(\lambda)$ is used to denote that x is a Poisson variate with parameter λ.

Uses

1. Number of deaths from a disease such as heart-attack or cancer, can be calculated.
2. This distribution can be used in finding the number of suicides reported in a particular city.
3. This distribution can be used in finding the number of defective blades in a packet of finite number of blades.
4. It can be used in finding the number of air accidents in some unit of time.

5. It can be used in finding the number of printing errors on each page of the book.
6. It can be used in finding the number of cars passing through a street in sometime.

Mean and Variance

Mean $= E(x) = \lambda,$

and variance = $V(x) = \lambda$

∵ Expected value and variance of a Poisson random variable are both equal to its parameter λ.

Example For Poisson distribution, find probability that the ace of spades will be drawn pack of well shuffled cards atleast once in consecutive trials $(e^{-2} = 0.136)$.

Sol.∵ $p = \frac{1}{52}$ and $n = 104$

So, $\lambda = np = \frac{104}{52} = 2$

So, probability (atleast once) $= P(r \geq 1) = 1 - P(0)$

$$= 1 - \frac{e^{-\lambda}.\ \lambda^0}{0!}$$

$$= 1 - e^{-2}$$

$$= 1 - 0.136$$

$$= 0.864$$

Example Let a book of 600 pages contains 40 printing mistakes. Let these errors are randomly distributed throughout the book and r, the number of errors per page has a Poisson distribution. Then, find the probability that 10 pages selected at random will be free from error.

Sol. ∵ $P = \frac{40}{600} = \frac{1}{15}$

And $n = 0$

So, $\lambda = np = \frac{1}{15} \times 10 = \frac{2}{3}$

So, $P(r) = \frac{e^{-\lambda} \cdot \lambda^r}{r!} = \frac{e^{-23} \times \left(\frac{2}{3}\right)^r}{r!}$

So, $P(0) = \frac{e^{-23} \times \left(\frac{2}{3}\right)^0}{o!} = e^{-23} = 0.51$

15.7 Continuous Distribution

Let X be a continuous random variable. A continuous distribution of X can be defined by a probability density function $f(x)$ such that

$$p(-\infty \leq x \leq \infty) = \int_{-\infty}^{\infty} f(x)dx = 1$$

The expected value of x is given by

$$\mu_x = E(x) = \int_{-\infty}^{\infty} x\, f(x)\, dx$$

This is also called mean and variance

$$V(x) = \int_{-\infty}^{\infty} (x - x)^{-2}\, f(x)\, dx$$

Hence, $f(x)$ is called probability density function, if

1. $fx) \geq 0$ for every value of x
2. $\int_{-\infty}^{\infty} f(x)\ dx = 1$
3. $\int_a^b f(x)\ dx = P \qquad (a < x < b)$

Example The probability density function $f(x)$ of a contonuous random variable x is defined by

$$f(x) = \begin{cases} \frac{A}{x^3}, & 5 \leq x \leq 10 \\ 0 & ,otherwise \end{cases}$$

then find the value of A.

Sol. Here, $f(x) = \frac{A}{x^3} \qquad (5 \leq x \leq 10)$

$\because f(x)$ is probability density function, so

$$\int_5^{10} \frac{A}{x^3}\, dx = 1$$

$$\left[\frac{-A}{2x^2}\right]_5^{10} = 1$$

$$\frac{3A}{200} = 1$$

$$A = \frac{200}{3}$$

Example Let $f(x)$ be the continuous probability function of a random variable X. Find the of $a \leq X \leq b$.

Sol. $\int_a^b f(x)dx$

$\because f(x)$ is a continuous probability density function of a variable X, then

$$P(a \leq X \leq b) = \int_a^b f(x)\, dx$$

Generally we say that X is a uniform random variable on (a, b) then

$$F(x) = \begin{cases} \frac{1}{\beta - \alpha}, & a < x < \beta \\ 0, & otherwise \end{cases}$$

$\because f(x)$is a constant, so, all values of x between α and β are likely or uniformly distributed.

Example If probability density function of a variable X is

$$(x) = \begin{cases} x^2, & for -1 \leq x \leq 1 \\ 0, & for\ any\ other\ value\ of\ X \end{cases}$$

Then, find the percentage probability $P\left(-\frac{1}{3} \leq x \leq \frac{1}{3}\right)$

Sol. $f(x) = \begin{cases} x^2, -1 \leq x \leq 1 \\ 0, \ otherwise \end{cases}$

So, $P\left(-\frac{1}{3} \leq x \leq \frac{1}{3}\right) = \int_{-1/3}^{1/3} f(x)\, dx$

$$= \left[\frac{x^2}{3}\right]_{-1/3}^{1/3} = \frac{2}{81}$$

So, the probability in percentage, $P = \frac{2}{81} \times 100 = 2.47\%$

Example A probability density function is of the form $p(x) = ke^{-\alpha|X|}, x \in (-\infty, \infty)$ then, find the value of k.

Sol. $\because \int_{-\infty}^{\infty} P(x)dx = 1$

$$= \int_{-\infty}^{\infty} k\, e^{-\alpha|x|}\, dx = 1$$

$$= \int_{-\infty}^{0} e^{\alpha x}\, dx + \int_{0}^{\infty} e^{-\alpha x}\, dx = 1$$

$$\frac{2k}{\alpha} = 1$$

$$k = 0.5\,\alpha$$

15.8 Normal Distribution

Normal distribution was discovered by a English mathematician A. de. Moivre in the eighteenth century. This is the most important continuous distribution. The discovery was the result of observations by various scientists like Pierre Laplace, Karl Gauss etc. They studied the mathematical properties of these special curves.

Definition A random variable x is said to have a normal distribution with parameters μ (mean) and σ^2 (variance), if its probability density function is given by

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} \qquad (-\infty < x < \infty)$$

The notation $x \sim N(\mu, \sigma^2)$ is used to denote that x follows normal distribution with mean μ and variance σ^2.

Note If $x \sim N(\mu, \sigma^2)$

Then, $z = \frac{x-\mu}{\sigma} \sim N(0,1)$

Mean $= E(z) = E\left(\frac{x-\mu}{\sigma}\right) = \frac{E(x)-\mu}{\sigma} = 0$

Mean $= 0$

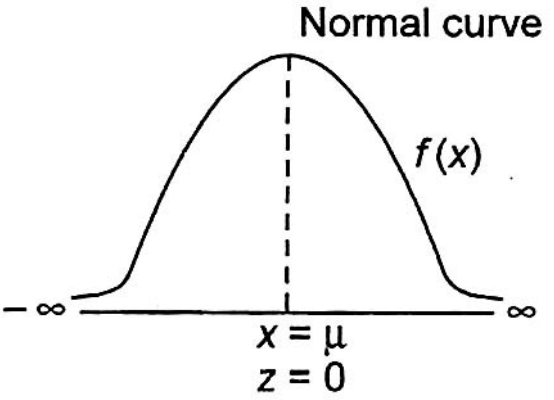
$$V(z) = V\left(\frac{x-\mu}{\sigma}\right) = \frac{V(x)-0}{\sigma^2} = \frac{\sigma^2-1}{\sigma^2} = 1$$

The probability density function of the standard normal variate is given by

$$f(z) = \frac{1}{\sqrt{2\pi}} e^{-\frac{z^2}{2}} \qquad (-\infty < z < \infty)$$

Properties of Normal Distribution

1. The mean, median and mode of a normal distribution are identical,
   i.e., mean = mode = median Normal curve



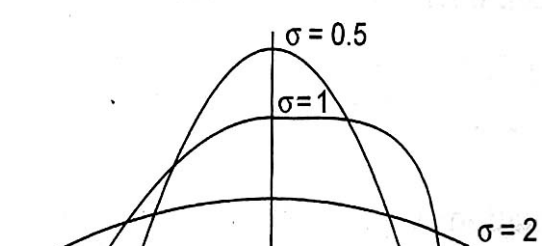
2. The total area under the curve and above the horizontal axis is equal to unity from $-\infty\ to + \infty.$
3. The curve is smooth regular and bell shaped and symmetric about the line $x\ = \mu$, because the expansion of

$$y = f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

   does not contain the odd powers of $\left(x - \frac{\mu}{\sigma}\right)$
4. The curve extends from $-\infty\ to + \infty.$
5. Area of normal curve bounded by X −axis and two ordinates equal to the probability for the interval marked on X −axis by the two ordinates.
6. The ordinate of the curve decreases rapidly as $|x|$ increases. The maximum ordinate at $x\ = \mu$ is given by

$$y\_max=1/(\sigma\sqrt{2\pi})$$

7. As σ becomes larger, the ordinate of y decreases.



i.e., the curve spreads out more but flattened at the top. On the other hand, when σ becomes smaller y increases.

8. Area of normal curve between $(\mu - \sigma)$ and $(\mu + \sigma)$ is 68.27%.
9. Area between $(\mu - 26)$ and $(\mu + 26)$is 95.45%.
10. For normal distribution mean deviation is $\frac{4}{5}\sigma' / \ quartile\ deviation\ is \frac{2}{3}\sigma.$

So, $QD : MD : SD = 10 : 12 : 15$

Standard Normal Variate

Let us assume that $X - N(\mu, \sigma^2)$ Now, let us introduce another variable Z such that

$$Z = \frac{x - \mu}{\sigma}$$

It can be seen that $Z \sim N(0, 1)$ and it is called standard normal variate with mean zero and variance unity. This variable Z is deliberately used most of the times as it simplifies calculations of probabilities concerning normally distributed variates.

The distribution of the random variable $Z = \frac{x-\mu}{\sigma}$ is called the standard normal distribution.

The probability density function of the standard normal variate Z is given by

$$\phi(z) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}z^2} \qquad (-\infty\ to + \infty)$$

and the corresponding distribution is given by

$$\phi(z) = \int_{-\infty}^{Z} \phi(u)du = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-\frac{1}{2}z^2} \qquad (-\infty \; to + \infty)$$

Mean Deviation about Mean for Normal Distribution

The mean deviation distribution about mean for normal distribution is

$$E(|X-\mu|) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} |x-\mu| e^{-(x-\mu)^2/2\sigma^2}$$

$$= \frac{\sigma}{\sqrt{2\pi}} \int_{-\infty}^{\infty} |z| e^{-\frac{1}{2}z^2} \qquad (Where\ z \frac{x-\mu}{\sigma})$$

$$= \frac{\sigma}{\sqrt{2\pi}} \left[\int_{-\infty}^{\infty} (z)^2 e^{-\frac{1}{2}z^2}\, dz + \int_{0}^{\infty} (z)\, e^{-\frac{1}{2}z^2}\, dz \right]$$

$$= \frac{\sigma}{\sqrt{2\pi}} \int_{0}^{\infty} z\, e^{-\frac{1}{2}z^2} dz$$

Let $t = \frac{1}{2}z^2, then$

$$E(|X-\mu|) = \frac{2\sigma}{\sqrt{2\pi}} \int_{0}^{\infty} e^{-t}\, dt$$

$$= \frac{2\sigma}{\sqrt{2\pi}} \int_{0}^{\infty} [e^{-t}]_0^{\infty} = \frac{2\sigma}{\sqrt{2\pi}} = \sigma\sqrt{\frac{2}{\pi}}$$

$$= 0.7979\, \sigma = \frac{4}{5}\, \sigma\ (approx)$$

The mean deviation about mean for normal distribution is $\frac{4}{3}\sigma$.

Mean and variance of Normal Distribution

The probability density function of a normal random variable X is given by

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

The expected value of the random variable X is given by

$$E(X) = \int_{-\infty}^{\infty} x\, f(x)dx$$

$$= \int_{-\infty}^{\infty} x\, \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}\, dx$$

Let $z = \frac{x-\mu}{\sigma}$, then

$$E(X) = \int_{-\infty}^{\infty} (\mu + 2\sigma) \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}z^2}\, dz$$

$$= \mu \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}z^2}\, dz + \sigma \int_{-\infty}^{\infty} z\, e^{-\frac{1}{2}z^2}\, dz$$

$$= \mu \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}z^2}\, dz + 0$$

(∵ The integrand in the second term is odd))

$$= 2\mu \int_{0}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}z^2}\, dz$$

$$= \mu \frac{\sqrt{2}}{\sqrt{\pi}} \int_{0}^{\infty} e^{-t}\, \frac{dt}{\sqrt{2t}} \qquad (where\ t = \frac{z^2}{2}, dt = z\, dz)$$

$$= \mu \frac{1}{\sqrt{\pi}} \int_{0}^{\infty} e^{-t}.\ t^{-(1/2)}\, dt$$

$$= \mu \frac{1}{\sqrt{\pi}} \int_{0}^{\infty} e^{-t}.\ t^{\frac{1}{2}-1}\, dt$$

$$= \mu \frac{\Gamma(1/2)}{\sqrt{\pi}} = \pi\, \frac{\sqrt{\pi}}{\sqrt{\pi}}$$

The variance of the random variable X is given by

$$V(X) = E(X-\mu)^2$$

$$= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (x-\mu)^2 e^{-(x-\mu)^2/2\sigma^2}\, dx$$

$$= \frac{\sigma^2}{\sqrt{2\pi}} \int_{-\infty}^{\infty} z^2 e^{-\frac{1}{2}z^2}\, dz \left(\because z = \frac{x-\mu}{\sigma}\right)$$

$$= \frac{2\sigma^2}{\sqrt{2\pi}} \int_{0}^{\infty} z^2 e^{-\frac{1}{2}z^2}\, dz$$

Let $t = \frac{z^2}{2} = dt = dz$

Thus

$$V(X) = \frac{2\sigma^2}{\sqrt{2\pi}} \int_0^{\infty} 2t\, .e^{-t}\, \frac{dt}{\sqrt{2t}}$$

$$= \frac{2\sigma^2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-t}\ t^{1/2}\, dt$$

$$= \frac{2\sigma^2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-t}\ t^{\frac{3}{2}-1}\, dt$$

$$= \frac{2\sigma^2}{\sqrt{\pi}}\, \Gamma\left(\frac{3}{2}\right) = \frac{2\sigma^2}{\sqrt{\pi}} \frac{1}{2} \sqrt{\pi}$$

$$= \sigma^2$$

The mean and the variance of normal distribution are given respectively by μ and σ^2, which are also the parameters of the normal distribution.

15.9 Continuous Random Variables

1. Uniform

A random variable X is said to be uniformly distributed in the interval $a \leq x \leq b$ if,

$$f_x(x) = \begin{cases} \frac{1}{a-b}, & a < x < b \\ 0, & elsewhere \end{cases}$$

A plot of $f_x(x)$ is shown in figure

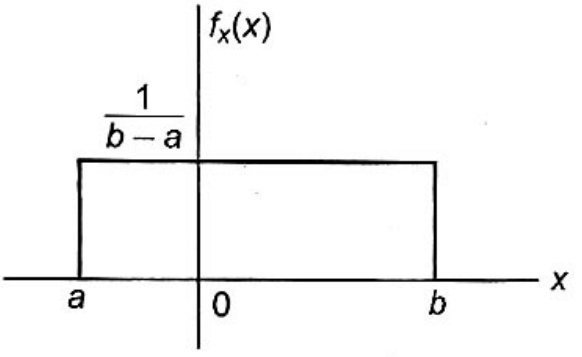


Fig. Uniform PDF

It is easy to show that

$$E[X] = \frac{a+b}{2}$$

$$and \qquad \sigma_x^2 = \frac{(b-a)^2}{12}$$

that the variance of the uniform PDF depends only on the width of the interval $(b - a)$. Therefore, X is uniform in $(-1, 1)$ or $(2, 4)$, it has the same variance, namely $\frac{1}{3}$.

2. Rayleigh

An $RV\ X$ is said to be Rayleigh distributed if,

$$f_{(x)}(x) = \begin{cases} \frac{x}{b}\exp\left(-\frac{x^2}{2b}\right), & x \geq 0 \\ 0 & , elsewhere \end{cases}$$

Where, b is a positive constant.

A typical sketch of the Rayleigh PDF is given in figure

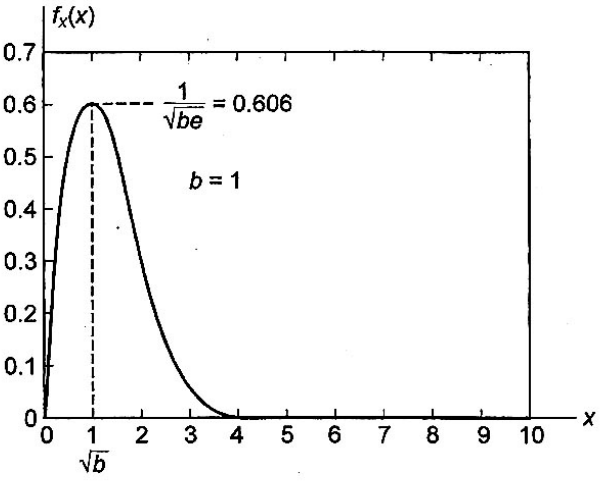


Fig. Rayleigh PDF

Rayleigh PDF frequently arises in radar and communication problems. We will encounter it later in the study of narrow-band noise processes.

3. Gaussian

By far the most widely used PDF, in the context of communication theory is the Gaussian (also called normal) density, specified by

$$f_x(x) = \frac{1}{\sqrt{2\pi}\,\sigma_x}\exp\left[-\frac{(x-m_x)^2}{2\sigma_x^2}\right], \quad -\infty < x < \infty$$

where, $m_x$is the mean value and σ_x^2 the variance. That is, the Gaussian PDF is completely specified by the two parameters, m_x and σ_x^2. We use the symbol $N(m_x, \sigma_x^2)$ to denote the Gaussian density. $f_x(x)$ as given by Eq. is a valid PDF.

As can be seen from the figure. The Gaussian PDF is symmetrical with respect to m_x.

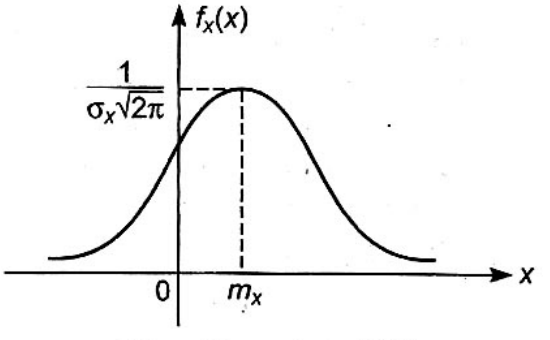


Fig. Gaussian PDF

Hence, $F_x(m_x) = \int_{-\infty}^{m_x} f_x(x)dx = 0.5$

Consider $P[X \geq a]$ We have,

$$P[X \geq a] = \int_0^{\infty} \frac{1}{\sqrt{2\pi}\sigma_x} \exp\left[-\frac{(x-m_x)^2}{2\sigma_x^2}\right] dx$$

1 1 (x — mx)2 P[X a] = expI a 2TC x [2a2x

This integral cannot be evaluated inclosed form. By (making a change of variable $z = \left(\frac{x-m_x}{\sigma_x}\right)$ we have

$$P[X \geq a] = \int_{\frac{a-m_x}{\sigma_x}}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-\frac{z^2}{2}}\, dz$$

$$= Q\left(\frac{a-m_x}{\sigma_x}\right)$$

where, $Q(y) = \int_y^{\infty} \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{x^2}{2}\right) dx$

Note that the integrand on the RHS of Eq. (4.13) is $N\ (0,1)$.

Note In this notation, $N(0,1)$ denotes the Gausian PDF with zero mean and unit variance. Note that if X and $N(m_x, \sigma_x^2)$, then $Y = \left(\frac{X-m_x}{\sigma_x}\right)$ is $N(0,1)$.

The importance of Gaussian density in communication theory is due to a theorem called central limit theorem.

Central Limit Theorem

If the $RV\ X$ is the weighted sum of N independent random components, where, each components makes only a small contribution to the sum, then $F_x(x)$ approaches Gaussian as N becomes large, regardless of the distribution of the individual components.

For a more precise statement and a through dicussion of this theorem. The electrical noise in a communication system is often due to the cumulative effects of a large number of randomly moving charged particles, each particle making an independent

contribution of the same amount, to the total. Hence, the instantaneous value of the noise can be fairly adequately modeled as a Gaussian variable.

Example A random variable Y is said to have a log-normal PDF if $X = ln\, Y$ has a Gaussian (normal) PDF.

Let Y have the PDF, $f_y(y)$ given by,

$$f_y(y) = \begin{cases} \frac{1}{\sqrt{2\pi}\,\gamma\,\beta} \exp\left[\frac{(In\,\gamma - \alpha)^2}{2\beta^2}\right], & \gamma \geq 0 \\ 0 & ,otherwise \end{cases}$$

where, α and β are given constants.

(a) Show that Y is log-normal

(b) Find $E(Y)$

(c) If m is such that $F_y(m) = 0.5$, find m.

Sol. (a) Let $X = In\, Y$ or $x = In\, y$ (Note that the transformation is one-to-one).

$$\frac{dx}{dy} = \frac{1}{y} \rightarrow |J| = \frac{1}{y}$$

also as $y \rightarrow 0, x \rightarrow -\infty$ and as $y \rightarrow \infty, x \rightarrow \infty$

Hence, $f_x(x) = \frac{1}{\sqrt{2\pi}\,\beta} \exp\left[\frac{(x-\alpha)^2}{2\beta^2}\right], -\infty < x < \infty$

Note that X is $N(\alpha, \beta^2)$

(b) $\overline{Y} = E[e^x] = \frac{1}{\sqrt{2\pi}\,\beta} \int_{-\infty}^{\infty} e^x \left[e^{\frac{(x-\alpha)^2}{2\beta^2}}\right] dx$

$$= e^{\alpha+\frac{\beta^2}{2}} \left[\int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\,\beta} e^{-\frac{[x-(\alpha+\beta^2)]^2}{2\beta^2}} dx\right]$$

As the brackted quantity being the integral of a Gaussian PDF between the limits $(-\infty, \infty)$ is 1, we have

$$\overline{Y} = e^{\alpha+\frac{\beta^2}{2}}$$

(c) $P[Y \leq m] = P[X \leq In\, m]$

Hence, if $P[Y \leq m] = 0.5$, then $P[X \leq In\, m] = 0.5$

That is, $ln\, m = \alpha$ or $m = e^{\alpha}$.

4. Bivariate Gaussian

As an example of a two dimensional density, we will consider the bivariate Gaussian PDF, $f_{x,y}(x,y), -\infty < x,y < \infty$ given by,

$$f_{x,y}(x,y) = \frac{1}{k_1}\exp\left[-\frac{1}{k_2}\left\{\frac{(x-m_x)^2}{\sigma_x^2} + \frac{(y-m_y)^2}{\sigma_y^2} - 2\rho\,\frac{(x-m_x)(y-m_y)}{\sigma_x\sigma_y}\right\}\right]$$

Where $k_1 = 2\pi\sigma_x\sigma_y\sqrt{1-\rho^2}$

$k_2 = 2(1-\rho^2)$

$\rho = correlation\ coefficient\ between\ X\ and\ Y.$

The following properties of the bivariate Gaussian density can be verified :

1. If $X\ and\ Y$ are jointly Gaussian, then the marginal density of $X\ or\ Y$ is Gaussian; that X is $N(m_x, \sigma_x^2)\ and\ Y\ is\ N(m_y, \sigma_y^2)$.
2. $f_{xy}(x,y) = f_x(x)f_y(y) iff\ \rho = 0$
   That is, if the Gaussian variables are uncorrelated then they are independent. That is not true, general, with respect to non-Gaussian variables.
3. If $Z = \alpha X + \beta Y$ where, α and β are constants and $X\ and\ Y$ are jointly Gaussian, then Z is Gaussian. Therefore, $f_Z(z)$ can be written after computing m_Z, and σ_Z^2Figure gives the plot of a bivariate Gaussian PDF for the case of $\rho = 0$ and$\sigma_x = \sigma_y$.

Note that the converse is not necessarily true. Let f_x and f_y be obtained from $f_{x,y}$and let $f_x$and $f_y$be Gaussian. This does not imply $f_{x,y}$ is jointly Gaussian, unless $X\ and\ Y$ are independent. We can construct examples of a joint PDF $f_{x,y}$which is not Gaussian but results in $f_x$and $f_y$that are Gaussian.

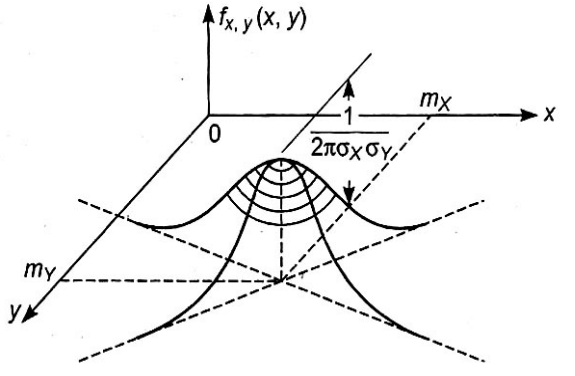


Fig. Bivariate Gaussian PDF ($\sigma_x = \sigma_y$ and $\rho = 0$)

For $\rho = 0$ and $\sigma_x = \sigma_y, f_{x,y}$ resembles a (temple) bell, with, of course, the striker missing! For $\rho \neq 0$, we have Uiwo cases, (i) ρ, positive and (ii) ρ, negative. If $\rho > 0$, imagine the bell being compressed along the $X = -Y$ axis so that it elongates along the $X = Y$ axis. Similarly, $\rho < 0$.

Example Let $X \; and \; Y$ be jointly Gaussian with $\overline{X} = -\overline{Y} = 1, \sigma_x^2 = \sigma_y^2 = 1$ and $\rho_{xy} = -\frac{1}{2}$. Let us find the probability of (X, Y) lying in the shaded region D shown figure.

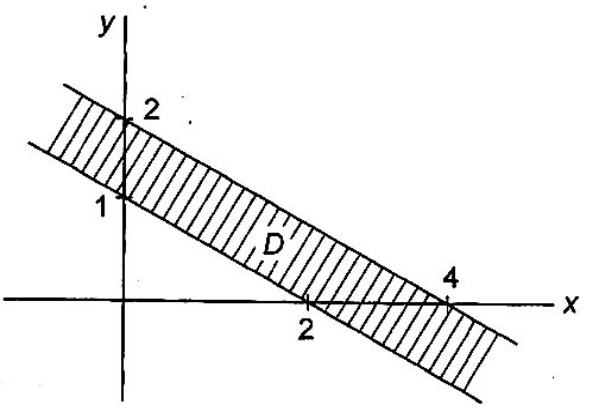


Fig. The region D of example 100

Let A the shaded region shown in Fig. (a) and B be the shaded region in Fig. (b).

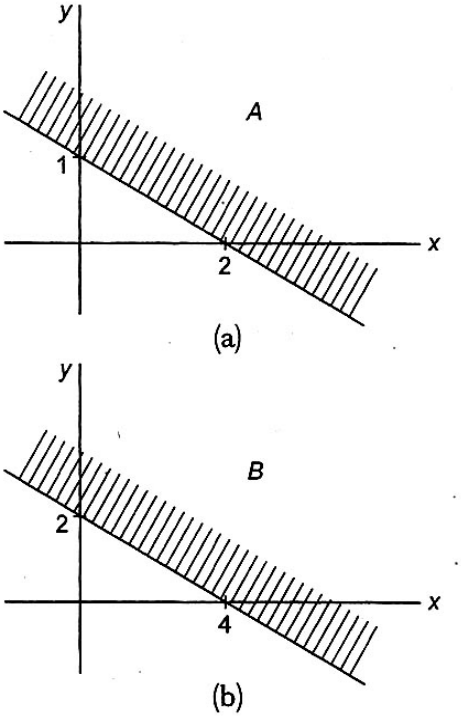


Fig. (a) Region A and (b) Region B used to obtain

The required probability$P[(x,y) \in A] - P[(x,y) \in B]$

For the region A, we have $y \geq -\frac{1}{2}x + 2$ and for the region B, we have $y \geq -\frac{1}{2}x + 2$. Hence, the required probability is,

$$P\left[Y + \frac{X}{2} \geq 1\right] - P\left[Y + \frac{X}{2} \geq 2\right]$$

Z is Gaussian with the parameters,

$$\bar{Z} = \bar{Y} + \frac{1}{2}, \bar{X} - \frac{1}{2}$$

$$\sigma_z^2 = \frac{1}{4}\sigma_x^2 + \sigma_y^2 + 2\frac{1}{2}\rho_{xy} = \frac{1}{4} + 1 - 2.\frac{1}{2}.\frac{1}{2} = \frac{3}{4}$$

That is, Z is $B\left(-\frac{1}{2}, \frac{3}{4}\right)$ $Then, W = \frac{Z+\frac{1}{2}}{\sqrt{\frac{3}{4}}}$ $is\ N(0,1)$

$$P[Z \geq 1] = P[W \geq \sqrt{3}]$$

$$P[Z \geq 2] = P\left[W \geq \frac{5}{\sqrt{3}}\right]$$

Hence, the required probability

$$= Q(\sqrt{3}) - Q\left(\frac{5}{\sqrt{3}}\right)$$

$$= (0.04 - 0.001) = 0.039$$

15.10 Self Assessment Test

1. State Bayes' theorem and prove it.
2. Write down Physical condition for Binomial Distribution

15.11 Reference books

1. Schaum's Outline of Vector Analysis, 2ed by Murray Spiegel, Seymour Lipschutz.
2. Mathematical Physics with Classical Mechanics by Satya Prakash.
3. Mathematical Physics by H.K. Das.

Unit-16 : Curve Fitting & R.M.S. Value

Structure of Unit

16.1 Objectives

The Objective of this unit is to theoretically describe experimental data with a model (may be function or equation) & to find the parameter associated with this model & to find R.M.S. Value and its use in Chemical Science.

16.2 Introduction

In this unit we shall consider the process of approximating a function when the function is known only in tabular form using least square approximation. Mechanistic models are specifically formulated to provide in sight into chemical, biological or

physical process. By curve fitting we means an expression of the relationship between two variables by an equation. If there are n pair of observed values, then it is possible to fit the given data to an equation that contains an arbitrary constants for we can solve n simultaneous equation for n unknown.

16.3 Principle of Least Square

Principle of least square is the most systematic procedures to fit a unique curve through given data. It states "Curve of best fit for a given data is that for which sum of square of deviation is minimum".

Suppose we have to fit the curve $y = f(x)$ for given set of data (x_i, y_i) (I = 1, 2 …..n) At $x = x_i$ the experimental value of the ordinate is y_i& the corresponding value on fitting curve is $f(x)$.

If e_i be the error of Approximation at $x = x_i$ then we have

$$e_i = y_i - f(x_i)$$

e_i may be (–ve) or (+ve) so by giving equal weightage to each residuals consider

$$S = \sum_{i=1}^{n} e^2{}_i = \sum_{i=1}^{n} (y_i - f(x_i))^2$$

Now according to principal of least square curve of best fit is that for which S is minimum.

16.4 Fitting a straight line

Let $\{(x_i, y_i)/i = 1,2, \ldots\ldots, m\}$ be a set of observations. We have to fit a straight line $Y = a + bx$ (2)

and corresponding observed value is y_i. Let e_i be the error at $x = x_i$, then

$$e_i = y_i - Y_i, \qquad \text{i = 1, 2, ……., m}$$

Or $$e_i = y_i - (a + bx_i), \qquad \text{i = 1, 2, ……., m}$$

The sum of squares S (say) of this error is given by

$$S = \sum_{i=1}^{n} [y_1 - (a + bx_i)^2] \qquad (3)$$

Least squares principle requires that S be minimum. Form(3), it is clear that S depends on a and b, that is, S is a function of a and b. Thus, we have to find the value of a and b so that S become minimum. By the theory of maxima-minima,the necessary conditions for S to be minimum are

$$\frac{\partial S}{\partial a} = 0 = \frac{\partial S}{\partial b},$$

Form (3), we have

$$-\sum_{i=1}^{n} 2[y_i - (a + bx_i)] = 0$$

and $$-\sum_{i=1}^{n} 2x_i[y_i - (a + bx_i)] = 0$$

On simplification of these two equations, we have

$$\sum_{i=1}^{n} y_i = na + b\sum_{i=1}^{n} x_i \qquad (\therefore \sum_{i=1}^{m} a = ma)$$

Or $$\sum y_i = na + b\sum x_i \qquad (4)$$

and $$\sum_{i=1}^{n} x_i y_i = a\sum_{i=1}^{n} x_i + b\sum_{i=1}^{n} {x_i}^2$$

$$\sum x_i\, y_i = a\sum x_i + b\sum {x_i}^2 \qquad (5)$$

Equation (4) & (5) are said to be normal equations. We can determine values of a & b by solving these equations.

16.5 Fitting of a Parabola

Let $y = a + bx + cx^2$ be a parabola to be fitted for the data (x_i, y_i)

(i =1,2,3….n) the error at $x = x_i$ is

$$e_i = y_i - f(x_i) = \ e_i = y_i - (a + bx_i + c{x_i}^2)$$

Let $S = \ \sum_{i=1}^{n} {e_i}^2 = \sum_{i=1}^{n} (y_i - (a + bx_i + c{x_i}^2)$

Now by principal of least square for best fit S is minimum i.e.

$$\frac{\partial S}{\partial a} = 0, \frac{\partial S}{\partial b} = 0 \ \& \frac{\partial S}{\partial c} = 0$$

$$\sum_{i=1}^{n} 2(y_i - (a + bx_i + c{x_i}^2)) = 0$$

$$\sum_{i=1}^{n} 2(y_i - (a + bx_i + c{x_i}^2))x_i = 0$$

$$\sum_{i=1}^{n} 2(y_i - (a + bx_i + cx_i^2))x_i^2 = 0$$

On solving

$$\sum_{i=1}^{n} y_i = an + b\sum_{i=1}^{n} x_i + c\sum_{i=1}^{n} x_i^2$$

$$\sum_{i=1}^{n} x_i y_i = a\sum_{i=1}^{n} x_i + b\sum_{i=1}^{n} x_i^2 + c\sum_{i=1}^{n} x_i^3$$

$$\sum_{i=1}^{n} x_i^2 y_i = a\sum_{i=1}^{n} x_i^2 + b\sum_{i=1}^{n} x_i^3 + c\sum_{i=1}^{n} x_i^4$$

Note : (1) For fitting parabola $y = a + bx^2$

Normal equations are

$$\sum_{i=1}^{n} y_i = an + b\sum_{i=1}^{n} x_i^2$$

& $$\sum_{i=1}^{n} x_i^2 y_i = a\sum_{i=1}^{n} x_i^2 + b\sum_{i=1}^{n} x_i^4$$

(2) For fitting parabola $y = ax + bx^2$

Normal equations are

$$\sum_{i=1}^{n} x_i y_i = a\sum_{i=1}^{n} x_i^2 + b\sum_{i=1}^{n} x_i^3$$

& $$\sum_{i=1}^{n} x_i^2 y_i = a\sum_{i=1}^{n} x_i^3 + b\sum_{i=1}^{n} x_i^4$$

Self Assessment Questions

Q.1 Derive normal equations for fitting parabola $y = a + bx^2$.

Ans. Normal equations are

$$\sum_{i=1}^{n} y_i = an + b\sum_{i=1}^{n} x_i^2$$

$$\sum_{i=1}^{n} x_i^2 y_i = a\sum_{i=1}^{n} x_i^2 + b\sum_{i=1}^{n} x_i^4$$

Q.2 Derive normal equations for fitting parabola $y = ax + bx^2$.

Ans. Normal equations are

$$\sum_{i=1}^{n} x_i y_i = a\sum_{i=1}^{n} x_i^2 + b\sum_{i=1}^{n} x_i^3$$

$$\sum_{i=1}^{n} x_i^2 y_i = a\sum_{i=1}^{n} x_i^3 + b\sum_{i=1}^{n} x_i^4$$

16.6 Fitting of General Polynomial

We can fit a general polynomial of degree n by using principal of least square let polynomial be

$$y = a_o + a_1x + a_2x^2 + \cdots + a_nx^n$$

Which is to be filled to given data (x_i, y_i), i=1,2,3,…….n then

$$S = \sum_{i=1}^{n}(y_i - Y_i)$$

Where

$$Y_i = Y(x_i)$$
$$= a_o + a_1x_i + a_2{x_i}^2 + \cdots + a_n{x_i}^n$$

so $$S = \sum_{i=1}^{n}[y_i - (a_o + a_1x_i + a_2{x_i}^2 + \cdots + a_n{x_i}^n)]$$

For S to be minimum, we must have

$$\frac{\partial S}{\partial a_0} = 0, \frac{\partial S}{\partial a_1} = 0, \ldots\ldots, \frac{\partial S}{\partial a_n} = 0,$$

That is,

$$\frac{\partial S}{\partial a_0} = \sum_{i=1}^{n} -2[y_i - (a_o + a_1x_i + a_2{x_i}^2 + \cdots + a_n{x_i}^n)] = 0,$$

$$\frac{\partial S}{\partial a_1} = \sum_{i=1}^{n} -2x_i[y_i - (a_o + a_1x_i + a_2{x_i}^2 + \cdots + a_n{x_i}^n)] = 0,$$

$$\frac{\partial S}{\partial a_2} = \sum_{i=1}^{n} -2{x_i}^2[y_i - (a_o + a_1{x_i}^2 + a_2{x_i}^2 + .. + a_n{x_i}^n)] = 0,$$

…. …. ….

$$\frac{\partial S}{\partial a_n} = \sum_{i=1}^{n} -2{x_i}^n[y_i - (a_o + a_1x_i + a_2{x_i}^2 + .. + a_n{x_i}^n)] = 0,$$

Simplifying above (n+1) equations, we get following normal equations,

$$\sum y_i = a_0m + a_1\sum x_i + a_2\sum {x_i}^2 + \cdots + a_n\sum {x_i}^n$$
$$\sum x_iy_i = a_0\sum x_i + a_1\sum {x_i}^2 + a_2\sum {x_i}^3 + \ldots + a_n\sum {x_i}^{n+1},$$
$$\sum {x_i}^2y_i = a_0\sum {x_i}^2 + a_1\sum {x_i}^3 + a_2\sum {x_i}^4 + \cdots + a_n\sum {x_i}^{n+2},$$

……..

$$\sum x_i{}^n y_i = a_0 \sum x_i{}^2 + a_1 \sum x_i{}^{n+1} + a_2 \sum x_i{}^{n+2} + \cdots + a_n \sum x_i{}^{2n} \quad \ldots.(6)$$

These (n+1) equations can be solved for (n+1) unknowns

$a_0, a_1, a_2, \ldots \ldots \ldots a_n.$

16.7 Fitting of curve of $y = ax^b$

Let, for the given data (x_i, y_i), I =1,2,……,m, we have to fit a curve of the from

$$y = ax^b \quad \ldots. (8)$$

Taking logarithm of both sides, we get

$$\log_e y = \log_e a + b \log_e x \quad \ldots. (9)$$

Let $\log_e y = Y, \log_e x = X, \log_e a = A$, then equation (9) becomes

$$Y = A + bX$$

Which is a straight line so the normal equations are given by

$$\sum Y_i = nA + b \sum X_i$$

and $$\sum X_i Y_i = A \sum X_i + b \sum X_i{}^2$$

where m is total number of given data.

Solving these equations, we can get values of A and b, using the relation

$\log_e a = A$, we can get value of a.

16.8 Fitting of Curve $y = ae^{bx}$

Let the equation of curve $y = ae^{bx}$

Which is to be fitted for data $(x_1 y_1)$ (i=1,2,…..n)

Taking logarithim both side

$$\log_e y = \log_e a + bx$$

Y = A+bx

Where $Y = \log_e y$ & $A = \log_e a$

Which is a straight line in Y & x for which norma l equations are

$$\sum_{i=1}^{n} y_i = nA + b\sum_{i=1}^{n} x_i$$

and $\sum_{i=1}^{n} x_i y_i = A\sum_{i=1}^{n} x_i + b\sum_{i=1}^{n} {x_i}^2$

Self Assessment Questions

Q.1 Derive normal equations for fitting curve $y = e^{bx}$.

Ans. Normal equation $\sum_{i=1}^{n} x_i logy_i = b\sum_{i=1}^{n} x_i^2$.

Q.2 Derive normal equations for fitting curve $y = x^b$.

Ans. Normal equation $\sum_{i=1}^{n}(logx_i)(logy_i) = b\sum_{i=1}^{n}(logx_i)^2$.

16.9 Illustrative Example' s

Example 16.1 : Using the method of least-squares find a straight line that fits the following data:

x	71	68	73	69	67	65	66	67
y	69	72	70	70	68	67	68	64

Also find the value of y at x = 68.5.

Solution : Let the required straight line be

$$y = a + bx \quad \ldots(i)$$

The normal equations are

$$\sum y_i = na + b\sum x_i \quad \ldots(ii)$$

and $$\sum x_i y_i = a\sum x_i + b\sum {x_i}^2 \quad \ldots(iii)$$

Now, to get the values of $\sum y_i, \sum x_i, \sum x_i y_i$ and $\sum {x_i}^2$, we construct following table:

i	x_i	y_i	$x_i y_i$	${x_i}^2$
1	71	69	4899	5041
2	68	72	4896	4624
3	73	70	5110	5329
4	69	70	4830	4761
5	67	68	4556	4489
6	65	67	4355	4225
7	66	68	4488	4356
8	67	64	4288	4489
Sum	546	548	37422	37314

Hence, $\sum x_i = 546, \sum y_i = 548$

$$\sum x_i y_i = 37422, \sum {x_i}^2 = 37314$$

and total number of given data m =8,

substituting these values in (ii) and (iii), we get

548 = 8a + 546b

37422 = 546a + 37314 b

Solving these two equations for a and b, we get

$$a = 39.545484 \text{ and } b = 0.424242$$

Thus, the required straight line is

$$y = 39.545484 + 0.424242x$$

Now at x = 68.5, value of y is given by

$$y = 39.545484 + 0.424242 \times 683.5$$
$$= 68.606061$$

Example 16.2 : Fit a straight line to the given data

x	1	2	3	4	5	6
Y	2.6	2.7	2.9	3.025	3.2	3.367

Also find value of y at x = 5.5.

Solution : Let the required straight lne be

$$y = a + bx$$

then, the normal equation are

$$\sum y_i = na + b\sum x_i$$

and $\sum x_i y_i = a\sum x_i + b\sum {x_i}^2$

Now, from the given data, we have following table :

i	x_i	y_i	$x_i y_i$	${x_i}^2$
1	1	2.6	2.6	1
2	2	2.7	5.4	4
3	3	2.9	8.7	9
4	4	3.025	12.1	16
5	5	3.2	16	25
6	6	3.367	20.202	36
Sum	21	17.792	65.002	91

Hence,

$$\sum x_i = 21, \sum y_i = 17.792,$$
$$\sum x_i\, y_i = 65.002, \sum {x_i}^2 = 91$$

and m = 6

then, the normal equations become

$$17.792 = 6a + 21b$$

and $65.002 + 21a + 91b$

Solving these equations, we get

$$a = 2.419333, b = 0.156$$

Hence, required straight line is given by the equation

$$y = 2.419333 + 0.156\,x$$

Now at $x = 5.5$, value of y is given by

$$y = 2.419333 + 0.156 \times 5.5$$
$$= 3.277333$$

Example 16.3 : Let the required straight line be

$$y = a + bx$$

then, the normal equation are

$$\sum y_i = na + b\sum x_i$$

and $\sum x_i y_i = a\sum x_i + b\sum {x_i}^2$

Now, we construct following table, using the given data :

I	x_i	y_i	$x_i y_i$	${x_i}^2$
1	-1	10	-10	1
2	0	9	0	0
3	1	7	7	1
4	2	5	10	4
5	3	4	12	9
6	4	3	12	16
7	5	0	5	25

8	6	-1	-6	36
Sum	20	37	30	92

From the table we obtained following values,

$$\sum x_i = 20, \sum y_i = 37,$$
$$\sum x_i\, y_i = 30, \sum {x_i}^2 = 92$$

and m = 8

from then, the normal equations become

$$37 = 8a + 20b$$

and $30 = 20a + 92b,$

Solving above two equations, we get the values of a and b as

$$a = 8.345238, b = 1.488095$$

Thus, the equation of the straight line is

$$y = 8.345238 - 1.488095x$$

Now at $x = 3.5$, we have

$$y = 8.345238 - 1.488095 \times 3.5$$
$$= 6.857143$$

Example 16.4 : Fit a curve of the form $y = ax + bx^2$ to the given data:

X	1	1.5	2	2.5	3	3.5	4
Y	1.1	1.95	3.2	5	8.1	11.9	16.4

Solution : Equation of the required curve is

$$y = ax + bx^2$$

Which can be written as

$$\frac{y}{x} = a + bx \qquad \text{....(i)}$$

Let $\frac{y}{x} = Y$, then the above equation becomes

$$Y = a + bx \quad \text{....(ii)}$$

Normal equation for this curve are given by

$$\sum Y_i = ma + b\sum x_i$$

and $$\sum x_i Y_i = a\sum x_i + b\sum {x_i}^2$$

Using given data, we construct following table:

I	x	Y	$Y = \frac{y}{x}$	xY	x^2
1	1	1.1	1.1	1.1	1
2	1.5	1.95	1.3	1.95	2.25
3	2	3.2	1.6	3.2	4
4	2.5	5	2.0	5	6.25
5	3	8.1	2.7	8.12	9
6	3.5	11.9	3.4	11.9	12.25
7	4	16.4	4.1	16.4	16
Sum	17.5	-	16.2	47.65	50.75

From the table we have

$$\sum x_i = 17.5, \sum y_i = 16.2,$$

$$\sum x_i\, y_i = 47.65, \sum {x_i}^2 = 50.75$$

and m = 7

substituting these values in normal equations, we get

$$16.2 = 7a + 17.5b$$

and $$47.65 = 17.5a + 50.75b,$$

Solving these equations, we get

$$a = 80.239827, b = 1.021429$$

Thus, from (ii) we have

$$y = 0.239287 + 1.021429x$$

Now at $Y = \frac{y}{x}$, we have

$$y = 0.239287x + 1.021429x^2$$

Which is the required equation.

Example 16.5 : Fit a second degree polynomial to given data:

x	-4	-3	-2	-1	0	1	2	3	4
y	-5	-1	0	1	3	4	4	3	2

Solution : Let the required equation of the curve be

$$y = a + bx + cx^2$$

Normal equation for this curve are

$$\sum y_i = na + b\sum x_i + c\sum {x_i}^2$$
$$\sum x_i y_i = a\sum x_i + b\sum {x_i}^2 + c\sum {x_i}^3$$
$$\sum {x_i}^2 y_i = a\sum {x_i}^2 + b\sum {x_i}^3 + c\sum {x_i}^4$$

From the given data we construct following table :

i	x_i	y_i	$x_i y_i$	${x_i}^2$	${x_i}^2 y$	${x_i}^3$	${x_i}^4$
1	-4	-5	20	16	-80	-64	256
2	-3	-1	3	9	-9	-27	81
3	-2	0	0	4	0	-8	16

4	-1	1	-1	1	1	-1	1
5	0	3	0	0	0	0	0
6	1	4	4	1	4	1	1
7	2	4	8	4	16	8	16
8	3	3	9	9	27	27	81
9	4	2	8	16	32	64	256
Sum	0	11	51	60	-9	0	708

Thus,

$$\sum x_i = 0, \sum y_i = 11, \sum x_i y_i = 51$$
$$\sum {x_i}^2 = 60, \sum {x_i}^2 y_i = -9, \sum {x_i}^3 = 0,$$
$$\sum {x_i}^4 = 708 \; and \; n = 9$$

Substituting above values in normal equations, we get

$11 = 9a + b.0 + 60c$ or $11 = 9a + 60c,$

$51 = a.0 + b.60 + c.0$ or $51 = 60b,$

$-9 = a.60 + b.0 + c.708$ or $-9 = 60a + 708c$

Solving above equations for a, b and c, we get

$$A = 3.004329, b = 0.85, c = -0.267316$$

So, the required equation is given by

$$Y = 3.004329 + 0.85x - 0.26731x^2$$

Example 16.6 : Population of a city in different years are given in the following table :

X	1970	1980	1990	2000	2010
Y (in thousands)	1450	1600	1850	2150	2500

Fit a parabola to the given data, using least squares principle. Also estimate the population of the city in 2005.

Solution : Sinc the magnitude of given data is large and values of x are given at equal intervals, therefore we reduce it by shift of origin and scale. Let $x_0 = 1990$ be origin of x-values and $y_0 = 1850$ be origin of y-values.

Then, let

$$x = \frac{x-1990}{10} \text{ and } y = \frac{y-1850}{50} \quad \ldots.(i)$$

Let required curve be $y = a + bx + cx^2$, after change of orogin and scale, it will be

$$Y = a + bX + cX^2 \quad \ldots.(ii)$$

Now, we construct following table:

x	X	Y	Y	XY	X^2	X^2Y	X^3	X^4
1970	-2	1450	-8	16	4	-32	-8	16
1980	-1	1600	-5	5	1	-5	-1	1
1990	0	1850	0	0	0	0	0	0
2000	1	2150	6	6	1	6	6	1
2010	2	2500	13	26	4	52	8	16
Sum	0	-	6	53	10	21	0	34

Normal equations, in new variables, will be

$$\sum Y_i = na + b\sum X_i + c\sum {X_i}^2$$
$$\sum X_iY_i = a\sum X_i + b\sum {X_i}^2 + c\sum {X_i}^3$$
$$\sum {X_i}^2Y_i = a\sum {X_i}^2 + b\sum {X_i}^3 + c\sum {X_i}^4$$

From the table, we have

$$\sum X_i = 0, \sum Y_i = 6, \sum X_iY_i = 53$$

$$\sum X_i^2 = 10, \sum X_i^2 Y_i = 21, \sum X_i^3 = 0,$$
$$\sum X_i^4 = 34 \; and \; n = 5,$$

Substituting above values in normal equations, we have

$$6 = 5a + b.0 + c.10$$

or $$6 = 5a + 10c,$$

$$53 = a.0 + b.10 + c.0$$

or $$53 = 10b,$$

and $$21 = a.10 + b.0 + c.34$$

or $$21 = 10a + 34c$$

Solving above equations for a, b and c, we get

$$a = -0.085714, b = 5.3, c = 0.642857$$

Now from (ii), we have

$$Y = -0.085714 + 5.3x + 0.642857x^2$$

…..(iii)

From (i), we have

$$\frac{y-1850}{50} =$$

$$-0.085714 + 5.3\left(\frac{x-1990}{10}\right) + 0.642857\left(\frac{x-1990}{10}\right)^2$$

On simplification, we have

$$Y = 1222008.286 - 1252.78543x + 0.3214285x^2$$

Which is the required equation of parabola. Now, in the year 2005, population of the city will be given by

$$Y = 1222008.286 - 1252.78543(2005) + 0.3214285(2005)^2$$
$$= 2324.10456$$
$$\approx 2324 \text{ thousands, approximately}$$

Example 16.7 : Fit a curve of the form $y = ax^b$ to the given data :

X	2	3	4	5	6
Y	144	1723.8	207.4	248.8	298.5

Solution : The curve to be fitted is

$$y = ax^b \qquad \text{.....(i)}$$

Taking logarithm of both sides of equation (i), we get

$$\log_e y = \log_e a + b \log_e x$$

Or $Y = A + bX$ ……(ii)

Where $Y = \log_e y$, $A = \log_e a$ *and* $\log_e x = X$

i	x	$X = \log_e x$	Y	$Y = \log_e y$	XY	X^2
1	2	0.6932	144	4.9698	3.4451	0.4808
2	3	1.0986	172.8	5.1521	5.6601	1.2069
3	4	1.3863	207.4	5.3346	7.3954	1.9218
4	5	1.6094	248.8	5.5166	8.8784	2.5902
5	6	1.7918	298.5	5.6988	10.2111	3.2105
Sum	-	6.5793	-	26.6719	35.5901	9.4099

From the table we obtained

$$\sum X_i = 6.5793, \sum Y_i = 26.6719,$$
$$\sum X_i Y_i = 35.5901, \sum {X_i}^2 = 9.4099,$$

and $n = 5$

Normal equations, for the curve (ii) are given by

$$\sum Y_i = mA + b\sum X_i$$

$$\sum X_i Y_i = A\sum X_i + b\sum {X_i}^2$$

Substituting values, obtained from the table, we get

$$26.6719 = 5A + 6.5793b,$$

$$35.5901 = 6.5793A + 9.4099b$$

Solving these equations, we get

$$A = 4.471176, b = 0.656$$

From the relation $\log_e a = A$, we get

$$A = 87.459515$$

Thus, the required curves is

$$Y = 87.459515(X)^{0.656}$$

Example 16.8 : Fit a curve $y = ax^b$ to the following data :

X	1	2	3	4
Y	5	7	9	10

Also estimate the value of y at $x = 2.5$

Solution : For the required curve

$$y = ax^b$$

Normal equations are given by

$$\sum Y_i = mA + b\sum X_i$$

$$\sum X_i Y_i = a\sum X_i + b\sum {X_i}^2$$

Where, $Y = \log_e y\,, X = \log_e x \; and \; A = \log_e a$

From the given data, we construct following table:

i	x	$X = \log_e x$	y	$Y = \log_e y$	XY	X^2
1	1	0	5	1.6094	0	0
2	2	0.6931	7	1.9459	1.3487	0.4804
3	3	1.0986	9	2.1972	2.4138	1.2069
4	4	1.3863	10	2.3026	3.1921	1.918
Sum	-	3.1780	-	8.0551	6.9546	3.6091

From the table, we obtained

$$\sum X_i = 3.175, \sum Y_i = 8.0551$$

$$\sum X_i Y_i = 6.9546, \sum {X_i}^2 = 3.6091$$

And m = 4

Substituting these values in normal equations, we get

$$8.0551 = 4A + 3.178b$$

$$-6.9546 = 3.178A + 3.6091b$$

Solving these equations, we get

$$A = 1.607194, b = 0.511745$$

By the relatin $\log_e a = A$, we get $a = 4.988793$

hence, the required equation is

$$y = 4.988793(X)^{0.511745}$$

Now at $x = 2.5, y = 4.988793(2.5)^{0.511745}$

$$= 7.973322$$

Example 16.9 : Fit a exponential curve of the form $y = ae^{bx}$ to the given data :

X	1	2	3	4	5	6
Y	1.6	4.5	13.8	40.2	125	300

Also find the value of y at $x = 4.5$

Solution : The required curve is

$$y = ae^{bx}$$

Normal equations are given by

$$\sum Y_i = mA + b\sum x_i$$

$$\sum x_i Y_i = A\sum x_i + b\sum {x_i}^2$$

Where, $Y = \log_e y$, $and\ A = \log_e a$

From the given data, we construct the table as follows:

i	x	y	$Y = \log_e y$	xy	x^2
1	1	1.6	0.4700	0.4700	1
2	2	4.5	1.5041	3.0082	4
3	3	13.8	2.6247	7.8741	9
4	4	40.2	3.6939	14.7756	16
5	5	125	4.8283	24.1415	25
6	6	300	5.7038	34.2228	36
Sum	21	-	18.8248	84.4922	91

From the table, we obtain following values

$$\sum x_i = 21, \sum Y_i = 18.8248$$

$$\sum x_i Y_i = 84.4922, \sum {x_i}^2 = 91$$

and m = 6

Substituting these values in normal equations, we get

$$18.8248 = 6A + 21b$$

and $84.4922 = 21A + 941b$

Solving these equations, we get

$$A = 0.583614, b = 1.063166$$

From the relatin $\log_e a = A$, we get $a = 0.557879$

Thus, the required curve is

$$y = (0.557879)e^{(1.063166)x}$$

Now at $x = 4.5$, value of y is given by

$$y = (0.557879)e^{(1.063166)(4.5)}$$
$$= 66.728611$$

16.10 Exercise

1. Fit a curve of the form $y = ax + bx^2$ to the given data :

x	1	2	3	4	5	6
y	2..6	5.4	8.7	12.1	16	20.2

(Ans. $y = 2.41973x + 0.15589x^3$)

2. Fit a straight line to the following data :

x	1	2	3	4	5	8
y	2.4	3	3.6	4	5	6

(Ans. $y = 1.76 + 0.506x, y = 3.747\ at\ x = 3.5$)

3. Compute the constants α and γ^{β} such that the curve $y = \alpha\gamma^{\beta x}$ fits the given data:

x	1	2	3	4	5	6

y	151	100	61	50	20	8

(Ans. $\alpha = 309, \gamma^{\beta} = 0.5754$)

4. Fit a curve of the form $y = ax^b$ to the given below :

x	2	4	7	10	20	40	60	80
y	43	25	18	13	8	5	3	2

(Ans. $a = 4.36, b = -0.7975$)

5. Fit the curve $pV^r = k$ to the data given in the table :

P	0.5	1	1.5	2	2.5	3
V	1.62	1	0.75	0.62	0.52	0.46

(Ans. $r = 1.4224, k = 0.9970$)

6. Fit the curve $y = ae^{bx}$ to the following data :

x	2	4	6	8	10
y	4.077	11.084	30.128	81.897	222.62

Also estimate y at $x = 7$.

(Ans. $a = 1.499, b = 0.5, c = 49.6401$)

7. Fit a second degree polynomial to the following data, taking x as independent variable:

x	1	1.5	2	2.5	3	3.5	4
y	1.1	1.3	1.6	2.0	2.7	3.4	3.1

(Ans. $y = 1.0368 - 0.1932x + 0.2429x^2$)

8. Fit a second degree parabola to the given data:

x	1929	1930	1931	1932	1934	1935	1936	1937
y	352	356	357	358	360	361	360	359

(Ans. $y = -1010135 + 1044.67x - 0.27x^2$)

9. Obtain a least-squares quadratic approximation to the function $y(x) = \sqrt{x}$ on $[0,1]$, with respect to the weight function $w(x) = 1.$

(Ans. $y = \frac{1}{35}(6 + 48x - 20x^2)$)

10. The temperature θ and length l of a heated rod are given below. Establish a relation between θ and l of the form $l = a + b\theta$ using least-squares principle.

$\theta(°C)$	20	30	40	50	60	70
l(mm)	800.3	800.4	800.6	800.7	800.9	800.10

(Ans. a = 800, b = 0.0146)

16.11 Mean and R.M.S. Values

1. Mean value : The mean value of the ordinate y, of a function $y = f(x)$ over the range $x = a$ to $x = b$ is the limit of mean value of the equidistant ordinates $y_1, y_2, \ldots . y_n$ as n tends to infinity. Thus, if is the mean value,

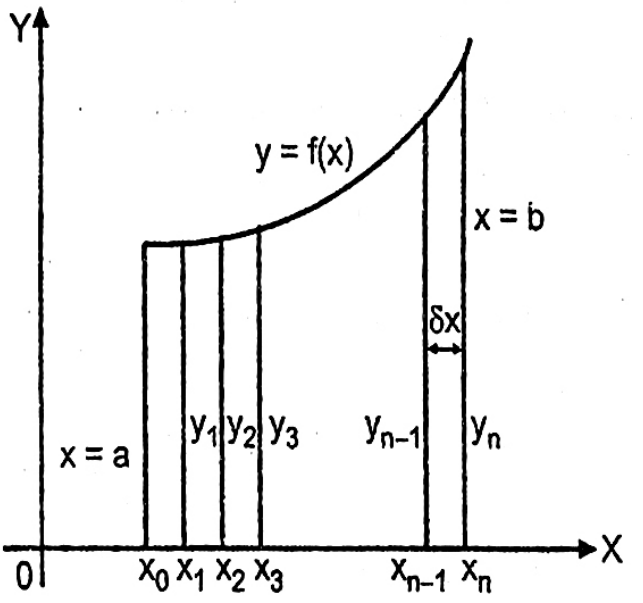
$$y_m = \lim_{n\to\infty} \frac{y_1 + y_2 + y_3 + \cdots + y_n}{n}$$

$$= \lim_{n\to\infty} \frac{y_1\delta x + y_2\delta x + \ldots + y_n\delta x}{n\delta x}$$

Now, $n\delta x = (b - a) = \int_a^b dx$ and $\lim_{n\to\infty}(y_1\delta x + y_2\delta x + \ldots + y_n\delta x)$

$= \lim_{n\to\infty} \sum_{x=a}^{x=b} y.\delta x = \int_a^b y dx$

$\delta x \rightarrow 0$



$$\therefore Y_m = \frac{\int_a^b y dx}{\int_a^b dx} = \frac{\int_a^b f(x) dx}{\int_a^b dx}$$

2. **Mean square value of $y = f(x)$ over (a, b) is defined as :**

$$M.S. of\ y = \frac{\int_a^b y^2 dx}{\int_a^b dx} = \frac{\int_a^b [f(x)]^2 dx}{\int_a^b dx}$$

The analysis can be extended to the mean values of the functions of two variables, say $z = f(x, y)$ over an area A is,

3. **Mean value $Z = f(x, y)$:**

$$Mean\ value\ of\ z = f(x,y) = Z_m = \frac{\iint_A f(x,y)dxdy}{\iint_A dxdy}$$

$$Over\ an\ area\ A$$

Similarly,

4.

$$Mean\ value\ of\ u = f(x,y,z) = U_m = \frac{\iiint f(x,y,z)dx\,dy\,dz}{\iiint dx\,dy\,dz}$$

$$Over\ a\ region\ of\ volume\ V$$

5. **Root mean square value (R.M.S. value) :** This term is usually applied in periodic functions. If y is a periodic function of x, of period p, the root mean square value of y is the square root of the mean value of y^2 over the range $x = c\ to\ x = c + p$ c being any constant.

$$\therefore \quad R.M.S.vaue\ of\ y = \sqrt{\frac{\int_c^{c+p} y^2 dx}{\int_c^{c+p} dx}}$$

Note : The R.M.S. value if very useful in calculation of A.C. electrical circuits.

Self Assessment Questions

Q.1 Write the formula formean square value of $y = f(x)$ over(a,b).

Ans.

$$M.S.of\ y = \frac{\int_a^b y^2 dx}{\int_a^b dx} = \frac{\int_a^b [f(x)]^2 dx}{\int_a^b dx}.$$

Q.2 Write the formula for root mean square value (R.M.S. value)

Ans. $R.M.S.vaue\ of\ y = \sqrt{\frac{\int_c^{c+p} y^2 dx}{\int_c^{c+p} dx}}$.

Example.16.10: Find the root mean square value of electric circuit given by

$$I = I_o + I_1 \sin\left(\frac{2\pi t}{T} + \alpha_1\right) + I_2 \sin\left(\frac{4\pi t}{T} + \alpha_2\right)$$

Solution : It is easily noted that for

$I = I_o + I_1 \sin\left(\frac{2\pi t}{T} + \alpha_1\right) + I_2 \sin\left(\frac{4\pi t}{T} + \alpha_2\right)$, the periodic time is T

$$\therefore\ I_{R.M.S.} = \sqrt{\frac{\int_0^T I^2 dt}{\int_0^T dt}} = \sqrt{\frac{1}{T}\int_0^T I^2 dt}$$

Consider

$$\int_0^T I^2 dt$$

$$= \int_0^T \left\{ {I_0}^2 + {I_1}^2 Sin^2\left(\frac{2\pi t}{T} + \alpha_1\right) + {I_2}^2 Sin^2\left(\frac{4\pi t}{T} + \alpha_2\right)\right\}$$

$$+2I_0 I_1 sin\left(\frac{2\pi t}{T} + \alpha_1\right) + 2.I_0.I_2 sin\left(\frac{4\pi t}{T} + \alpha_2\right) + 2I_1 I_2 sin\left(\frac{2\pi t}{T} + \alpha_1\right) sin\left(\frac{4\pi t}{T} + \alpha_2\right) dt$$

$$\int_0^T {I_0}^2 dt = {I_0}^2 T\ ;$$

$$\int_0^T {I_1}^2 sin^2\left(\frac{2\pi t}{T}+\alpha_1\right)dt$$

$$= \frac{{I_1}^2}{2}\int_0^T \left[1-cos\left(\frac{4\pi t}{T}+2\alpha_1\right)\right]dt$$

$$= \frac{{I_1}^2}{2}[T-0]$$

$$= \frac{{I_1}^2 T}{2}$$

$$\int_0^T {I_2}^2 sin^2\left(\frac{4\pi t}{T}+\alpha_1\right)dt = \frac{{I_2}^2 T}{2}$$

$$\int_0^T sin\left(\frac{2\pi t}{T}+\alpha_1\right)dt = 0 \int_0^T sin\left(\frac{4\pi t}{T}+\alpha_2\right)dt = 0$$

$$\int_0^T sin\left(\frac{2\pi t}{T}+\alpha_1\right) sin\left(\frac{4\pi t}{T}+\alpha_2\right)dt$$

$$= \frac{1}{2}\int_0^T \left[cos\left(\frac{2\pi t}{T}+\alpha_1+\alpha_2\right)-cos\left(\frac{2\pi t}{T}+\alpha_1+\alpha_2\right)\right]dt$$

$$= 0$$

$$\frac{1}{T}\int_0^T I^2 dt = \frac{1}{T}\left[{I_0}^2 T + {I_1}^2\frac{T}{2}+{I_2}^2\frac{T}{2}\right] = {I_0}^2 + \frac{{I_1}^2}{2}+\frac{{I_2}^2}{2}$$

$$I_{r.m.s.} = \sqrt{{I_0}^2+\frac{{I_1}^2}{2}+\frac{{I_2}^2}{2}}$$

Example.16.11: Find the R.M.S. value of a

$sin\, pt + b\cos qt + c\sin rt + d\cos st + \cdots p, q, r, s \ldots .$ being integers

Solution : Given function is a periodic function with period 2π.

Mean squre value = $\frac{\int_0^{2\pi}[a\, sin\, pt + b\cos qt + c\sin rt + d\cos st + \cdots]^2 dt}{\int_0^{2\pi} dt}$

$$= \frac{1}{2\pi}\int_0^{2\pi} \{a^2 sin^2 pt + b^2 cos^2 qt + c^2 sin^2 rt + d^2 cos^2 st + \cdots$$

$$+2ab \sin pt \cos qt + 2ac \sin pt \sin rt + \cdots\} dt$$

$\int_0^{2\pi} sin^2 pt\, dt = \int_0^{2\pi} \frac{1-cos2pt}{2} dt = \frac{2\pi}{2} - 0 = \pi$ and

$$\int_0^{2\pi} cos^2 qt\, dt = \pi$$

$\int_0^{2\pi} \sin pt \cos qt\, dt = 0$ and so on.

Mean square value $= \frac{1}{2\pi}[a^2\pi + b^2\pi + c^2\pi + d^2\pi + \cdots]$

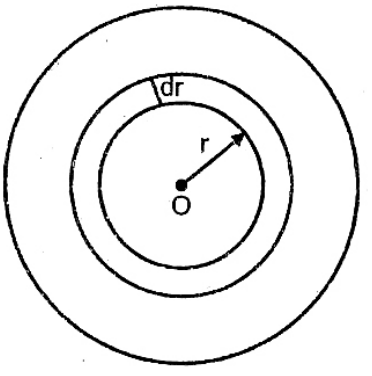
$$= \frac{1}{2}[a^2 + b^2 + c^2 + d^2 + \cdots]$$

$$R.M.S.Value = \sqrt{\frac{a^2+b^2+c^2+d^2+\cdots}{2}}$$

Example.16.12 : The law of density p of a sphere of radius a is $p = p_0 \frac{\sin(kr)}{nr}$, where 'r' distance from the centre , p_0, k and n are constants. Find the average density.

Solution : $Average\ density = \frac{Total\ mass}{Volume} = \frac{Total\ mass}{\frac{4}{3}\pi a^3}$

To find the total mas, divide the sphere into an infinite number of thin spjshells concentric with the sphere and consider a typical shell of radius r and this dr.



Its volume = $4\pi r^2 dr$

The mass of this shell = dm = $4\pi r^2 dr.p$

dm = $4\pi r^2 dr\ \frac{p_0 \sin kr}{nr} = \frac{4\pi p_0}{n}\ (r \sin kr)\ dr$

Since r varies from 0 to a.

Total mass = $\int_0^a dm = \int_0^a \frac{4\pi p_0}{n}\ (r \sin kr)\ dr$

$= \frac{4\pi p_0}{n}\left[r\left(\frac{-\cos kr}{k}\right) - (1)\left(\frac{-\sin kr}{K^2}\right)\right]^a$

$= \frac{4\pi p_0}{n}\left[\frac{-a\cos ka}{k} + \frac{\sin ka}{k^2}\right] = \frac{4\pi p_0}{nk^2}\ [\sin ak - ak\cos ak]$

Average density = $\frac{4\pi p_0}{n}\frac{(\sin ak - ak\cos ak)}{(4\pi a^3)/3}$

= $\frac{3p_0}{nk^2a^3}\ (\sin ak - ak\cos ak)$

Example.16.13: Find the M.V. and R.M.S. value of the ordinate of the cycloid $x = a\ (\theta + \sin\theta), y = a\ (I - \cos\theta)$ over the range $\theta = -\pi$ to $\theta = \pi$.

Solution: Let P(x,y) be any point on the cycloid. Its ordinate is y.

$$y_m = \frac{\int y\ dx}{\int dx} = \frac{\int_{-\pi}^{\pi}(1-\cos\theta)\ a\ (1+\cos\theta)\ d\theta}{\int_{-\pi}^{\pi} a(1+\cos\theta)\ d\theta}$$

$$y_m = \frac{a\int_{-\pi}^{\pi} sin^2\ \theta\ d\theta}{[\theta + \sin\theta]}$$

$$= \frac{a}{2\pi}\ 2\int_0^{\pi} sin^2\theta\ d\theta = \frac{a}{\pi}\ 2\int_0^{\pi/2} sin^2\theta\ d\theta$$

$$= \frac{2a}{\pi}\frac{1}{2}\frac{\pi}{2} = \frac{a}{2}$$

R.M.S. value = $\frac{\int y^2 dx}{\int dx} = \frac{1}{2\pi a}\int_{-\pi}^{\pi} a^2(1-\cos\theta)^2\ a(1+\cos\theta)d\theta$

$= \frac{a^2}{2\pi} = 2\int_0^{\pi} sin^4\frac{\theta}{2}2cos^2\frac{\theta}{2}d\theta \qquad \left(\therefore \frac{\theta}{2} = t\right)$

$$= \frac{8a^2}{\pi} = \int_0^{\pi/2} sin^4 t\, cos^2 t\, 2dt = \frac{16a^2}{\pi}\frac{3.1.1}{6.4.2}\frac{\pi}{2} = \frac{a^2}{2}$$

$$= \frac{a^2}{2} \qquad \therefore R.N.S.value = \frac{a}{\sqrt{2}}$$

Example.16.14: If a point move with constant acceleration, show that the space average of velocity over any distance is $\frac{2}{3}\left(\frac{{v_1}^2+v_1v_0+{v_0}^2}{v_1+v_0}\right)$, where v_0 and v_1 are the initial and find velocities.

Solution: $v\frac{dv}{ds} = acceleration = f\ say, ds = \frac{1}{f}\ v\ dv$

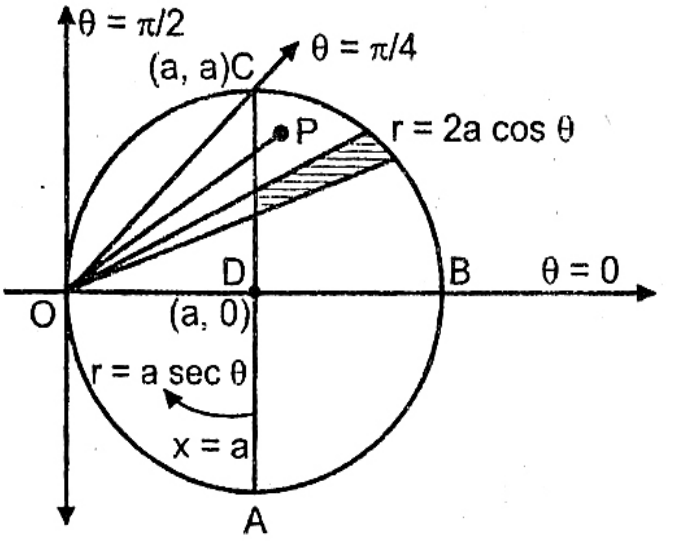
$\therefore$ Space average of velocity over any distance $= \frac{\int v\, ds}{\int ds} = \frac{\int v\frac{v}{f}dv}{\int \frac{v}{f}dv}$

$$= \frac{\int_{v_0}^{v_1} v^2 dv}{\int_{v_0}^{v_1} v\, dv} = \frac{({v_1}^3 - {v_0}^3)/3}{({v_1}^2 - {v_0}^2)/2} = \frac{2}{3}\frac{(v_1-v_0)({v_1}^2+v_1v_0+{v_0}^2)}{(v_1-v_0)\,(v_1-v_0)}$$

$$= \frac{2}{3}\left(\frac{{v_1}^2+v_1v_0+{v_0}^2}{v_1v_0}\right)$$

Example.16.15: Find R.M.S. value of distances from origin of points within $x^2 + y^2 - 2ax = 0$ cut off by $x = a$ where $x \geq a$.

Solution: Givenregion is ABCDA shown in fig.



$$x = a \implies e\cos\theta = a \; or \; r = a\sec\theta$$

$$\therefore \qquad x^2 + y^2 = 2ax \implies r = 2a\cos\theta$$

The distance of any point $P\ (r, \theta\ )$ from origin O being r, then the

$$\text{M.S. value} = \frac{\iint r^2 r\, dr\, d\theta}{\iint r\, dr\, d\theta} = \frac{2\int_0^{\pi/4} d\theta \int_{a\sec\theta}^{2a\cos\theta} r^3\, dr}{\frac{\pi a^2}{2}}$$

$$= \frac{4}{\pi a^2}\int_0^{\pi/4} \frac{16a^2\cos^4\theta - a^4\sec^4\theta}{4}\, d\theta$$

$$= \frac{a^2}{\pi}\left\{\int_0^{\pi/4} 16\frac{(1+\cos 2\theta)^2}{4}\, d\theta \int_0^{\pi/4} sec^2\,\theta\,(1+tan^2\theta)d\theta\right\}$$

$$= \frac{a^2}{\pi}\left\{4\int_0^{\frac{\pi}{2}} (1+2\cos t + cos^2\, t)\frac{dt}{2} - \int_0^1 (1+u^2)du\right\}$$

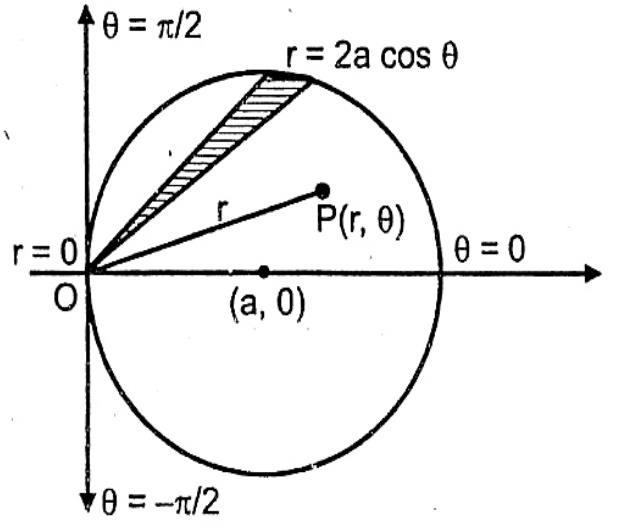
$$\begin{cases} 2\theta = t \\ \tan\theta = u \end{cases}$$

$$= \frac{a^2}{\pi}\left\{2\left(\frac{\pi}{2} + 2 + \frac{1}{2}\frac{\pi}{2}\right) - \left(1 + \frac{1}{3}\right)\right\} = a^2\left(\frac{3}{2} + \frac{8}{3\pi}\right)$$

R.M.S. value = $a\sqrt{\frac{3}{2}+\frac{8}{3\pi}}$

Example.16.16: Prove that the mean distance of points within a circular area of a radius a from a fixed point on the circumference is $\frac{32a}{9\pi}$

Solution: Take the fixed point O in the circumference as the pole and the diameter through O as the initial line. Then the polar equation of the circle $s\, r = 2a\cos\theta$. Refer fig. by summetry we may consider only the upper semi-circle for the required mean distance. The distance of any point $P(r,\theta)$ of the region from O being r, the required M.V. of the distance is



$$M.V. = \frac{\iint r\, r\, dr\, d\theta}{\iint r\, dr\, d\theta} = \frac{\int_0^{\pi/2}\int_0^{2a\cos\theta} r^2\, dr\, d\theta}{\frac{\pi a^2}{2}}$$

$$= \frac{2}{\pi a^2}\int_0^{\pi/2}\frac{8a^3\cos^3\theta}{3}\,d\theta = \frac{16a}{3\pi}\frac{2}{3} = \frac{32a}{9\pi}$$

16.12 Exercise

1. Find the average density of the sphere of radius a whose density at a distance r from the centre of the sphere is $p = p_0\left(1 + k\frac{r^3}{a^3}\right)$

(Ans. $p_0\left(1+\frac{k}{2}\right)$) (Refer solvedEx/7)

2. A point moves from rest with uniform acceleration. Prove that in any interval from the start, the space average of velocity is $\frac{4}{3}$ of the time average.

3. Find M.V. of rectangle contained by the abscissa and ordinate of any oint in first quadrant of ellipse $\frac{x^2}{a^2}+\frac{y^2}{b^2}=1.$

(Ans.$\frac{ab}{2\pi}$)

4. A particle moves from rest with uniform acceleration. Prove that in any interval of time from starting point, the space average of velocity is $\frac{2}{3}v$, where v is final velocity. **Hint :** Space average velocity = $\frac{\int v\,ds}{\int ds}=\frac{\int_0^v v^2dv}{\int_0^v v\,dv}=\frac{2}{3}v$

5. Find the M.S. value and R.M.S. value of the distance from a point within a cardiode $r = a\,(1+\cos\theta)$ from vertex.

(Ans.$\frac{35a^2}{24},\frac{a}{2}\sqrt{\frac{35}{6}}$)

6. If the density at a distance r from centre of sphere is given by $p_0\left(1-\frac{kr^2}{a^2}\right)$, prove that the average density is $p_0\left(1-\frac{3k}{5}\right)$, where a is radius of sphere.

Hint: Average density = $\frac{\int p\,dv}{\int dv}$ and use $v=\frac{4}{3}\pi r^3, dv=4\pi r^2dr.$

7. If in a spherical mass whose density p is a function of r where r is distance from the centre. If D denotes mean density of mater of the mass included within a concentric sphere of radius r, prove that $p = D+\frac{r}{3}.\frac{dD}{dr}$.

Hint : $D=\frac{\int p\,dv}{\int dv},\frac{4}{3}\pi r^3D=\int p\,4\pi r^2\,dr,\frac{r^3}{3}D=\int p\,r^2dr.$
Now differentiate w.r.t.r.

16.13 Summary

Principle of least square is the most systematic procedures to fit a unique curve through given data. It states "Curve of best fit for a given data is that for which sum of square of deviation is minimum".

Suppose we have to fit the curve $y = f(x)$ for given set of data (x_i, y_i) (I = 1, 2 …..n) At $x = x_i$ the experimental value of the ordinate is y_i& the corresponding value on fitting curve is $f(x)$.

If e_i be the error of Approximation at $x = x_i$ then we have

$$e_i = y_i - f(x_i)$$

e_i may be (–ve) or (+ve) so by giving equal weightage to each residuals consider

$$S = \sum_{i=1}^{n} e^2{}_i = \sum_{i=1}^{n} (y_i - f(x_i))^2$$

Now according to principal of least square curve of best fit is that for which S is minimum.

Root mean square value (R.M.S. value) : This term is usually applied in periodic functions. If y is a periodic function of x, of period p, the root mean square value of y is the square root of the mean value of y^2 over the range $x = c \; to \; x = c + p$ c being any constant.

$$\therefore \quad R.M.S.vaue\ of\ y = \sqrt{\frac{\int_c^{c+p} y^2 dx}{\int_c^{c+p} dx}}$$

16.14 Glossary

- Curve Fitting: An expression of the relationship between two variables by an equation.
- Straight Line: A length without breadth or thickness.

- Parabola: A symmetrical open plane curve formed by the intersection of a cone with a plane parallel to its side.
- Least: Smallest in amount, extent, or significance
- Minimum: The smallest value.
- Least Square: The overall solution minimizes the sum of the squares of the errors made in the results of every single equation.
- Mean: The mean is the average of the numbers.
- Root Mean Square Value: A statistical measure of the magnitude of a varying quantity.

16.15 References

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Unit – 9 : Cell Structure

Structure of Unit :

9.0 Objective

After reading this unit you can understand:

- The basic structure and functions of prokaryotic and eukaryotic cells differentiation between plant and animal cells.
- The cellular structure, cell organelles and their role in our cells.
- The structure of ATP, its formation and energy is production from ATP.
- Origin of life and about the existence of the building blocks of macromolecules.

9.1 Introduction

In 1665, an Englishman by the name of Robert Hooke examined thin slices of cork and observed that it was composed of numerous little boxes, fitted together like honey comb. Since these boxes resembled the compartment of monastery he named them as cells. The cork cells studied by Hooke were really empty boxes; they had lost their living matter, the protoplasm. After his discovery, the protoplasm in living cells were largely over looked due to its transparency. Today, with the help of special techniques, we are able to see not only the protoplasm but also many bodies inside it. This unit let you examine the structure and functions of most of your cell organelles in relation to why they are present.

There are many theories regarding how life may have originated on earth, but there is very little that we know for sure. New hypotheses are being proposed constantly, and old ones reevaluated. In this unit some of the ideas presented here about the origin of life will surely be obsolete. Thus, the contesting ideas are presented in this chapter in an open-ended format, attempting to make clear that there is as yet no one answers to the question of how life originated on earth. The origin of life seems to have taken just the right combination of physical events and chemical processes.

9.2 Structure of prokaryotic and eukaryotic cells

The cell is the basic structural, functional and biological unit of all known living organisms. Cells are the smallest unit of life that can replicate independently, and are often called the "building blocks of life". The study of cells is called cell biology. There are two types of cells - Prokaryotic and Eukaryotic.

a. Prokaryotic cells: Prokaryotic cells were the first form of life on Earth. They are simpler and smaller than eukaryotic cells, and lack membrane-bound organelles such as the nucleus. Prokaryotes include two of the domains of life, bacteria and archaea. The DNA of a prokaryotic cell consists of a single chromosome that is in direct contact with the cytoplasm. The nuclear region in the cytoplasm is called the nucleoid.

A prokaryotic cell has three architectural regions:

- On the outside, flagella and pili project from the cell's surface. These are structures (not present in all prokaryotes) made of proteins that facilitate movement and communication between cells.
- Enclosing the cell is the cell envelope – generally consisting of a cell wall covering a plasma membrane though some bacteria also have a further covering layer called a capsule. The envelope gives rigidity to the cell and separates the interior of the cell from its environment, serving as a protective filter. Though most prokaryotes have a cell wall, there are exceptions such as *Mycoplasma* (bacteria) and *Thermoplasma* (archaea). The cell wall consists of peptidoglycan in bacteria, and acts as an additional barrier against exterior forces. It also prevents the cell from expanding and bursting (cytolysis) from osmotic pressure due to a hypotonic environment. Some eukaryotic cells (plant cells and fungal cells) also have a cell wall.
- Inside the cell is the cytoplasmic region that contains the genome (DNA), ribosomes and various sorts of inclusions. The prokaryotic chromosome is usually a circular molecule (an exception is that of the bacterium *Borrelia burgdorferi*, which causes Lyme disease). Though not forming a *nucleus*, the DNA is condensed in a *nucleoid*. Prokaryotes can carry extrachromosomal DNA elements called plasmids, which are usually circular. Plasmids encode additional genes, such as antibiotic resistance genes.

b. Eukaryotic cells

Plants, animals, fungi, slime moulds, protozoa and algae are all eukaryotic. These cells are about fifteen times wider than a typical prokaryote and can be as much as a thousand times greater in volume. The main distinguishing feature of eukaryotes as compared to prokaryotes is compartmentalization: the presence of membrane-bound compartments in which specific metabolic activities take place. Most important among these is a cell nucleus, a membrane-delineated compartment that houses the eukaryotic cell's DNA. This nucleus gives the eukaryote its name, which means "true nucleus." Other differences include:

- The plasma membrane resembles that of prokaryotes in function, with minor differences in the setup. Cell walls may or may not be present.
- The eukaryotic DNA is organized in one or more linear molecules, called chromosomes, which are associated with histone proteins. All chromosomal DNA is stored in the cell nucleus, separated from the cytoplasm by a membrane. Some eukaryotic organelles such as mitochondria also contain some DNA.
- Many eukaryotic cells are ciliated with primary cilia. Primary cilia play important roles in chemosensation, mechanosensation, and thermosensation. Cilia may thus be viewed as a sensory cellular antennae that coordinates a large number of cellular signaling pathways, sometimes coupling the signaling to ciliary motility or alternatively to cell division and differentiation

- Eukaryotes can move using motile cilia or flagella. Eukaryotic flagella are less complex than those of prokaryotes.

9.3 Intracellular organelles and their functions

The endomembrane system includes the:

- plasma membrane
- nuclear envelope
- endoplasmic reticulum
- Golgi apparatus or Golgi bodies
- Vesicles
- Vacoulles
- Lysosomes

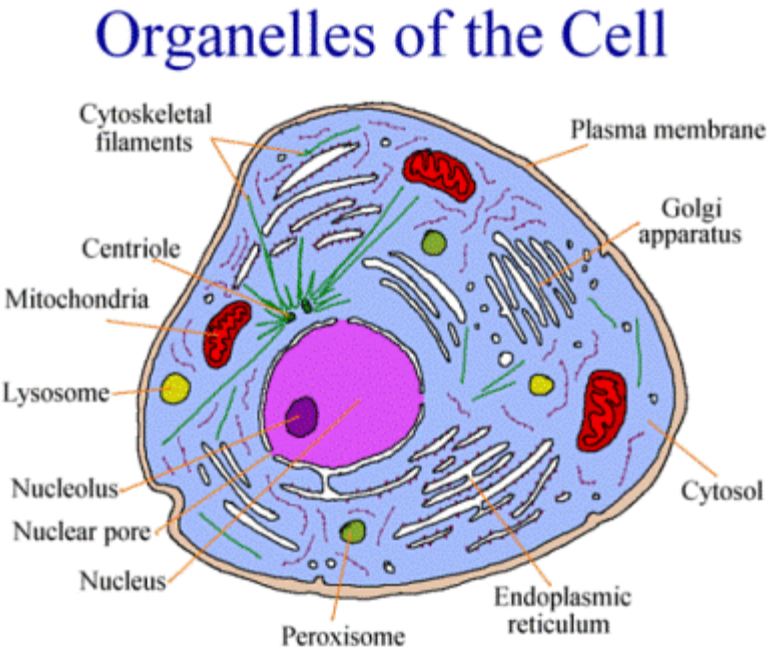

Fig. 9.1 Organelles of the Cell

The membrane of all of these is composed of two layers of phospholipids with embedded proteins. Membrane has a consistency of a light oil allowing its membranes

to diffuse throughout. Autogenous hypothesis states that the endomembrane system evolved from invagination of the plasma membrane.

a.Cell or Plasma Membrane

The cell membrane is possibly the most important organell in the cell. It holds the cell together, keeping everything intact. It is mobile & moves along paths that membranes follow. It is composed of a phosolipid bilayer.

The cell membrane is the thin layer that forms the outer boundary of a living cell or of an internal cell compartment The outer boundary is the plasma membrane, and the compartments enclosed by internal membranes are called organelles. Cell membranes have a dual function: (1) they both separate important but incompatible processes conducted in the organelles and keep toxic substances out of the cell; and (2) they allow specific nutrients, wastes, and metabolic products to pass between organelles and between the cell and the outside environment.

Structure:

The plasma membrane (also called the cell membrane) forms the outer limits of the cell. As with other membranes, the plasma membrane is made up of proteins and lipids, especially phospholipids which consist of both a hydrophilic head and 2 hydrophobic fatty acid tails (amphipathic). These lipids occur in two layers, often called the bi-layer. The bi-layer has globular proteins that seem to float in the lipid layer. This type of structure is in continual motion, giving it a fluid appearance. This appearance is often called the fluid mosaic structure. The plasma membrane uses this fluid mosaic structure to control the environment of the cell. The lipid bilayer is the main fabric of the membrane but proteins in this lipid layer are very important because they carry out many of the activities that the plasma membrane performs. Membrane carbohydrates on surface of the plasma membrane recognize other cells (glycoproteins).

Functions:

- Transport proteins: allow water-soluble substances to move through their interior, which opens on both sides of the bi-layer. Some transport proteins hydrolyze ATP as an energy source to actively pump substances across the membrane.

- Enzymatic activity: A protein built into the membrane may be an enzyme with its active site exposed to substances in the adjacent solution.
- Signal transduction: A membrane protein may have a binding site with a specific shape that fits the shape of a chemical messenger, such as hormones & other extracellular substances that trigger changes in cellular activity
- Intercellular joining: Membrane proteins of adjacent cells may be hooked together in various kinds of junctions.
- Cell-cell recognition: Some glycoproteins serve as identification tags that are specifically recognized by other cells.
- Adhesion proteins: Microfilaments or other elements of the cytoskeleton may be bonded to membrane proteins, a function that helps maintain cell shape and fixes the location of certain membrane proteins. Proteins that adhere to the extracellular matrix (ECM) can coordinate extra cellular and intracellular changes.

Fluid Mosaic Structure

- Membranes are fluid because:
- Membranes are not static sheets, but rather held together by hydrophobic attraction (= weaker than covalent bonds)
- Lipids and some of proteins can drift about randomly, but rarely flip flop.
- Fluidity is affected by the type of bonds within the membrane.
- Membranes are mosaic because membrane is a collage of different proteins within the bi-layer.
- Proteins determine most of the specific functions of membrane Different proteins are found in different membranes (More than 50 kinds of proteins have been found to date in the plasma membrane of red blood cells, for example)

Structure: Cell (plasma) membranes are made of lipids, proteins and carbohydrates.

a. Lipids –These are barriers separating the interior of the cell from its environment. Also act as a barrier between the solutions inside the cell, separating contents of an organelle from the cell cytoplasm. For example, the nucleus is surrounded by two

layers of membranes that are actually extensions of the membrane surrounding the cell. These nuclear membranes keep the DNA inside of the nucleus. Lipid molecules are called Phosopholipids made of fatty acids, glycerol, phosphate and hydrophilic organic derivative. The lipids are amphipathic in nature that means one end of molecule is hydrophobic (hates water) and the other side is hydrophilic (loves water).

b. Proteins

The proteins within the plasma membrane are the functional and part of the membrane, allowing for transport of materials through the membrane and sending and receiving signals to and from other cells. Basically these proteins can act as, pumps, gates, receptors, engery transducers, and enzymes or receptors for the endocytosis of material and cell-cell signaling. The proteins associated with the outside surface of the lipid bilayer are called extrinsic proteins. These can be easily removed. The proteins that are embedded in the membrane are called intrinsic proteins. They can only removed with detergents that disrupt the cell membrane. Integral proteins also have a hydrophobic portion (amino acids or fatty acid tail) that spans the hydrophobic interior of the lipid bilayer. Some of these inner proteins also have integrins to connect the outside proteins to the cytoskeleton inside the cell.

c. Carbohydrates – The carbohydrates modify the lipid and protein molecules and the modified molecules are called glycoproteins and glycolipids.

- Glycolipids are located mainly in the plasma membrane, and they are found only in the noncytosolic half of the bilayer. Their sugar groups therefore are exposed on the exterior of the cell, where they form part of the protective coat of carbohydrate that surrounds most animal cells. This protective coat is the glycocalyx. The glycolipid molecules acquire their sugar groups in the Golgi apparatus. The enzymes that add the sugar groups are confined to the inside of the Golgi apparatus so that the sugars are added to lipid molecules in the noncytosolic half of the lipid bilayer. Once a glycolipid molecule has been created in this way, it remains trapped in this monolayer. As there are no flippases to transfer the glycolipid to the cytosolic side of the membrane. Two broad types of glycolipids can be distinguished:

i) Glycerol-Based: Fatty acid chains attached to the glycerol molecule. A carbohydrate group linked to the 3rd carbon of glycerol with no bridging phosphate group. Glycerol-based glycolipids are the primary form in plants and bacteria.

ii) Sphingolipid-Based: These are based on the addition of carbohydrate units to the sphingolipid nucleus. This type of glycolipid is the main form in animal cell membranes. Simple glycolipids formed by the addition of a single sugar unit are called cerebrosides. The addition of straight or branched sugar chains produces gangliosides. The carbohydrates added can be have considerable variation in structure.

b. Nucleus

It contains and protects the majority of the cell's DNA in the form of chromosomes. DNA also occurs in the mitochondria and chloroplasts. The nucleus occupies about 10% of volume of cell and typically averages 5 microns in diameter. Surrounded by nuclear envelope with pores. Nuclear pores regulate the passage of materials between the nucleus and the cytoplasm. Double membrane has an inner and outer membrane separated by a space. Outer membrane is continuous with the membrane of the rough endoplasmic reticulum (RER) and has ribosomes attached to its surface. Nucleoplasm (gel) contains the chromatin (chromosomes) and a nucleolus (plural nucleoli).

While DNA is found in the chloroplast and mitochondria of eukaryotic cells, the majority of the DNA is located and protected within the cell’s nucleus. The nucleus is the largest organelle and is most visible in slides. It occupies about 10% of volume of cell and typically averages 5 microns in diameter.

During the first part of a cell’s life cycle (growth phase 1), the DNA molecules exist as long threads surrounded by proteins. In this state the DNA lengths are called chromatin. Were you to view a slide of a cell during this stage, you would not be able to see the DNA as discrete units. The nucleus would simply appear as a dark nut or kernel thus the organelle’s name nucleus (=kernel). During the synthesis stage (second part of the cell growth phase), the chromatin threads replicate in preparation for mitosis or meiosis I. The original chromatin length and its copy are called chromatids and are temporarily joined together at a point called a centromere. It is not until the

first phase of mitosis or meiosis I (prophase) that the DNA lengths condense into the shorter, thicker and finally visible chromosomes. It is important to realize that a DNA molecule, a length of chromatin, a chromatid and a chromosome are all the same unit.

The DNA material takes up most of the volume of the nucleus. Surrounding it and protecting it is a nucleoplasm, much like the cytosol found in the rest of the cell. The nucleoplasm is rich in nucleotides to make nucleic acids and amino acids to make proteins. Two types of organelles exist inside the nucleus: ribosomes and one or more nucleoli (singular nucleolus).

The nucleus is part of the endomembrane system. A double layer of semipermeable (porous) membranes (nuclear envelope) surrounds it. The nuclear envelope is a bilayer of lipids and proteins.

The two layers are separated by a space of about 20-40 nm. The outer membrane is studded with ribosomes and is continuous with the membranes of the rough endoplasmic reticulum (ER). The space between the two layers of nuclear membranes is also continuous with the space of the rough ER.

This space in between the nuclear membranes and the space in the ER can fill with proteins and proteins can pass between the two organelles. True of all the membranes of the endomembrane system, the nuclear envelope is strengthened by a mesh of protein filaments. Both the endoplasmic reticulum and nucleus membranes are connected via membranous extensions to the plasma membrane and Golgi apparatus. The nuclear pores regulate the passage of materials between the nucleus and the cytoplasm.

Lining the inside of the inner membrane is a layer of intermediate protein filaments 30-100 nm thick (nuclear lamina), which is hypothesized to add strength and shape to the nucleus, to control the assembly and disassembly of the nuclear membrane during prophase. After the proteins making up these laminas are phosphorylated, the nuclear membrane begins breaking up into vesicles that appear to disappear during nuclear division. During telophase these proteins lose the phosphate group (dephosphorylation) and the proteins reassemble forming the nuclear membrane.

It is clear that laminas control this process because when antibodies to laminas are injected into a cell, the nucleus cannot reform during telophase.

c. Nuclear Pores: pores about 100 nm in diameter perforate the nuclear envelope.

Occur in areas of the nuclear envelope, where the inner and outer membranes are joined. At the lip of each pore, the inner and outer membranes are fused. An intricate structure of proteins, called a "pore complex" lines each pore and regulates the entry and exit of certain large macromolecules and particles. The pore is formed by a ring of eight spokes that point to the center of the pore. Each spoke is a subunit 15 – 20 nm in diameter. At the center is a diaphragm or plug. The pore itself acts as a water-filled channel 10 nm in diameter. Molecules of 5,000 MW are freely diffusable, while those of 60,000 MW cannot enter by diffusion. This means that mature ribosomes with both subunits attached together are too large to reenter the nucleus. So this means that the translation of mRNA occurs outside the nucleus. The pore can be caused to dilate open up to 26 nm when the pore recognizes certain peptide sequences rich in lysine, arginine and proline. These proteins control the direction molecules can actively be transported (active transport requires an expenditure of ATP energy, so it costs the cell) through the pore. In tests, gold-labeled tRNA or 5S RNA could exit through the pore, but not enter. Transport of RNA is inhibited by alteration of the 3' end or the 5' cap structure. The protein signal is so refined and specific, that if the sequence is altered by even one amino acid the peptide no longer passes through the pore. While proteins can bind to the surface of the nuclear membrane, they can only enter the pore in the presence of ATP. The nuclear lamina, a netlike array of protein filaments gives the nucleus its shape. This lamina lines the inner surface of the membrane.

d. Nucleolus: These organelles are not part of the endomembrane system—they are not surrounded by membranes nor are they extensions of the plasma membrane or associated membranous organelles makes the ribosomal subunits.Nonmembrane-bound cloud like mass composed of rRNA and proteins that are combined to form ribosome subunits.These subunits leave the nucleolus cloud and exit the nucleus through its pores. There is a region of the nucleolus that is called the "nucleolus organizer".Certain genes of chromosomes that are located here make many identical copies of the same rRNA gene. Humans have five pairs of chromosomes (13, 14, 15, 21 and 22) each that have a nucleolar organizer located at a constriction near one end of the chromosome (this is a second constriction, not the centromere). All of the copies of the rRNA are expressed within the same short period of time resulting in a large

number of rRNA molecules, which bond with proteins forming large and small ribosome subunits. Nuclear Organizer of an elongated chromosome singlet and a condensed chromosome singlet.

Functions:

- synthesizes ribosomal RNA
- assembles the ribosomal subunits into a complete, mature, functional ribosome

Structure: This is a spherical organelle within the nucleus. The nucleolus contains histones, enzymes, nucleotides, amino acids and RNA. Ribosomes are aggregates of copies of RNA (called ribosomal RNA) aggregate with certain proteins into three-dimensional bodies called "subunits". Two subunits join together to form a mature ribosome that then becomes a site for reading messenger RNA. There are certain blocks of genes (on chromosomes 13, 14, 15, 21 and 22 in humans) that code for the production of these particular proteins and for this type of rRNA.

Those chromosomes, that contain these genes, aggregate in the area making up the nucleolus. These blocks of active genes act as "nucleolar organizers". These genes are veritable copy machines continually "turning on" (gene expression), making sufficient copies of RNA to produce the proteins necessary for the production of ribosomes, which then become the site of further protein synthesis. An average, healthy cell reportedly can produce up to 10,000 ribosomes per minute.

e. Ribosomes

Ribosomes are composed of strands of ribosomal RNA (transcribed off of certain genes) and complex proteins that bind the rRNA strands together. These ribonucleoprotein complexes form two different sizes of units, one larger than the other. In order to be functional, a ribosome musthave one large and one small subunit attached together. These subunits are formed in the nucleolus and exit the nucleus via pores in the nuclear envelope. Once, these subunits join outside the nucleus they are too large to reenter the pores. Because proteins are synthesized in the nucleus as well as outside, we know that some ribosomes become complete and functional in the nucleus, but they stay inside while the nuclear membrane is intact, while the majority of ribosomes are not put together until the subunits are outside the nucleus. For more

information concerning the formation of rRNA refer to the section above concerning the nucleolus**.**

Structure:

Ribosomes are not organelles since they are non-membraneous. They are spherical bodies composed of RNA and protein enzyemes.Ribosomes are made up of two subunits or parts. There are two types of ribosomes: free ribsomes, which are suspended in the cytosol, and bound ribosomes, which are attached to the outside of a membranous network called the endoplasmic reticulum. In both cases the ribosomes often occur in clusters called polysomes.Ribosomes are found in the nucleus, cytosol, and are attached to the endoplasmic reticulum (ER) constituting rough ER.The messenger RNA molecule holds the two subunits of the ribosome together during protein synthesis. A ribosome has a mRNA binding site and three tRNA binding sites, known as the P, A and E binding sites. All are located on the large subunit.

Function of rRNA in the ribosome: rRNA is the catalyst for formation of the peptide bond. The P site holds the tRNA carrying the growing polypeptide chain. The A site holds the tRNA carrying the next amino acid to be added to the peptide chain. Discharged tRNAs leave the ribosome from the E site.

Ribosomes are not part of the endomembrane system in that they are not membranous, but the ones attached to the rough endoplasmic reticulum and nuclear envelope (bound ribosomes) interfunction with this system. Bound ribosomes make proteins that will be included into membranes, packaged within certain organelles such as lysosomes or exported from the cell. Free ribosomes, floating in the cytoplasm, have to do with the synthesis of hormones. The ribosomes bring together mRNA and tRNA.

Differences between the tRNA of prokaryotic and eukaryotic cells:

Predictably, eukaryotic and prokaryotic rRNAs are distinctly different but the rRNA inside mitochondria and chloroplasts are more similar to that found in prokaryotic cells. The length of rRNA varies between species from 4700 bases to about 120 bases. Eukaryotes contain 28, 18, 5.8 and 5 S rRNAs, while prokaryotes contain 23, 16 and 5 S rRNAs. The "S" symbolizes a **Svedberg unit** (s), which measures the rate of sedimentation of molecules and organelles during centrifugation. It is the sedimentation coefficient, and is a measure of relative size.

Differences in life span of messenger, transfer and ribosomal RNA:

A study using Escherichia coli found that in at least that species, most of the cell's RNA is ribosomal RNA, only a small portion (3%) of the cell's total RNA is made up of mRNA, but, that the cell uses almost 1/3 of its capacity for RNA synthesis to the production of mRNA. In fact, this value may increase to about 60% when the cell is growing slowly and does not need to replace ribosomes and tRNA. This probably is due to the fact that transfer and ribosomal RNA are very stable and do not need to be rebuilt, but the messenger RNA lives no longer than three minutes and then needs to be replaced. The average half-life of mRNA in eukaryotic cells is about 30 minutes.

Differences between ribosomes in prokaryotic and eukaryotic cells:

The differences in rRNA (detailed above) correlate to differences in ribosomes between bacteria and eukaryotic cells. The ribosomes found within mitochondria and chloroplasts distinctly more similar to those in bacteria.

a. Size: Eukaryotic ribosomes are large (80S), consisting of 40S and 60S subunits, whileprokaryotic ribosomes are smaller (70S), consisting of 30S and 50S subunits.
b. Antibiotics: Certain antibiotics including tetracycline, streptomycin and chloramphenicol, kill bacteria by binding to their ribosomes but do not affect the ribosomes of eukaryotes possibly due to their larger size.
c. Number: Eukaryotic cells contain far more ribosomes than do bacterial cells. A single human cell might contain several million ribosomes.

Function of Ribosome:

The function of a ribosome is to convert the genetic code into a sequence of amino acids that form a specific protein. Ribosomes are involved in protein synthesis. It creates protein for the cell. Ribosomes can occur freely in the cytosol and it boundes attached to the outer membrane (endoplasmic reticulum).

During protein synthesis, several ribosomes called polyribosomes (or polysomes) follow one another down the same messenger RNA molecule making it possible for tRNAs to bring amino acids to the mRNA and for the amino acids to bond forming a peptide chain. Each ribosome "car" "reads" the same mRNA and assembles the same amino acids that will result in molecules of the same protein being synthesized

repeatedly. Polyribosomes synthesize multiple copies of the same protein. Cells needing to make proteins most frequently, such as pancreatic, liver and muscle cells have the greatest number of ribosomes.

f. Endoplasmic reticulum

Throughout the eukaryotic cell, especially those responsible for the production of hormones and other secretory products, is a vast amount of membrane called the endoplasmic reticulum, or ER for short. The ER membrane is a continuation of the outer nuclear membrane and its function suggests just how complex and organized the eukaryotic cell really is. When viewed by electron microscopy, some areas of the endoplasmic reticulum look "smooth" (smooth ER) and some appear "rough" (rough ER).

The rough endoplasmic reticulum consists of a system of membranous sacs and tubules known as cisternae. It derives its name from the fact that it is coated with numerous ribosomes, which line the cytoplasmic surface of its membrane. This causes the surface of rough ER to appear studded or "rough" under the electron microscope. An electron microscope must be used to view the rough ER due to its extremely small size; 0.005 um in diameter.

The rough ER has two primary functions; make more membrane and convert polypeptide chains into a variety of functional proteins. Information coded in DNA sequences in the nucleus is transcribed as messenger RNA. Messenger RNA exits the nucleus through small pores to enter the cytoplasm. At the ribosomes on the rough ER, the messenger RNA is translated into proteins. The proteins are then delivered into the endoplasmic cisterns.

In most instances, polypeptide chains require a considerable amount of processing before they are ready for shipment. Some are fitted with carbohydrate side-chains, that contain as many as ten or more sugar molecules (glycosylation). The smooth endoplasmic reticulum is an extensive membranous network, and like the rough ER, it is continuous with the outer nuclear membrane.

The smooth ER is a network of interconnected tubules that lack ribosomes. Much of its activity results from enzymes embedded in its membrane. One of the most important functions of the smooth ER is the synthesis of lipids, which includes fatty acids, phospholipids, and steroids. Each of these products is made by particular kinds of cells. In mammals, for example, smooth ER in cells of the ovaries and testes synthesizes the steroid sex hormones.

These proteins are then transferred to the golgi in transport vesicles where they are further processed and packaged into lysosomes, peroxisomes, or secretory vesicles.

Our liver cells also have large amounts of smooth ER, with additional kinds of functions. Certain enzymes in the smooth ER of liver help regulate the amount of sugar released from liver cells into the bloodstream. While other liver enzymes help break down drugs and other potentially harmful substances. They are also used as a destruction of toxic substances in the liver cells. The drugs detoxified by these enzymes include sedatives such as barbiturates, stimulants such as amphetamines, and certain antibiotics.

Another function of the smooth ER is the storage of calcium ions. In the muscle tissue, these are necessary for contraction. When a nerve stimulates a muscle cell, calcium ions leak from the smooth ER into cytoplasmic fluid, where they trigger contraction of a cell. These proteins are then transferred to the golgi in transport vesicles where they are further processed and packaged into lysosomes, peroxisomes, or secretory vesicles. Living cells manufacture all sorts of export materials, which they assemble, process, package, and transport in a chain of interconnected,membrane-limited organelles. Biologists refer to this cytoplasmic network as the endomembrane system. The endoplasmic reticulum is only one of the many organelles in the system responsible for the synthesis, storage, and export of important molecules.

Endoplasmic reticulum is an interconnected canal of membranes. Half of the membranes within a typical animal cell are endoplasmic reticulum. It comprises the largest portion of the endomembrane system of membrane-bound organelles that interrelate or interfunction through the production and distribution of membranes. Canal system of ER is composed of two connected subdivisions:

a. Rough endoplasmic reticulum (RER): Consists of layers (cisternae) with attached ribosomes on outer surface.

b. Smooth endoplasmic reticulum (SER): Consists of a network of interconnecting tubules without ribosomes.

Function of Rough ER:

The polyribosome (subunits of rRNA + proteins) is connected or held together by a molecule of messenger RNA, which runs between the two subunits. As the polypeptide chain grows it projects down from the large subunit and is inserted into the membrane of the endoplasmic reticulum and then into the internal cisterae of the RER. The membrane of the RER has a receptor site that binds the larger subunit of the polyribosome. Adjacent to this receptor site is the pore through which the polypeptide chain will pass into the cisternae of the ER. The membranous sacs of the rough endoplasmic reticulum connect with the rest of the endomembrane system, with the nuclear envelope, plasma membrane and golgi apparatus (etc.), and the proteins synthesized by the ribosomes on the surface of the RER are passed through membranous canals or channels to the rest of the cell.

Function of the Smooth ER:

- Produces enzymes for synthesis of lipids. phospholipids, steroids, hormones
- Metabolism of carbohydrates. In the hydrolysis of glycogen in liver cells, glucose phosphate (the first product of the reaction) cannot leave the cell and enter the blood until an enzyme embedded in the cell's smooth ER remove the phosphate from the glucose.
- Detoxification of drugs and proteins. Smooth ER adds hydroxyl groups to drugs such as barbiturates or alcohol, making them more soluble and easier to flush from the body. Drugs induce a proliferation of smooth ER that leads to an increased tolerance of the drug that then requires higher does and this causes further proliferation of the smooth ER.
- Contraction of muscle cells. ER membrane pumps calcium ions from the cytosol into the cisternal space. When a nerve impulse stimulates a muscle cell, calcium rushes back across the ER and triggers the contraction.

g. Golgi apparatus

The Golgi apparatus is part of the endomembrane system and represents the structural connection to other Organelles. The GA is connected at points to the ER. The forming face lies near the nucleus and the maturing face and secretory vesicles lie near the cell membrane at the surface opposite to the one where the raw materials enter.

Function

The function of the Golgi apparatus involves interaction with other organelles, but is not connected by membrane with the other organelles. The function is to chemically modify the secretory proteins and lipids transported from the ER in a transport vesicle. The transport vesicle enters the golgi sac through the bottom, the receiving side. Each sac in the golgi apparatus body contains a different enzyme (remember enzymes have active sites that only accept specific molecules) therefore there are many different modifications taking place. The mature cells are then marked with a sequence of molecules and sorted into different batches for various destinations within the cell including the lyosomal membrane, plasma membrane and many others.

- The Golgi apparatus is responsible for modifying proteins that were produced in the endoplasmic reticulum. It is here that export proteins and membrane proteins mature and where polysaccharides, to be exported, are synthesized.
- The GA receives newly synthesized proteins from the ER and then modifies them chemically.
- The GA collects, prepares, packages, and releases secretory materials to the surface of the cell in vesicles pinched off from the GA. After a secretory vesicle has ruptured and expelled its secretory materials form the cell; its membrane often becomes part of the plasma membrane. This is the last stage in the directional flow of membrane that exists in cells.
- It also produces lysosomes, vesicles that contain powerful hydrolytic enzymes for digesting particles taken into the cell during endocytosis.
- Transfer vesicles carry secretory proteins from the ER to the GA.

- The RER and GA maintain cell membranes.

h. Lysosomes

Lysosomes are membrane-bound sacs of hydrolytic enzymes, which the cell uses to digest macromolecules. Lysosomes come from the endomembrane system. The rough ER makes both the hydrolytic enzymes that are found in lysosomes as well as the membranes that form the lysosome to carry the enzymes. Both products that are made in the RER are then sent to the GA for further processing.The enzymes that are contained in the lysosomes have varying functions. Some hydrolyze proteins, polysaccharides, fats, and nucleic acids. Lysosomes provide a safe way for the cell to digest products without having to deal with the destructive possibilities of hydrolytic enzymes. Lysosomes not only digest food products, but they also aid in the recycling of materials from defective or dying cell parts. Lysosomes also work closely with food vacuoles, which basically hold food products waiting for enzymes from lysosomes to come and continue with the cellular digestion of food. Interestingly enough, when lysosomes have small breaks in their membrane, the neutral environment of the cytosol will make the enzymes that leak out less active, thus limiting their damage to the cell itself. Large leaks, however, do cause autodigestion of the cell. They are capable of killing the bacteria.

i. Peroxisomes

Unlike lysosomes, peroxisomes do not bud from the endomembrane system. They are semi-spherical in shape and often have a granular or crystalline core. The core is probablymade up of a collection of enzymes.The enzymes that are found in peroxisomes take hydrogen from various substrates and bind it to oxygen, making the by-product hydrogen peroxide. In other peroxisomes, oxygen is used to break fatty acids into smaller molecules. The broken acids are then transported to the mitochondria and used as that organelle's source of fuel for cellular respiration. Peroxisomes play an important role in the liver, where they detoxify alcohol by removing hydrogen to form H_2O_2. Although, hydrogen peroxide is toxic, enzymes do exist in peroxisomes that convert it into water.

j. Vacuoles

Vacuoles are membranous sacs that belong to the endomembrane system. Vaculoes are found both all eukaryotic cells. Plant cells have a large central water-filled vacuole enclosed by a membranous extension of the endomembrane system. Vacuoles vary widely in size, shape, content, and function, and are considered in most occurrences to be true organelles of the cytoplasm.

Structure: The structure of vacuoles is very simple. They consist of a single membrane surrounding the liquid or solid contents. There are different kind of vacuole including plant cell central vacuole, food vacuole, autophagic vacuole, and contractile vacuole. A plant cel's central vacuole is formed from the fusion of smaller vacuoles that occur universally in plants. Plant cells are characteristically large and may constitute the greater part of the total size of the cell. The central vacuole of the plant cell may occupy as much as 90% of the volume of the mature cell. The large central vacuole may contain many diverse substances including salts, sugars, organic acids, amino acids, proteins and pigments.

Functions:

- Vacuoles play many roles in the maintenance and functioning of the cell. Vacuoles are primarily storage bins that hold a variety of substances, which in turn determine their function. For example, food vacuole hold food (leucoplasts hold starch). A lysosome(s) will fuse with the vacuole and hydrolytic enzymes will then mix with the food digesting it.
- In plants, some vacuoles are mainly for storing organic compounds. Others hold and/or help with the disposal of metabolic by-products that could be harmful were they to be in the cytosol. The color of flowers is the result of the pigments being stored in the petals' vacuoles.
- The colors of many flowers and some leaves are due to pigments contained in the central vacuole. Plant cells central vacuole can serve as a large lysosome. The central vacuole may also help the plant cell grow in size by absorbing water, and it can store vital chemicals or waste products of cell metabolism.
- Food vacuoles are common in most protozoan and some algae. They form where the surface of the cell contacts a particle of food. The plasma membrane at the surface forms an in-pocketing to engulf the food, which is then detached

from the plasma membrane and becomes a vacuole in the cytoplasm. Lysosome fuses with the food vacuoles, exposing the nutrients to hydrolytic enzymes that digest them.

- Autophagic vacuoles in needed for cell to digest portions of itself. This often happens in response to starvation.

k. Mitochondria

The mitochondria have certain similar features that resemble those of prokaryotes, which are primitive cells that lack a nucleus. Some of the same features that these two have are: circular DNA, and ribosomes. Also, the mitochondria divide independently of the cell through binary fission, which is the method of cell division prokaryotes commonly use. These similarities lead scientists to support what is called the Endosymbiosis hypothesis, which states that millions of years ago, prokaryotes capable of aerobic respiration were engulfed by other, larger prokaryotes but not digested; it may be because they were able to resist digestive enzymes. The two cells then developed a symbiotic relationship the made the host provided the nutrients to carry aerobic respiration, which provided the host cell with ATP. The engulfed cells evolved into mitochondria, which retain the DNA and ribosomes characteristic of their prokaryotic ancestors.

Structure

Structure of the mitochondrion is long and slender, or even bean-shaped, or oval through an electron microscope. They are anywhere from 0.5 micrometer (0.000005 in) to 1 micrometer (0.0001 in) long. The mitochondria have two membranes protecting it on the outside. The outer most layer is smooth, and also contains transport proteins that passes materials in and out of the mitochondrion. The outer compartment, the area between the two membranes, is filled with liquid. The inner membrane is call cristae. It looks like folds and are the sites of ATP synthesis. The structure of cristae is very important. The folds allow more surface area for ATP synthesis to occur. Transport proteins are molecules also known as electron transport chains. The

enzymes that synthesize ATP are in the folds of the cristae. Within the cristae is a liquid filled area known as the inner compartment, or matrix. In the inner compartment is where the enzymes that are used in aerobic respiration.

Function:

- The main function of the mitochondria is to make energy for cellular activity by the process of aerobic respiration. During aerobic respiration glucose is broken down in the cell's cytoplasm to make pyruvic acid, which is transported into the mitochondrion. A sequence of reactions, called Krebs cycle, the pyruvic acid reacts with water to make carbon dioxide and ten hydrogens. The hydrogen atoms are then tranported by coenzymes to the cristae.
- It has the region of electron transport chain (ETC). ETC separates the electron and proton of the hydrogens. The electrons and protons are sent through the ETC to combine with oxygen to make water. Energy is released when electrons flow from the coenzymes to the electron transport chain to the oxygen atoms. This energy is trapped by the ETC. As the electrons travel from one component to another it releases protons from the inner compartment to the outer compartment. The protons can only return by the enzyme ATP synthetase, which is only found in the inner membrane. As protons go back into the inner membrane, ATP synthesis adds a phosphate group to a molecule from the inner membrane, adenosine diphosphate (ADP). Therefore, making it into ATP.

L. Chloroplast

Chloroplast is found in all algae cells and in photosynthetic cells of plants, is the site of photosynthesis. Using solar energy chloroplasts form sugar from carbon dioxide and water. It is not part of the endomembrane system, is a member of a family of organelles called "plastids", which are storage vacuoles. Chloroplasts store chlorophyll on their thylakoid membranes, are lens shaped organelles measuring 2 – 5 microns. Contents are partitioned from the cytosol by an envelope made of two membranes separated by a narrow intermembrane space. Inside the chloroplast is another membranous system arranged into flattened discs called thylakoids. The fluid outside the thylakoids is called the stroma. The thylaloid membrane divides the interior of the chloroplast into two compartments: the tylakoid space and the stroma. Chloroplasts are

mobile and move around the cell with the mitochondria and other organelles along tracks of the cytoskeleton.

9.4 Difference between plant and animal cell

Key difference: Animal cells do not have rigid cell walls and chloroplasts, and they have smaller vacuoles. Plant cells have a rigid cell wall and chloroplasts and have a large central vacuole.

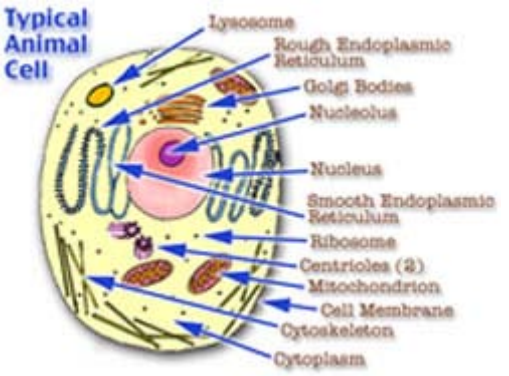

Fig. 9.2 : Typical Animal Cell

Cells are the smallest unit of life and are microscopic in nature, which means that they can't be seen with the naked eye. Cells were discovered in 1665 by Robert Hooke and were named for the small "cells" (rooms) in a monastery. There are two types of cells, the prokaryotic cells and the eukaryotic cells. The prokaryotic cells are self-sufficient in nature, such as bacteria and archaea. On the other hand, the cells of all multi-cellular beings are eukaryotic cells. Both the animal cells and plant cells are eukaryotic cells, but they have different structures.

The main difference between an animal cell and a plant cell is that, plant cells have a cell wall, which the animal cell lacks. The cell wall which is made up of cellulose gives the plant cell rigidity resulting in a fixed, rectangular shape. Animal cells lack the rigidity hence, they tend to have a round and irregular shape. Animal cells tend to vary greatly in appearance. The cell wall allows high pressure to build inside of the plant cell without bursting. Due to this, the plant cell is able to accept large amounts of liquid through osmosis without bursting. Animal cells, which only have a thin

membrane restricting access to the cell, tend to burst if they absorb too much extra water.

Both animal cells and plant cells have a defined nucleus, which contains chromosomes. The nucleus is protected and surrounded by cytoplasm, a watery or gel-like liquid that holds all the organelles in place. The cytoplasm, in turn is held in by the cell membrane.

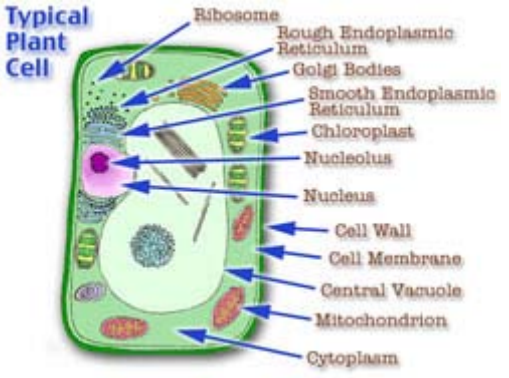

Fig. 9.2 : Typical Plant Cell

However, all animal cells have centrioles whereas only some lower plant forms have it. Also, plant cells tend to have one large central vacuole that can take up to 90% of cell volume. Animal cells tend to have one or more small vacuoles. Vacuoles contain waste materials, water, and nutrients that can be used or secreted as necessary. In plant cells, vacuoles store water and maintain turgidity of the cell. In animal cells, they store water, ions and waste.

Another difference among them is that plant cells have chloroplasts for photosynthesis, which allows them to covert sunlight into food for the cell. Chloroplasts have its own DNA and tend to direct their own work. Animal cells lack chloroplasts and hence this ability, which is why we can't live off of sunlight, sadly.

Table 9.1 : comparison between animal cells and plant cells:

	S.No,	Animal Cell	Plant Cell

Type of cell		Eukaryotic	Eukaryotic
Cell walls	1	No cell walls	Rigid cell walls
Shape	2	Round (irregular shape)	Rectangular (fixed shape)
Organelles	3	Cell membrane Nuclear membrane One or more small vacuoles Centrioles present Cytoplasm Endoplasmic Reticulum Ribosomes Mitochondria Golgi Apparatus Microtubules/ Microfilaments present Flagella in some cells Lysosomes Nucleus Cilia DNA	Cell membrane Cell wall Nuclear membrane Plasmodesma present Large Vacuole Plastids Chloroplast Leucoplast Chromoplast, present Golgi Bodies Ribosome Endoplasmic reticulum Mitochondria Lysosome Cytoplasm Nucleus DNA Chromatin RNA Cytoskeleton

			Nucleolus

9.5 Overview of metabolic processes - Anabolism and Catabolism

An anabolic metabolic pathway is a controlled series of reactions in which smaller, lower energy, less complex molecules are built up into larger, higher energy, and more complex molecules. This requires a net input of energy. Anabolic pathways can consist of both exergonic and endergonic reactions, but the net input of energy will always exceed the net output.

A catabolic metabolic pathway is a controlled series of reactions in which larger, higher energy, and more complex molecules are broken down into smaller, lower energy, less complex molecules. This results in a net release of energy. Catabolic pathways can consist of both exergonic and endergonic reactions, but the net input of energy will always be less than the net output.

9.6 ATP: The Biological Energy Currency for the Cell

In order to function, every machine requires specific parts such as the screws, springs, cams, gears, and pulleys. Likewise, all biological machines must have many well-engineered parts to work. Examples include units called organs such as the liver, kidney and heart. These complex life units are made from still smaller parts called cells which in turn are constructed from yet smaller machines known as organelles. Cell organelles include mitochondria, Golgi complexes, microtubules, and centrioles. Even below this level are other parts so small that they are formally classified as macromolecules (large molecules).

A critically important macromolecule—arguably "second in importance only to DNA"—is ATP. ATP is a complex nano machine that serves as the primary energy currency of the cell. A nanomachine is a complex precision microscopic-sized machine that fits the standard definition of a machine. ATP is the "most widely distributed high-energy compound within the human body". This ubiquitous molecule is "used to build complex molecules, contract muscles, generate electricity in nerves,

and light fireflies. All fuel sources of Nature, all foodstuffs of living things, produce ATP, which in turn powers virtually every activity of the cell and organism. Imagine the metabolic confusion if this were not so: Each of the diverse foodstuffs would generate different energy currencies and each of the great variety of cellular functions would have to trade in its unique currency".

ATP is an abbreviation for adenosine triphosphate, a complex molecule that contains the nucleoside adenosine and a tail consisting of three phosphates. (See Figure for a simple structural formula and a space filled model of ATP.) As far as known, all organisms from the simplest bacteria to humans use ATP as their primary energy currency. The energy level it carries is just the right amount for most biological reactions. Nutrients contain energy in low-energy covalent bonds which are not very useful to do most of kinds of work in the cells.

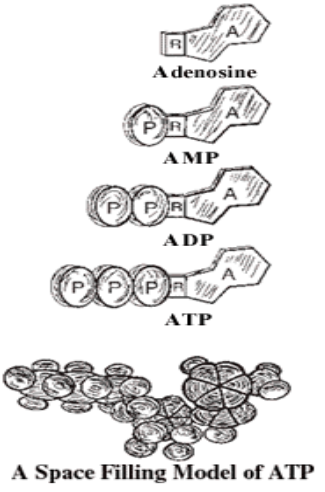

Fig. 9.4 Views of ATP and related structures.

These low energy bonds must be translated to high energy bonds, and this is a role of ATP. A steady supply of ATP is so critical that a poison which attacks any of the proteins used in ATP production kills the organism in minutes. Certain cyanide compounds, for example, are poisonous because they bind to the copper atom in cytochrome oxidase. This binding blocks the electron transport system in the mitochondria where ATP manufacture occurs.

Energy Transfers from ATP

Energy is usually liberated from the ATP molecule to do work in the cell by a reaction that removes one of the phosphate-oxygen groups, leaving adenosine diphosphate (ADP). When the ATP converts to ADP, the ATP is said to be spent. Then the ADP is usually immediately recycled in the mitochondria where it is recharged and comes out again as ATP.

The enormous amount of activity that occurs inside each of the approximately one hundred trillion human cells is shown by the fact that at any instant each cell contains about one billion ATP molecules. This amount is sufficient for that cell's needs for only a few minutes and must be rapidly recycled. Given a hundred trillion cells in the average male, about 10^{23} or one sextillion ATP molecules normally exist in the body. For each ATP the terminal phosphate is added and removed 3 times each minute.

The total human body content of ATP is only about 50 grams, which must be constantly recycled every day. The ultimate source of energy for constructing ATP is food; ATP is simply the carrier and regulation-storage unit of energy. The average daily intake of 2,500 food calories translates into a turnover of a whopping 180 kg (400 lbs) of ATP (Kornberg, 1989, p. 65).

The Structure of ATP

ATP contains the purine base adenine and the sugar ribose which together form the nucleoside adenosine. The basic building blocks used to construct ATP are carbon, hydrogen, nitrogen, oxygen, and phosphorus which are assembled in a complex that contains the number of subatomic parts equivalent to over 500 hydrogen atoms. One phosphate ester bond and two phosphate anhydride bonds hold the three phosphates (PO_4) and the ribose together. The construction also contains a b-N glycoside bond holding the ribose and the adenine together.

Phosphates are well-known high-energy molecules, meaning that comparatively high levels of energy are released when the phosphate groups are removed. Actually, the high energy content is not the result of simply the phosphate bond but the total interaction of all the atoms within the ATP molecule.

Because the amount of energy released when the phosphate bond is broken is very close to that needed by the typical biological reaction, little energy is wasted. Generally, ATP is connected to another reaction—a process called coupling which

means the two reactions occur at the same time and at the same place, usually utilizing the same enzyme complex. Release of phosphate from ATP is exothermic (a reaction that gives off heat) and the reaction it is connected to is endothermic (requires energy input in order to occur). The terminal phosphate group is then transferred by hydrolysis to another compound, a process called phosphorylation, producing ADP, phosphate (P_i) and energy.

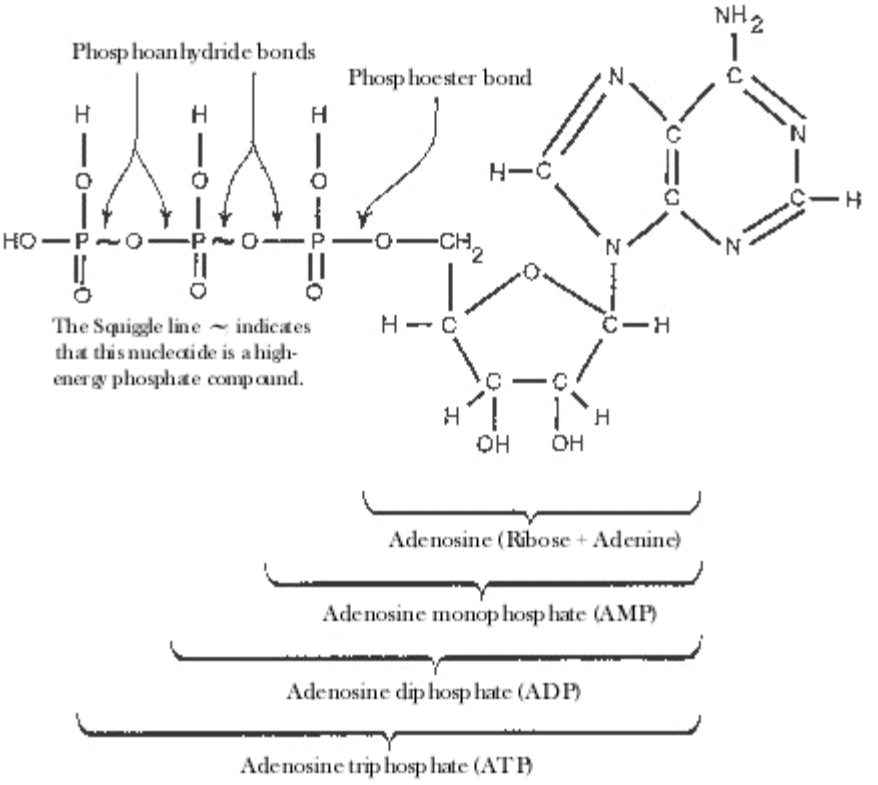

Fig. 9.5 : The two-dimensional stick model of adenosine phosphate family of molecules, showing the atom and bond arrangement.

The self-regulation system of ATP has been described as follows:

The high-energy bonds of ATP are actually rather unstable bonds. Because they are unstable, the energy of ATP is readily released when ATP is hydrolyzed in cellular reactions. Note that ATP is an energy-coupling agent and not a fuel. It is not a store house of energy set aside for some future need. Rather it is produced by one set of reactions and is almost immediately consumed by another. ATP is formed as it is needed, primarily by oxidative processes in the mitochondria. Oxygen is not consumed unless ADP and a phosphate molecule are available, and these do not become

available until ATP is hydrolyzed by some energy-consuming process. Energy metabolism is therefore mostly self-regulating.

ATP is not excessively unstable, but it is designed so that its hydrolysis is slow in the absence of a catalyst. This insures that its stored energy is released only in the presence of the appropriate enzyme.

The Function of ATP

The ATP is used for many cell functions including transport work moving substances across cell membranes. It is also used for mechanical work, supplying the energy needed for muscle contraction. It supplies energy not only to heart muscle (for blood circulation) and skeletal muscle (such as for gross body movement), but also to the chromosomes and flagella to enable them to carry out their many functions. A major role of ATP is in chemical work, supplying the needed energy to synthesize the multi-thousands of types of macromolecules that the cell needs to exist.

ATP is also used as an on-off switch both to control chemical reactions and to send messages. The shape of the protein chains that produce the building blocks and other structures used in life is mostly determined by weak chemical bonds that are easily broken and remade. These chains can shorten, lengthen, and change shape in response to the input or withdrawal of energy. The changes in the chains alter the shape of the protein and can also alter its function or cause it to become either active or inactive.

The ATP molecule can bond to one part of a protein molecule, causing another part of the same molecule to slide or move slightly which causes it to change its conformation, inactivating the molecule. Subsequent removal of ATP causes the protein to return to its original shape, and thus it is again functional. The cycle can be repeated until the molecule is recycled, effectively serving as an on and off switch. Both adding a phosphorus (phosphorylation) and removing a phosphorus from a protein (dephosphorylation) can serve as ATP is used in conjunction with enzymes to cause certain molecules to bond together. The correct molecule first docks in the active site of the enzyme along with an ATP molecule. The enzyme then catalyzes the transfer of one of the ATP phosphates to the molecule, thereby transferring the energy stored in the ATP molecule. Next a second molecule docks nearby at a *second* active

site on the enzyme. The phosphate is then transferred to it, providing the energy needed to bond the two molecules now attached to the enzyme. Once they are bonded, the new molecule is released. This operation is similar to using a mechanical jig to properly position two pieces of metal which are then welded together. Once welded, they are released as a unit and the process then can begin again.

9.7 Origin of life-unique properties of carbon chemical evolution and rise of living systems

There are a great many scientists with intriguing ideas that explain how life may have originated on earth, but there is very little that we know for sure. New hypotheses are being proposed constantly, and old ones reevaluated. By the time this text is published, some of the ideas presented here about the origin of life will surely be obsolete. Thus, the contesting ideas are presented in this chapter in an open-ended format, attempting to make clear that there is as yet no one answer to the question of how life originated on earth. Although recent photographs taken by the Hubble Space Telescope have revived controversy about the age of the universe, it seems clear the earth itself was formed about 4.6 billion years ago. The oldest clear evidence of life—microfossils in ancient rock—are 3.5 billion years old. The origin of life seems to have taken just the right combination of physical events and chemical processes The earth formed as a hot mass of molten rock about 4.6 billion years ago. As the earth cooled, much of the water vapor present in its atmosphere condensed into liquid water, which accumulated on the surface in chemically rich oceans. One scenario for the origin of life is that it originated in this dilute, hot smelly soup of ammonia, formaldehyde, formic acid, cyanide, methane, hydrogen sulfide, and organic hydrocarbons.

Whether at the oceans' edge, in hydrothermal deep-sea vents, or elsewhere, the consensus among researchers is that life arose spontaneously from these early waters less than 4 billion years ago. While the way in which this happened remains a puzzle, one cannot escape a certain curiosity about the earliest steps that eventually led to the origin of all living things on earth, including ourselves. How did organisms evolve from the complex molecules that swirled in the early oceans?

Theories about the Origin of Life

The question of how life originated is not easy to answer because it is impossible to go back in time and observe life's beginnings; nor are there any witnesses. There is testimony in the rocks of the earth, but it is not easily read, and often it is silent on issues crying out for answers. There are, in principle, at least three possibilities:

1. **Special creation.** Life-forms may have been put on earth by supernatural or divine forces.
2. **Extraterrestrial origin.** Life may not have originated on earth at all; instead, life may have infected earth from some other planet.
3. **Spontaneous origin.** Life may have evolved from inanimate matter, as associations among molecules became more and more complex.
4. **Special Creation.** The theory of special creation, that a divine God created life is at the core of most major religions. It is the oldest hypothesis about life's origins, it is also the most widely accepted.
5. **Extraterrestrial Origin.** The theory of **panspermia** proposes that meteors or cosmic dust may have carried significant amounts of complex organic molecules toearth, kicking off the evolution of life. Hundreds of thousands of meteorites and comets are known to haveslammed into the early earth, and recent findings suggestthat at least some may have carried organic materials.Nor is life on other planets ruled out. For example, the discovery of liquid water under the surface of Jupiter'sice-shrouded moon Europa and suggestions of fossils in rocks from Mars lend some credenceto this idea. The hypothesis that anearly source of carbonaceous materialis extraterrestrial is testable, although it has not yet been proven. Indeed,NASA is planning to land on Europa,drill through the surface, and send a probe down to see if there is life.
6. **Spontaneous Origin.** Most scientists tentatively accept the theory of spontaneous origin, that life evolved from inanimate matter. In this view, the force leading to life was selection.

As changes in molecules increased their stability and caused them to persist longer, these molecules could initiate more and more complex associations, culminating in the evolution of cells.

Did Life Originate at the Ocean's Edge?

The more we learn about earth's early history, the more likely it seems that earth's first organisms emerged and lived at very high temperatures. Rubble from the forming solar system slammed into early earth from 4.6 to 3.8 billion years ago, keeping the surface molten hot. As the bombardment slowed down, temperatures dropped. By about 3.8 billion years ago, ocean temperatures are thought to have dropped to a hot 49° to 88°C (120° to 190°F). Between 3.8 and 3.5 billion years ago, life first appeared, promptly after the earth was inhabitable. Thus, as intolerable as early earth's infernal temperatures seem to us today, they gave birth to life. Very few geochemists agree on the exact composition of the early atmosphere. One popular view is that it contained principally carbon dioxide (CO_2) and nitrogen gas (N_2), along with significant amounts of water vapor (H_2O). It is possible that the early atmosphere also contained hydrogen gas (H_2) and compounds in which hydrogen atoms were bonded to the other light elements (sulfur, nitrogen, and carbon), producing hydrogen sulfide (H_2S), ammonia (NH_3), and methane (CH_4).

We refer to such an atmosphere as a reducing atmosphere because of the ample availability of hydrogen atoms and their electrons. In such a reducing atmosphere it would not take as much energy as it would today to form the carbonrich molecules from which life evolved. The key to this reducing atmosphere hypothesis is the assumption that there was very little oxygen around. In an atmosphere with oxygen, amino acids and sugars react spontaneously with the oxygen to form carbon dioxide and water. Therefore, the building blocks of life, the amino acids, would not last long and the spontaneous formation of complex carbon molecules could not occur. Our atmosphere changed once organisms began to carry out photosynthesis, harnessing the energy in sunlight to split water molecules and form complex carbon molecules, giving off gaseous oxygen

molecules in the process. The earth's atmosphere is now approximately 21% oxygen. Critics of the reducing atmosphere hypothesis point out that no carbonates have been found in rocks dating back to the early earth. This suggests that at that time carbon dioxide was locked up in the atmosphere, and if that was the case, then the prebiotic atmosphere would not have been reducing. Another problem for the reducing atmosphere hypothesis is that because a prebiotic reducing atmosphere would have

been oxygen free, there would have been no ozone. Without the protective ozone layer, any organic compounds that might have formed would have been broken down quickly by ultraviolet radiation.

9.8 Introduction to biomolecules, building blocks of bio-macromolecules in existence

Amino acids are the basic building blocks of proteins, and proteins are one of the major kinds of molecules of which organisms are composed. In similar experiments performed later by other scientists, more than 30 different carbon compounds were identified, including the amino acids glycine, alanine, glutamic acid, valine, proline, and aspartic acid. Other biologically important molecules were also formed in these experiments. For example, hydrogen cyanide contributed to the production of a complex ring-shaped molecule called adenine, one of the bases found in DNA and RNA. Thus, the key molecules of life could have formed in the atmosphere of the early earth. Here are some probable reasons of rising macromolecules in earth:

Under frozen oceans. One hypothesis proposes that life originated under a frozen ocean, not unlike the one that covers Jupiter's moon Europa today. All evidence suggests, however, that the early earth was quite warm and frozen oceans quite unlikely.

Deep in the earth's crust. Another hypothesis is that life originated deep in the earth's crust. In 1988 Gunter Wachtershauser proposed that life might have formed as a by-product of volcanic activity, with iron and nickel sulfide minerals acting as chemical catalysts to recombine gases spewing from eruptions into the building blocks of life. In later work he and coworkers were able

to use this unusual chemistry to build precursors for amino acids (although they did not actually succeed in making amino acids), and to link amino acids together to form peptides. Critics of this hypothesis point out that the concentration of chemicals used in their experiments greatly exceed what is found in nature.

Within clay. Other researchers have proposed the unusual hypothesis that life is the result of silicate surface chemistry. The surface of clays have positive charges to

attract organic molecules, and exclude water, providing a potential catalytic surface on which life's early chemistry might have occurred. While interesting conceptually, there is little evidence that this sort of process could actually occur.

At deep-sea vents. Becoming more popular is the hypothesis that life originated at deep-sea hydrothermal vents, with the necessary prebiotic molecules being synthesized on metal sulfides in the vents. The positive charge of the sulfides would have acted as a magnet for negatively charged organic molecules. In part, the current popularity of this hypothesis comes from the new

science of genomics, which suggests that the ancestors of today's prokaryotes are most closely related to the bacteria that live on the deep-sea vents. No one is sure whether life originated at the ocean's edge, under frozen ocean, deep in the earth's crust, within clay, or at deep-sea vents. Perhaps one of these hypotheses will be proven correct. Perhaps the correct theory has not yet been proposed.

When life first appeared on earth, the environment was very hot. All of the spontaneous origin hypotheses assume that the organic chemicals that were the building blocks of life arose spontaneously at that time. How is a matter of considerable disagreement.

The Miller-Urey Experiment

An early attempt to see what kinds of organic molecules might have been produced on the early earth was carried out in 1953 by Stanley L. Miller and Harold C. Urey. In what has become a classic experiment, they attempted to reproduce the conditions at ocean's edge under a reducing atmosphere. Even if this assumption proves incorrect—the jury is still out on this—their experiment is critically important, as it ushered in the whole new field of prebiotic chemistry. To carry out their experiment, they (1) assembled a reducing atmosphere rich in hydrogen and excluding gaseous oxygen; (2) placed this atmosphere over liquid water, which would have been present at ocean's edge; (3) maintained this mixture at a temperature somewhat below 100°C; and (4) simulated lightning by bombarding it with energy in the form of sparks.

They found that within a week, 15% of the carbon originally present as methane gas (CH_4) had converted into other simple carbon compounds. Among these compounds were formaldehyde (CH_2O) and hydrogen cyanide (HCN). These compounds then

combined to form simple molecules, such as formic acid (HCOOH) and urea (NH2CONH2), and more complex molecules containing carbon-carbon bonds, including the amino acids glycine and alanine.

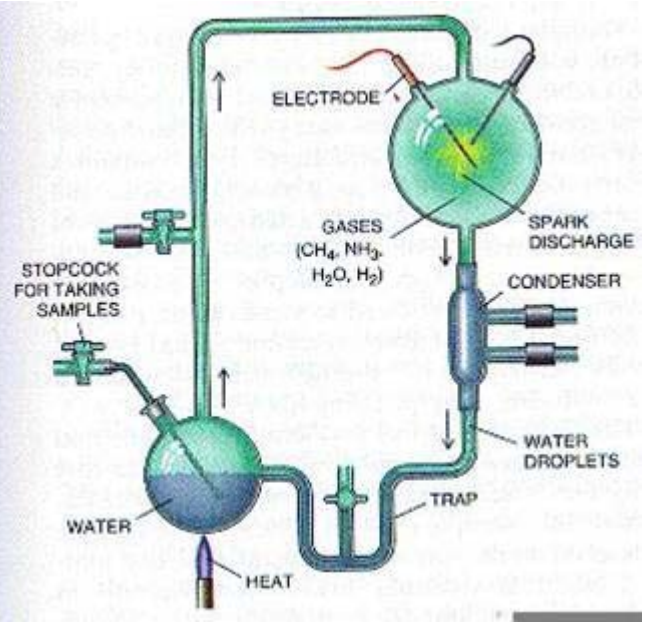

Fig. 9.6 : The Miller-Urey experiment

Procedure: The apparatus consisted of a closed tube connecting two chambers. The upper chamber contained a mixture of gases thought to resemble the primitive earth's atmosphere. Electrodes discharged sparks through this mixture, simulating lightning. Condensers then cooled the gases, causing water droplets to form, which passed into the second heated chamber, the "ocean." Any complex molecules formed in the atmosphere chamber would be dissolved in these droplets and carried to the ocean chamber, from which samples were withdrawn for analysis.

The Path of Chemical Evolution

A raging debate among biologists who study the origin of life concerns which organic molecules came first, RNA or proteins. Scientists are divided into three camps, those that focus on RNA, protein, or a combination of the two. All three arguments have their strong points. Like the hypotheses that try to account for where life originated, these competing hypotheses are diverse and speculative.

An RNA World. The "RNA world" group feels that without a hereditary molecule, other molecules could not have formed consistently. The "RNA world" argument earned support when Thomas Cech at the University of Colorado discovered ribozymes, RNA molecules that can behave as enzymes, catalyzing their own assembly. Recent work has shown that the RNA contained in ribosomes catalyzes the chemical reaction that links amino acids to form proteins. Therefore, the RNA in ribosomes also functions as an enzyme. If RNA has the ability to pass on inherited information and the capacity to act like an enzyme, were proteins really needed?

A Protein World. The "protein-first" group argues that without enzymes (which are proteins), nothing could replicate at all, heritable or not. The "protein-first" proponents argue that nucleotides, the individual units of nucleic acids such as RNA, are too complex to have formed spontaneously, and certainly too complex to form spontaneously again and again. While there is no doubt that simple proteins are easier to synthesize from abiotic components than nucleotides, both can form in the laboratory under the right conditions.

A Peptide-Nucleic Acid World. Another important and popular theory about the first organic molecules assumes key roles for both peptides and nucleic acids. Because RNA is so complex and unstable, this theory assumes there must have been a pre-RNA world where the peptide-nucleic acid (PNA) was the basis for life. PNA is stable and simple enough to have formed spontaneously, and is also a selfreplicator.

Molecules that are the building blocks of living organisms form spontaneously under conditions designed to simulate those of the primitive earth**.** Other chemists have created synthetic nucleotide-likemolecules in the laboratory that are able to replicate.Moving even further, Rebek and his colleagues have createdsynthetic molecules that could replicate and "makemistakes." This simulates mutation, a necessary ingredientfor the process of evolution.

A Peptide-Nucleic Acid World. Another important and popular theory about the first organic molecules assumes key roles for both peptides and nucleic acids. Because RNA is so complex and unstable, this theory assumes there must have been a pre-RNA world where the peptide-nucleic acid (PNA) was the basis for life. PNA is stable and simple enough to have formed spontaneously, and is also a selfreplicator.

9.9 Summary

It is important that different cellular functions be carried out by distinct organelles so that all the functions that need to be done are completed. Each organelle has its own function, even though more than one organelle can work together to function. Hence this unit is designed to understand the cellular structure and functions. The origin of life seems to have taken just the right combination of physical events and chemical processes. Now the student also know that how the earth formed as a hot mass of molten rock about 4.6 billion years ago. As the earth cooled, much of the water vapor present in its atmosphere condensed into liquid water, which accumulated on the surface in chemically rich oceans. One scenario for the origin of life is that it originated in this dilute, hot smelly soup of ammonia, formaldehyde, formic acid, cyanide, methane, hydrogen sulfide, and organic hydrocarbons.

9.10 Self Learning Exercise

Section A

1 Give the name of prokaryotdes nothave calicula.
2 Write down major function of muclolours.
3 Which gases used in philler way experiments.
4 Meation the basis for life that assumed in pei-RNA world.
5 Who discovered callfor the firtttim?
6 Write true.false
   a) Calls are invisible to the nobid human eye
   b) Animalcellshaw a cellwall
   c) Cell wall is hon-living

Section B

1 Diffeerntit between plant and animal cell.
2 Write a short note on ATP molecule.
3 Brifly discuss major thiries about origin of life.
4 Maksa drawing ofmitochondria
5 Plat cells aren more rigid in shope than animal cell justipy the statements.

Section C

1. Describe the function of mitochondria and write down the role of cristae.
2. What evidence supports the argument that RNA evolved first on the early earth? What evidence supports the argument that proteins evolved first?
3. What molecules are thought to have been present in the atmosphere of the early earth? Which molecule that was notably absent then is now a major component of the atmosphere?
4. What characteristics of living things are necessary characteristics (possessed by all living things), and which are sufficient characteristics (possessed only by living things)?

Answer Key (Section A)

1 Mycoplasma

2 Synthesis r-RNA & Ribosomes

3 NH_3, CH_4, H_2 riducning gases

4 Peptide –nucleic acid

5 Robert Hoops (2665)

6 a) True b) false c) true

9.11 References and Suggested Readings

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6. Structure and function ofcellular organelles margie l. stinson

Unit-10 : Carbohydrates I

Structure of Unit

10.0 Objective

After reading this unit you will be able to understand:

- Arrangements of monosaccharides & sugars
- The structure and functions of important derivatives of monosaccharides, disaccharides and polysaccharides.
- The storage forms and structural forms of these polysaccharides.

10.1 Introduction

Carbohydrates are the most abundant biomolecules on earth. Each year, photosynthesis by plants and algae converts more than 100 billion metric tons of CO_2 and H_2O into cellulose and other plant products. Certain carbohydrates (sugar and starch) are a staple of the human diet in most parts of the world, and the oxidation of carbohydrates is the central energy-yielding pathway in most nonphotosynthetic cells. Insoluble carbohydrate polymers serve as structural and protective elements in the cell walls of bacteria and plants and in the connective tissues and cell coats of animals. Other carbohydrate polymers lubricate skeletal joints and provide adhesion between cells. Complex carbohydrate polymers, covalently attached to proteins or lipids, act as signals that determine the intracellular location or the metabolic fate of these

glycoconjugates. This chapter introduces the major classes of carbohydrates and glycoconjugates, and provides a few examples of their many structural and functional roles.

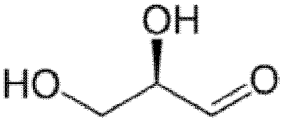
Carbohydrates are polyhydroxy aldehydes or ketones, or substances that yield such compounds on hydrolysis. Most substances of this class have empirical formulas suggesting that they are carbon "hydrates," in which the ratio of C : H : O is 1: 2 : 1. For example, the empirical formula of glucose is $C_6H_{12}O_6$, which can also be written $(CH_2O)_6$ or $C_6(H_2O)_6$. Although many common carbohydrates conform to the empirical formula $(CH_2O)_n$, others do not; some carbohydrates also contain nitrogen, phosphorus, or sulfur.

10.2 Conformation and examples of Monosaccharides

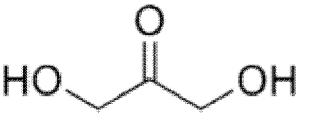
Monosaccharides are the simplest carbohydrates in that they cannot be hydrolyzed to smaller carbohydrates. They are aldehydes or ketones with two or more hydroxyl groups. The general chemical formula of an unmodified monosaccharide is $(C{\bullet}H_2O)n$, literally a "carbon hydrate." Monosaccharides are important fuel molecules as well as building blocks for nucleic acids. The smallest monosaccharides, for which n = 3, are dihydroxyacetone and D- and L-glyceraldehyde. These are some monosaccharides described below :

1. Triose

A triose is a monosaccharide containing three carbon atoms. There are only two trioses, an aldotriose (glyceraldehyde) and a ketotriose (dihydroxyacetone). Trioses are important in respiration. Namely, lactic acid and pyruvic acid are derived from aldotriose and ketotriose, respectively. The D-aldotriose is D-Glyceraldehyde

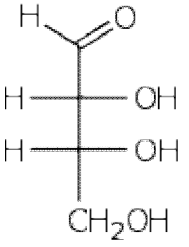


The ketotriose is dihydroxyacetone:

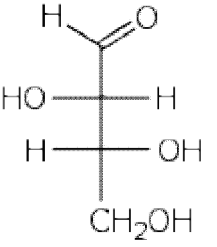


2. Tetrose

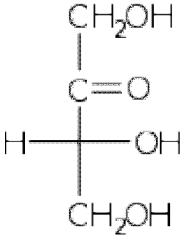
A tetrose is a monosaccharide with 4 carbon atoms. They have either an aldehyde functional group in position 1 (aldotetroses) or a ketone functional group in position 2 (ketotetroses).The aldotetroses have two chiral centers ("asymmetric carbon atoms") and so 4 different stereoisomers are possible. There are two naturally occurring stereoisomers, the enantiomers of erythrose and threose having the D configuration but not the L enantiomers. The ketotetroses have one chiral center and, therefore, two possible stereoisomers: erythrulose (L- and D-form). Again, only the D enantiomer is naturally occurring.



D-Erythrose



D-Threose



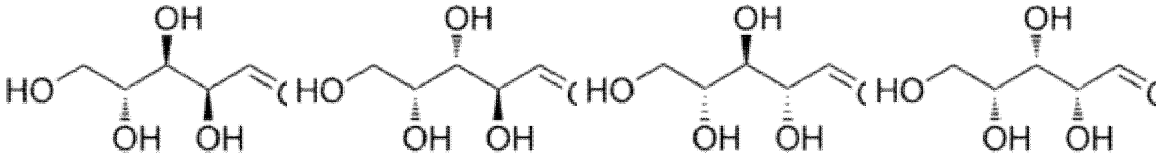
D-Erythrulose

3. Pentose

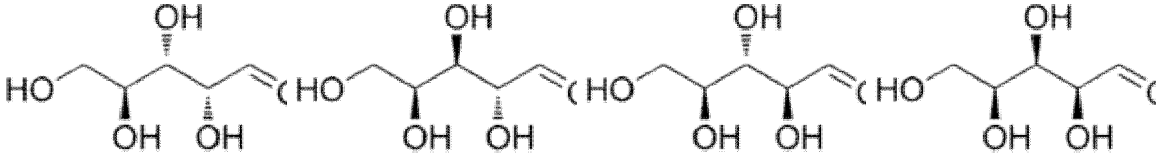
A pentose is a monosaccharide with five carbon atoms. Pentoses are organized into two groups. Aldopentoses have an aldehyde functional group at position 1. Ketopentoses have a ketone functional group in position 2 or 3.The aldehyde and

ketone functional groups in these carbohydrates react with neighbouring hydroxyl functional groups to form intramolecular hemiacetals and hemiketals, respectively. The resulting ring structure is related to furan, and is termed a furanose. The ring spontaneously opens and closes, allowing rotation to occur about the bond between the carbonyl group and the neighbouring carbon atom — yielding two distinct configurations (α and β). This process is termed mutarotation. Ribose is a constituent of RNA, and the related deoxyribose of DNA. A polymer composed of pentose sugars is called a pentosan.

Aldopentoses The aldopentoses have three chiral centers and therefore eight different stereoisomers are possible.

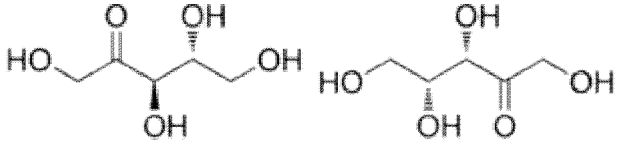


D-Arabinose D-Lyxose D-Ribose D-Xylose

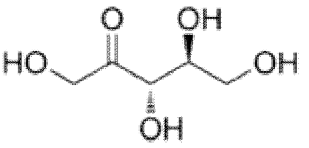
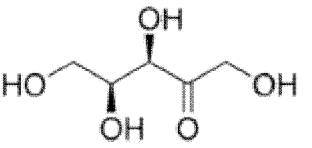


L-Arabinose L-Lyxose L-Ribose L-Xylose

Ketopentoses The 2-ketopentoses have two chiral centers and therefore four different stereoisomers are possible. The 3-ketopentoses are rare.



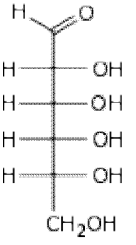
D-Ribulose D-Xylulose

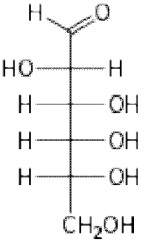
L-Ribulose L-Xylulose

4. Hexose In Biochemistry, a **hexose** is a monosaccharide with six carbon atoms, having the chemical formula $C_6H_{12}O_6$. Hexoses are classified by functional group, with **aldohexoses** having an aldehyde at position 1, and **ketohexoses** having a ketone at position 2.

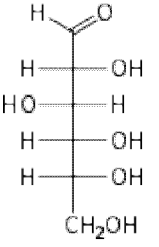
Aldohexoses The aldohexoses have four chiral centres for a total of 16 possible aldohexose stereoisomers (2^4). The D/L configuration is based on the orientation of the hydroxyl at position 5, and does not refer to the direction of optical activity. The eight D-aldohexoses are:



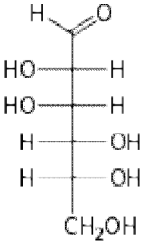
D-Allose



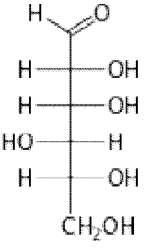
D-Altrose



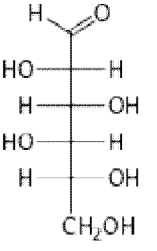
D-Glucose



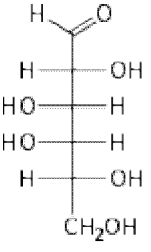
D-Mannose



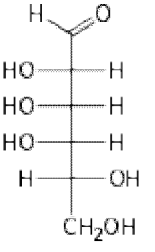
D-Gulose



D-Idose



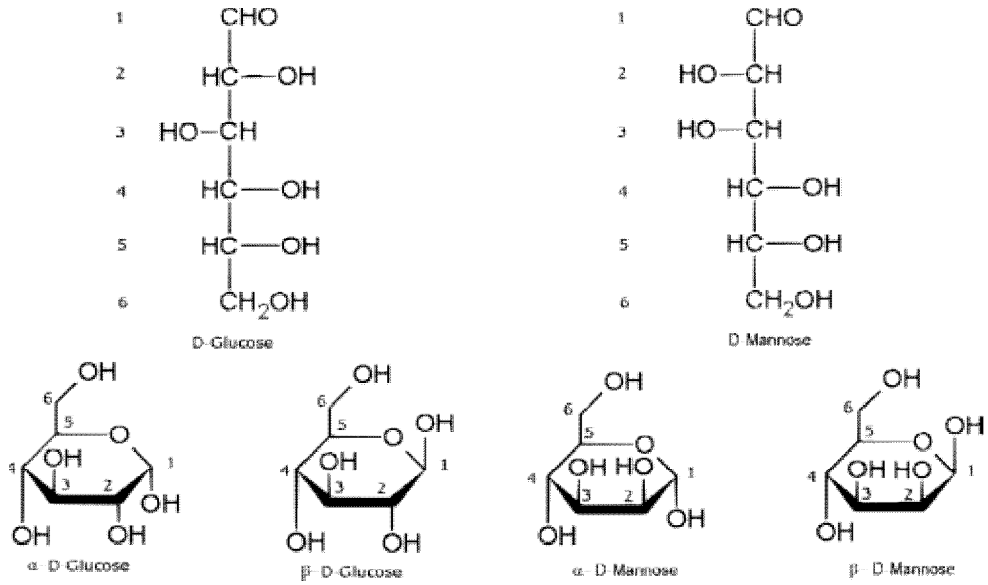
D-Galactose



D-Talose

Of these D-isomers, all except D-altrose are naturally occurring. L-Altrose, however, has been isolated from strains of the bacterium *Butyrivibrio fibrisolvens*.

Cyclic hemiacetals It has been known since 1926 that 6-carbon aldose sugars form cyclic hemiacetals. The diagram below shows the hemiacetal forms for D-glucose and D-mannose.



The numbered carbons in the open-chain forms correspond to the same numbered carbons in the hemiacetal forms. The formation of the hemiacetal causes carbon number 1, which is symmetric in the open-chain form, to become asymmetric in the cyclic version. This means that both glucose and mannose (as well as all the other aldohexoses) each have two cyclic forms. In solution, both of these exist in equilibrium with the open-chain form. The open-chain form, however, does not crystallize. Hence the two cyclic forms become separable when they are crystallized. For example, D-glucose forms an alpha crystal that has specific rotation of +112° and melting point of 146 °C, as well as a beta crystal that has specific rotation of +19° and melting point of 150 °C.

Ketohexoses The ketohexoses have 3 chiral centres and therefore eight possible stereoisomers (2^3). Of these, only the four D-isomers are known to occur naturally. Only the naturally occurring hexoses are capable of being fermented by yeasts.

Mutarotation: The aldehyde and ketone functional groups in these carbohydrates react with neighbouring hydroxyl functional groups to form intramolecularhemiacetals and hemiketals, respectively. The resulting ring

structure is related to pyran, and is termed a pyranose. The ring spontaneously opens and closes, allowing rotation to occur about the bond between the carbonyl group and the neighbouring carbon atom, yielding two distinct configurations (α and β). This process is termed mutarotation. Hexose sugars can form dihexose sugars with a condensation reaction to form a 1,6-glycosidic bond.

5. Heptose A heptose is a monosaccharide with seven carbon atoms. They have either an aldehyde functional group in position 1 (aldoheptoses) or a ketone functional group in position 2 (ketoheptoses). There are few examples of C-7 sugars in nature, among which are:

10.3 Structure and functions of important derivatives of monosaccharides

Sugar derivatives (Structure, occurrence & functions)

Various sugar derivatives, which are essential participants in various reactions, are known and well characterized. Some of them participate in the transformations of simple sugars to other simple sugars or sugar derivatives. Here properties of some of the important derivatives of the sugars will be presented.

1. Derivatives of Monosaccharide

Monosaccharide undergoes a number of reactions to form biologically important derivatives. Three common types of monosaccharide derivatives are amino sugars, carboxylic acid sugars and sugar alcohols.

A. Amino sugars and N-acetylated sugars

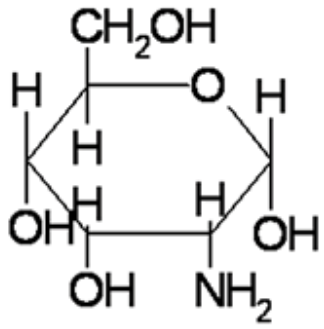
An amino sugar contains an amine group in place of a hydroxyl group. Derivatives of amine containing sugars, such as N-acetylglucosamine and sialic acid, while not formally containing an amine, are also considered amino sugars. N-acetylated sugars are derivatives of amino sugars. The N in "N-acetyl" refers to the fact that the acetyl group is bonded to the nitrogen. The acetyl group here replaces one of the amine hydrogens. Connective tissue polysaccharides, such as cartilage, contain amino sugar and N-acetyl sugar monomers.

Significant amounts of glucosamine have been found in the intestinal mucin, which binds chloresterol, thereby limiting its absorption. Glucosamine has proven to decrease insulin secretion without suppressing liver glucose production.

i) Glucosamine

Systematic name: **2-Amino-2-deoxy-D-glucose**

Molecular Formula: $\mathbf{C_6H_{13}NO_5}$



Glucosamine is an amino sugar derived from glucose, produced in the body from the sugar glucose and the amino acid glutamine through the action of the enzyme glucosamine synthetase.

It's used as a precursor in the biochemical synthesis of glycosylated proteins and lipids. Glucosamine stimulates the synthesis of proteoglycans, glycosaminoglycans (more commonly referred to as mucopolysaccharides), and collagen. It therefore plays a role in the formation of cartilage and the cushioning synovial fluid between the joints; hence it's classified as "chondroprotective" agent. Supplementary glucosamine can be an important source of this vital amino sugar for those with reduced capacity to produce glucosamine, such as the elderly.

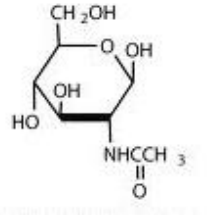
Glucosamine acts as an immune modulator with antitumor and antiviral properties, as well as it has some activity against HIV. Oral glucosamine is commonly used for the treatment of osteoarthritis. Since glucosamine is a precursor for glycosaminoglycans, and glycosaminoglycans are a major component of joint cartilage, supplemental glucosamine may help to rebuild cartilage and treat arthritis. Deficiencies or malfunctions in the ability to metabolize this sugar have been linked to diseases of the bowel and bladder. Glucosamine has been shown to help repair the mucosal-lining defensive barrier called the glycosaminoglycan layer (GAG). Defects in the GAG layer have been implimented in Crohn's disease, ulcerative colitis, and interstitial cystitis.

ii) N-Acetylglucosamine (N-Acetyl-D-Glucosamine, or GlcNAc, or NAG)

Systematic name: **2-(Acetylamino)-2-deoxy-D-glucose**

Molecular formula: $\mathbf{C_8H_{15}NO_6}$

It is a monosaccharide derivative of glucose. Chemically it is an amide between glucosamine and acetic acid; and is significant in several biological systems.



N-Acetylglucasamine

N-acetylglucosamine is part of a biopolymer in the bacterial cell wall, built from alternating units of GlcNAc and N-acetylmuramic acid (MurNAc), cross-linked with oligopeptides at the lactic acid residue of MurNAc. This layered structure is called peptidoglycan. GlcNAc is the monomeric unit of the polymer chitin, which forms the outer coverings of insects and crustaceans. GlcNAc is also of note in neurotransmission, where it is thought to be an atypical neurotransmitter functioning in nocioceptive (pain) pathways.

N-acetylglucosamine (GlcNAc) carries out important roles in a broad range of cells from bacteria to humans. One aspect of GlcNAc function is to mediate cellular signaling. In bacteria, GlcNAc induces components that are important for colonization of human hosts, including fimbrins that mediate adhesion to host cells, multidrug exporter genes and Curli fibers that promote biofilm formation. In mammals, GlcNAc is a key sensor of nutrient status that is involved in insulin signaling, cell cycle control, and other essential processes.

N-AcetylGlucosamine (or glucosamine its metabolic derivative) helps in immune system functioning particular in regards to HIV and tumors. In addition, GlcNAc decreases pain and inflammation and increases range of motion in osteoarthritis patients and helps repair cartilage. GlcNAc has also been implicated as an aid to learning during certain mice studies. The saccharide or its derivative is found in the brains of mammal implying a relation to nerve functioning for learning.

In regards to disease processes, N-acetylglucosamine has been linked to Crohn's disease, interstitial cystitis and ulcerative colitis. Deficiencies of GlcNAc have

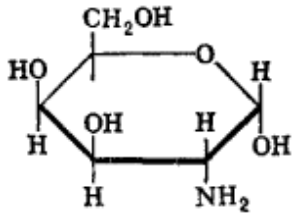
been linked to diseases of the bowels and bladder. Those with colon cancer show particular deficiencies.

N-acetylglucosamine has been shown to repair the mucosal-lining defensive barrier called the glycosaminoglycan layer (GAG). According to animal studies, N-acetylglucosamine helped prevent the flu virus and herpes virus from occurring. N-acetylglucosamine also has a hand in limiting chloresterol absorption and decreasing insulin secretion. It has been proposed as a treatment for autoimmune diseases.

iii) Galactosamine

Systematic name: ***2-Amino-2-deoxy-D-galactose***

Molecular formula: $\mathbf{C_6H_{13}NO_5}$



Galactosamine

Galactosamine is a hexosamine derived from galactose.

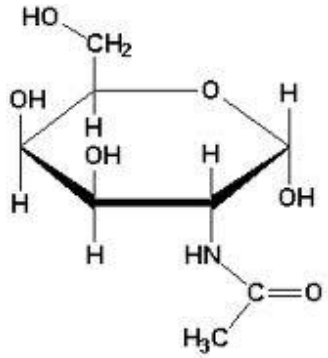
This amino sugar is a constituent of some glycoprotein hormones such as follicle-stimulating hormone (FSH) and luteinizing hormone (LH).

iv) N-Acetylgalactosamine (GalNAc, 2-Acetamido-2-deoxy-D-galactopyranose or N-Acetyl-D-galactosamine)

Systematic name: ***2-(Acetylamino)-2-deoxy-D-galactose***

Molecular formula: $\mathbf{C_8H_{15}NO_6}$

It is a monoacetylaminosaccharide derivative of galactose. Chemically it is an amide between galactosamine and acetic acid



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In humans it is the terminal carbohydrate forming the antigen of blood group A. N-Acetylgalactosamine is necessary for intercellular communication, and is concentrated in sensory nerve structures of both humans and animals. This saccharide may inhibit the growth of some tumors. Lower than normal levels of this sugar have been found in patients with heart disease implying that these conditions may be reversed if a supplementation of N-acetylgalactosamine were to be added to the diet. It appears that this sugar plays a role in joint function, scavenging harmful radicals like superoxide generated during the course of action of macrophage in inflammatory response.

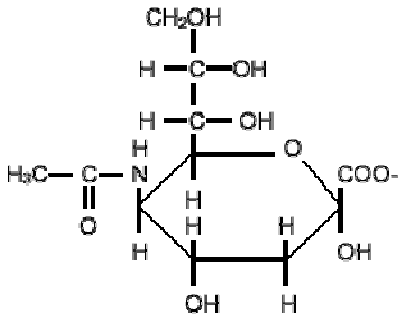
Functions: N-acetylgalactosamine also seems to play an important role in the immune system. Contained in macrophages and neutrophils, it may play a significant role in the etiolology of joint inflammation and could be important in such conditions as rheumatoid arthritis. N-acetylgalactosamine is localized in the golgi apparatus and ER – found in cell organelles and associated with synthesis of various proteins and enzymes. It is also found on the surface of cortical neurons and involved in synaptic function of the central nervous system and peripheral brain, suggesting its importance in nerve function. N-acetylgalactosamine is also concentrated in other sensory nerve structures especially in the retina, photoreceptors, optic nerve, and the epithelial pigment of the eyes of both humans and animals. This suggests that it may be extremely important for optimal vision. N- acetylgalactosamine is distributed to several other tissues, suggesting that it is important in the functional role of these tissues. Some of these tissues include the ducts of the kidney, the testes, the skin, and a variety of other structures including sweat glands, some blood vessel cells, and hair follicles. It is known that concentrations of N-acetylgalactosamine decrease with age.

v) Neuraminic acid & Sialic acid

Systematic name: **(Neuraminic acid)** ***5-amino-3,5-dideoxy- D-glycero-D-galacto-non-2-ulosonic acid***

Molecular formula: $C_9H_{17}NO_8$

Neuraminic acid is a 9-carbon monosaccharide. It may be theoretically visualized as the aldol-condensation product of pyruvic acid and D-mannosamine (2-amino-2-deoxy-mannose). The N- or O-substituted derivatives of neuraminic acid are collectively and commonly known as sialic acids, the predominant one being N-acetylneuraminic acid. The amino group bears either an acetyl or a glycolyl group. The hydroxyl substituents may vary considerably: acetyl, lactyl, methyl, sulfate and phosphate groups have been found.



Neuraminic Acid

Neuraminic acid does not occur naturally, but many of its derivatives are found widely distributed in animal tissues and in bacteria, especially in glycoproteins and gangliosides. N-acetylneuraminic acid (is widely distributed throughout the tissues of the body (brain, adrenal glands, and the heart). It is found mainly in the glycoproteins and glycolipids and also in many fluids including saliva, urine, cerebrospinal fluid, amniotic fluid, and breast milk.

It is important for brain development, learning, memory and cognitive performance. Cancer cells that can metastasize often have a lot of sialic acid rich glycoproteins. This helps these late stage cancer cells enter the blood stream.

During pregnancy, N-acetylneuraminic acid levels are raised suggesting its importance in the immune system along with other physical and mental development systems for infants. Disrupted N-acetylneuraminic acid metabolisms are seen in infants who are developmentally delayed, show a coarsening of facial

features, have enlarged livers and/or spleens and fail to produce skin and hair pigmentation.

Like the other glyconutrients, N-acetylneuraminic acid is important for cellular communication and is an immune system modulator. As an immune modulator, N-acetylneuraminic acid affects the viscosity of mucus, which in turn repels viruses, bacteria and other pathogens. In fact, N-acetylneuraminic acid has been shown to be effective in defending against viruses that cause hepatitis, viral pneumonia and cold sores as well as the common cold. This in turn decreased the severity of asthmatic bronchial spasms and allergic reactions as well. N-acetylneuraminic acid is rapidly expelled from the kidneys and bladder. N-acetylneuraminic acid also lowers the LDL (bad cholesterol) levels and influences blood coagulation.

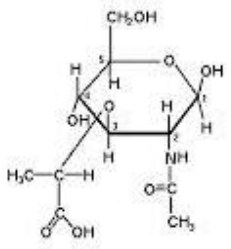
Sialic acid-rich oligosaccharides on the glycoconjugates found on surface membranes help keep water at the surface of cells. The sialic acid-rich regions contribute to creating a negative charge on the cells surface. Since water is a polar molecule, it has a partial positive charge on both hydrogen molecules, it is attracted to cell surfaces and membranes. This also contributes to cellular fluid uptake. Subjects with Sjogren's syndrome and alcohol dependency show markedly low levels of N-acetylneuraminic acid.

vi) N-Acetylmuramic acid, or MurNAc

Systematic name: ***(R)-2-(acetylamino)-3-O-(1-carboxyethyl)-2-deoxy-D-glucose***

Molecular formula: $\mathbf{C_{11}H_{19}NO_8}$

It is the ether of lactic acid and N-acetylglucosamine.



N-Acetylmuramic Acid

It is part of a biopolymer in the bacterial cell wall, built from alternating units of N-acetylglucosamine (GlcNAc) and N-acetylmuramic acid (MurNAc) linked by

β(1⟶4) glycosidic bonds, cross-linked with oligopeptides at the lactic acid residue of MurNAc. This layered structure is called peptidoglycan. (see below for specific linkages).

vii) Peptidoglycan

Peptidoglycan, also known as murein, is a polymer consisting of sugars and amino acids that forms a mesh-like layer outside the plasma membrane of eubacteria. Structurally, it consists of linear chains of two alternating amino sugars, *N*-acetylglucosamine (GlcNAc or NAG) and *N*-acetylmuramic acid (MurNAc or NAM). The alternating sugars are connected by a β (1, 4) - glycosidic bond.

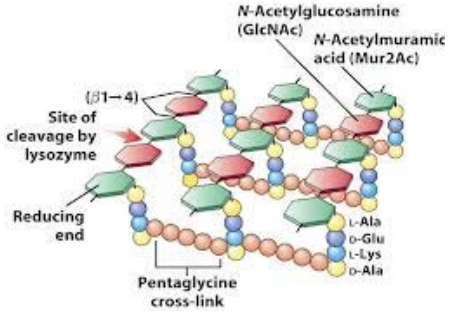
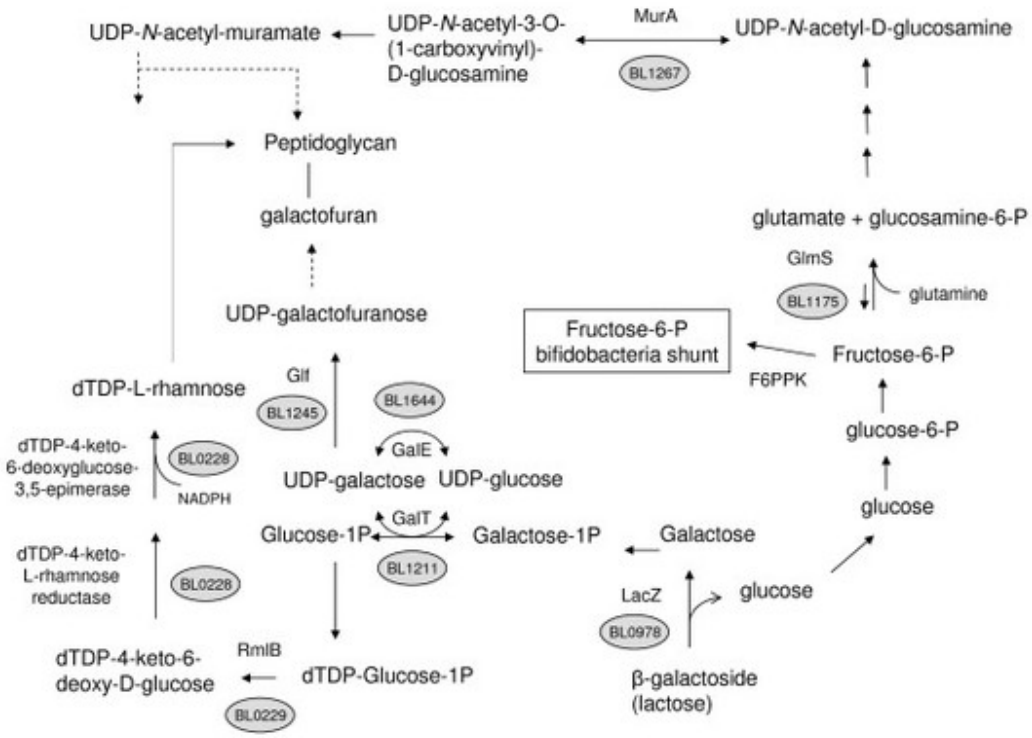


Fig. 10.1 : Structure of Peptidoglycan layer

Each MurNAc is attached to a short (4- to 5-residue) amino acid chain via its 3rd carbon, normally containing D-alanine, D-glutamic acid, and mesodiaminopimelic acid (Fig. 40b). These three amino acids do not occur in proteins and help protect against attacks by most peptidases. Cross-linking between amino acids in different linear amino sugar chains by an enzyme known as transpeptidase result in a 3-dimensional structure that is strong and rigid. The specific amino acid sequence and molecular structure vary with the bacterial species The peptide chain can be cross-linked to the peptide chain of another strand forming the 3D mesh-like layer. Some Archaea have a similar layer of pseudopeptidoglycan.



Schematic representation of peptidoglycan

Peptidoglycan serves a structural role in the bacterial cell wall, giving structural strength, as well as counteracting the osmotic pressure of the cytoplasmbinary fission Gram-positive bacteria nmS-layer. A common misconception is that peptidoglycan gives the cell its shape; however, whereas peptidoglycan helps maintain the structure of the cell. Peptidoglycan is also involved in during bacterial cell reproduction.The peptidoglycan layer is substantially thicker in (20 to 80) than in Gram-negative bacteria (7 to 8 nm), with the attachment of the . Peptidoglycan forms around 90% of the dry weight of Gram-positive bacteria but only 10% of Gram-negative strains. In Gram-positive strains, it is important in attachment roles and sterotyping purposes. For both Gram-positive and Gram-negative bacteria, particles of approximately 2 nm can pass through the peptidoglycan.

B. Carboxylic acid sugars

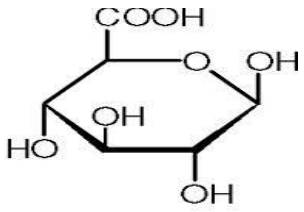
The carbonyl group at C1 of monosaccharides may be oxidized to generate aldonic acids while C-6 oxidation results in uronic acids.

i) Glucuronic acid

Systemic name: ***D-Glucuronic Acid***

Molecular formula: $\mathbf{C_6H_{10}O_7}$

Glucuronic acid is a carboxylic acid. Its structure is similar to glucose. However glucuronic acid's sixth carbon is oxidized to a carboxylic acid. The salts of glucuronic acid are known as glucuronates; the anion $C_6H_9O_7^-$ is the glucuronate ion.



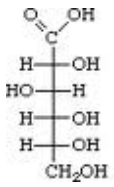
Glucuronic acid is highly soluble in water. In the animal body, glucuronic acid is often linked to poisonous substances, mainly in the liver, to allow for subsequent elimination, and to hormones to allow for easier transport. These linkages involve O-glycosidic bonds. The process is known as glucuronidation, and the resulting substances are known as glucuronides (or glucuronosides).

ii) Gluconic acid

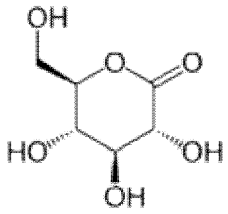
Systemic name***: D-Gluconic Acid***

Molecular formula: $\mathbf{C_6H_{12}O_7}$

Gluconic acid is the carboxylic acid formed by the oxidation of the first carbon of glucose and. When dissolved in water, it forms the gluconate ion $C_6H_{11}O_7$; the salts of gluconic acid are also known as gluconates. The chemical structure of gluconic acid consists of a six-carbon chain with five hydroxyl groups terminating in a carboxyl group (Fig.). This latter group can lose a hydrogen ion and thus turns the molecule into an acid. In aqueous solution, some gluconic acid molecules will convert to the cyclic ester Glucono delta lactone (Fig.), and the two exist in equilibrium.



Gluconic acid



Glucono delta lactone

Occurrence & Uses: Gluconic acid occurs naturally in fruit, honey, kombucha tea and wine and is used as a food additive, an acidity regulator. It is a strong chelating agent, especially in alkaline solution.

C. Sugar phosphates

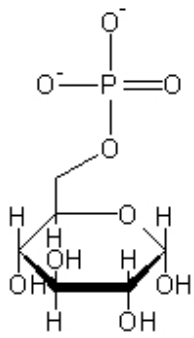
Phosphorylated sugars are another important class of derivatives of sugars. At the normal pH of a cell, most of the hydroxyl groups (OH) on the phosphates are ionized (O-). The hydroxyl group of sugars form ester bond with phosphates.

Phosphorylated sugars are key intermediates in energy generation and biosynthesis. Sugar phosphates are intermediates in monosaccharide metabolism and are building blocks for energy-providing nucleotides and for nucleic acids. Some important sugar phosphates are listed below.

i) Glucose 6 phosphate

Molecular formula: $\mathbf{C_6H_{13}O_9P}$

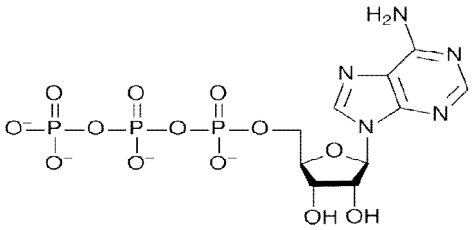
Glucose 6-phosphate (Fig. 44) (also known as Robison ester) is glucose sugar phosphorylated on carbon 6. This compound is very common in cells as the vast majority of glucose entering a cell is phosphorylated in this way. Because of its prominent position in cellular chemistry, glucose 6-phosphate has many roles within the cell. It lies at the start of two major metabolic pathways: Glycolysis and Pentose phosphate pathway. In addition, it may also be converted to glycogen or starch for storage. This storage is in the liver and muscles in the form of glycogen for most multicellular animals, and in intracellular starch or glycogen granules for most other organisms.



Glucose 6 phosphate

ii) Adenosine triphosphate (ATP)

Molecular formula: $C_{10}H_{16}N_5O_{13}P_3$



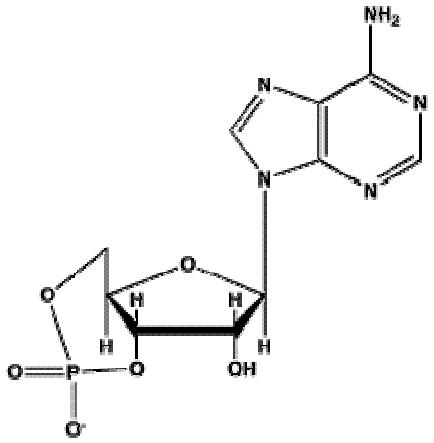
Adenosine 5'-triphosphate (ATP) (Fig.) is a multifunctional nucleotide that is most important as a "molecular currency" of intracellular energy transfer. In this role, ATP transports chemical energy within cells for metabolism. It is produced as an energy source during the processes of photosynthesis and cellular respiration and consumed by many enzymes and a multitude of cellular processes including biosynthetic reactions, motility and cell division. In signal transduction pathways, ATP is used by kinases that phosphorylate proteins and lipids, as well as by adenylate cyclase, which uses ATP to produce the second messenger molecule cyclic AMP.

iii) Cyclic Adenosine MonoPhosphate (cAMP)

Molecular formula: $C_{10}H_{12}N_5O_6P$

Cyclic adenosine monophosphate (cAMP, cyclic AMP or 3'-5'-cyclic adenosine monophosphate) is a molecule that is important in many biological processes (Fig. 46); it is derived from adenosine triphosphate (ATP). cAMP is synthesised from

ATP by adenylyl cyclase which is located in the cell membranes. Adenylyl cyclase is activated by the hormones glucagon and epinephrine. cAMP is a second messenger, used for intracellular signal transduction, such as transferring the effects of hormones like glucagon and adrenaline, which cannot get through the cell membrane. Its purposes include the activation of protein kinases and regulating the effects of adrenaline and glucagon. It is also used to regulate the passage of Ca^{2+} through ion channels.



Cyclic Adenosine monophosphate

E. Glycosides

Glycosides are formed by elimination of water between the anomeric hydroxyl of a cyclic monosaccharide and the hydroxyl group of another compound. Glycosides do not undergo mutarotation in the absence of an acid catalyst, so they remain locked in the α or β configuration. (Remember that the hydroxyl group on the anomeric carbon can undergo a change in orientation from the α to β position, or vice versa. This change is called mutarotation). Glycosidic bonds are very common in plant and animal tissues. Many glycosides are known. Some, such as ouabain or amygdalin are very poisonous. Others, such as the common oligosaccarides and polysaccharides found in our cells, are not.

i)Ouabain

Structure: Ouabain is also known as G-Strophanthin, Acocantherin, Purostrophan, Astrobain, Gratibain, Kombetin, Rectobaina, Solufantina, Strodival. It is a cardioactive glycoside consisting of rhamnose and ouabagenin, obtained from the seeds of Strophanthus gratus and other plants of the Apocynaceae; used like digitalis. it is commonly used in cell biological studies as an inhibitor of the na(+)-k(+)-exchanging ATPase

Molecular Formula: $C_{29}H_{44}O_{12}$

Molecular Weight: 584.65246

Function: Ouabain is a glycoside poison that binds to and inhibits the action of the Na^+/K^+ pump in the cell membrane. The Na^+/K^+ pump is essential for maintaining the balance of these ions across cell walls. Ouabain and digitoxin are used to stimulate the heart muscle. They work by binding to the Na^+/K^+ ATPase and inhibiting its action. The result of this is that Na^+ leaks back into the cell. When this happens, the cell tries to maintain the osmotic balance pumping the sodium out with the Na^+/Ca^{2+} pump. This pumps Ca^{2+} into the cell, which triggers muscle contraction.

ii)Amygdalin

Amygdalin is an O-linked glycoside found in the seeds of bitter almonds. Its poisonous nature results from the release of cyanide upon hydrolysis. **Amygdalin** is commonly called Laetrile.

Structure:

Molecular formula - $C_{20}H_{27}NO_{11}$

The chemical structure of amygdalin is well established and is clearly recorded in the *Merck Index*, (9^{th} Ed., p. 81, 1976) as D(1)-mandelonitrile-b -D-glucosido-6-b -D-glucoside (other synonyms: (R-a-[(6-O-b -D-Glocopyranosyl-b -D-

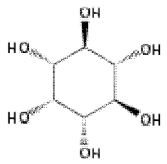
glucopyranosyl)] oxy benzeneacetronitrile; amygdaloidal; mandelanitrile-b -gentiobioside). The empirical formula is C20 H27 NO11. The molecular weight is 457.22. The element composition is C 52.51%, H 5.959%, N 3.06%, O 38.47%.

F. Myoinositol

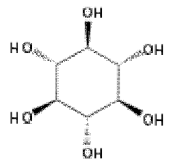
Inositol or cyclohexane-1,2,3,4,5,6-hexol is a chemical compound with formula $C_6H_{12}O_6$ or $(\text{-CHOH-})_6$, a sixfold alcohol (polyol) of cyclohexane. It exists in nine possible stereoisomers, of which the most prominent form, widely occurring in nature, is cis-1,2,3,5-trans-4,6-cyclohexanehexol, or myo-inositol (former name meso-inositol).Inositol is a carbohydrate, though not a classical sugar. It has a taste which has been assayed at half the sweetness of table sugar (sucrose).

Structure:

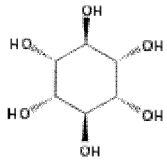
The isomer myo-inositol is a meso compound possessing an optically inactive plane of symmetry through the molecule, and meso-inositol is an obsolete name that refers to myo-inositol. Besides myo-inositol, the other naturally occurring stereoisomers (though in minimal quantities) are scyllo-, muco-, D-chiro-, and neo-inositol. The other possible isomers are L-chiro-, allo-, epi-, and cis-inositol. As their name denotes, the two chiro inositols are the only pair of inositol enantiomers, but they are enantiomers of each other, not of myo-inositol.



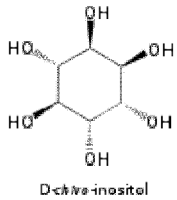
myo-



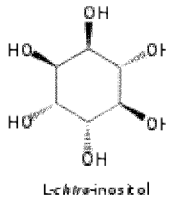
scyllo-

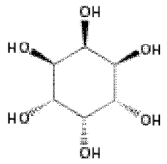


muco-

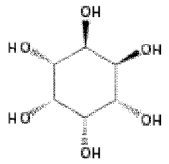


chiro-

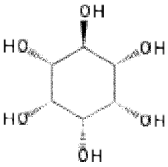




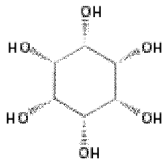
neo-



allo-



epi-



cis-

In its most stable conformational geometry, the myo-inositol isomer assumes the chair conformation, which puts the maximum number of hydroxyls to the equatorial position, where they are farthest apart from each other. In this conformation the natural myo isomer has a structure in which five of the six hydroxyls (the 1st, 3rd, 4th, 5th, and 6th) are equatorial, whereas the 2nd hydroxyl group is axial.

Synthesis: myo-Inositol is synthesized from glucose-6-phosphate (G-6-P) in two steps. First, G-6-P is isomerised by an inositol-3-phosphate synthase enzyme (called ISYNA1) to myo-inositol 1-phosphate, which is then dephosphorylated by an inositol monophosphatase enzyme (called IMPase 1) to give free myo-inositol. In humans most inositol is synthesized in the kidneys, in typical amounts of a few grams per day.

Function:

Inositol and some of its mono and polyphosphates function as the basis for a number of signaling and secondary messenger molecules. They are involved in a number of biological processes, including:

- Insulinsignal transduction
- Cytoskeleton assembly
- Nerve guidance (Epsin)
- Intracellularcalcium (Ca^{2+}) concentration control
- Cell membrane potential maintenance
- Breakdown of fats and reducing blood cholesterol
- Gene expression

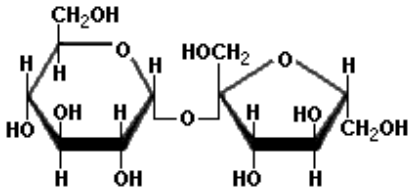
10.4 Disaccharides

A disaccharide consists of two monosaccharides joined by an O-glycosidic bond. Disaccharides can be homo- and heterodisaccharide (Fig. 5). Three most abundant disaccharides are sucrose, lactose, and maltose. In sucrose the anomeric carbon atoms of a glucose unit and a fructose unit are joined. Lactose, the disaccharide of milk, consists of galactose joined to glucose by a β (1⟶4) glycosidic linkage. In maltose, α (1⟶4) glycosidic linkage joins two glucose units. Sucrose and lactose are heterosaccharides and maltose is homosaccharide.

A. Sucrose

Systematic name: ***D-glucopyranosyl-(1↔2)-β-D-fructofuranoside***

Molecular formula: $C_{12}H_{22}O_{11}$



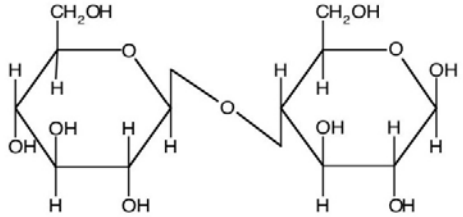
Sucrose (common name: table sugar, also called saccharose) is a disaccharide (glucose + fructose) best known for its role in human nutrition and is formed by plants but not by other organisms such as animals. Sucrose is an easily assimilated macronutrient that provides a quick source of energy to the body, provoking a rapid rise in blood glucose upon ingestion. However, pure sucrose is not normally part of a human diet balanced for good nutrition, although it may be included sparingly to make certain foods more palatable.

Sucrose, as a pure carbohydrate, has an energy content of 3.94 kilocalories per gram (or 17 kilojoules per gram). When a large amount of foods that contain a high percentage of sucrose is consumed, beneficial nutrients can be displaced from the diet, which can contribute to an increased risk for chronic disease such as defect in glucose metabolism or diabetes mellitus.

B. Cellobiose

Systemic name: *4-O- β-D-glucopyranosyl-D-glucose*

Molecular formula $C_{12}H_{22}O_{11}$



Cellobiose

Cellobiose is a disaccharide derived from the condensation of two glucose molecules linked in a β(1⟶4) bond. It can be hydrolyzed by bacteria or cationic ion exchange resins to give glucose. Cellobiose has eight free alcohol (COH) groups and three ether linkages, which give rise to strong inter- and intra-molecular hydrogen bonds.

C. Trehalose

Systemic name: *α-D-glucopyranosyl- α-D-glucopyranoside*

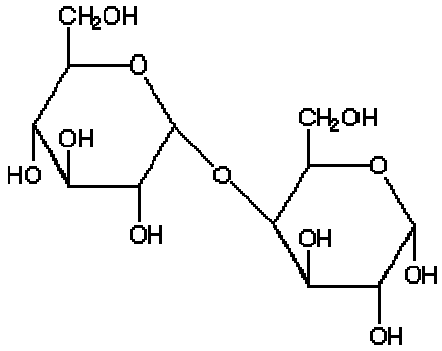


Fig. Trehalose

Molecular formula: $C_{12}H_{22}O_{11}$

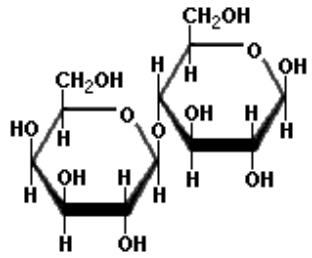
Trehalose, also known as mycose, is a natural alpha-linked disaccharide formed by an α, α-1, 1-glucoside bond between two α-glucose units (Fig.). It can be synthesised by fungi, plants, and invertebrate animals. It is implicated in anhydrobiosis — the ability of plants and animals to withstand prolonged periods of desiccation. It has high water retention capabilities and is used in food and cosmetics. The sugar forms a gel phase as cells dehydrate, which prevents disruption of internal cell organelles by effectively splinting them in position. Rehydration then allows normal cellular activity to be resumed without the major, lethal damage that would normally follow a dehydration/reyhdration cycle. Trehalose has the added advantage of being an antioxidant. Trehalose can be found in nature, animals, plants, and microorganisms. In animals, trehalose is prevalent in shrimp, and also in insects, including grasshoppers, locusts, butterflies, and bees, in which blood-sugar is trehalose. The trehalose is then broken down into glucose by the catabolic enzyme trehalase for use. In plants, the presence of trehalose is seen in sunflower seeds, selaginella mosses, and sea algae. Within the fungus family, it

is prevalent in mushrooms shiitake (*Lentinula edodes*), maitake (*Grifola fondosa*), nameko (*Pholiota nameko*), and Judas's ear (*Auricularia auricula-judae*) contain 1% to 17% percent of trehalose in dry weight form. Trehalose is found in such microorganisms as baker's yeast and wine yeast. When tardigrades (water bears) dry out, the glucose in their bodies changes to trehalose when they enter a state called cryptobiosis - a state wherein they appear dead. However, when they receive water, they revive and return to their metabolic state.

D. Lactose

Systemic name: ***4-O- β-D-galactopyranosyl-D-glucose***

Molecular formula: $\mathbf{C_{12}H_{22}O_{11}}$



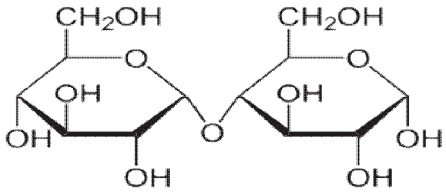
Lactose (also referred to as milk sugar) is a sugar, which is found most notably in milk (Fig**.**). Lactose makes up around 2–8% of milk (by weight). The name comes from the Latin word for milk, plus the -ose ending used to name sugars. Lactose is the only significant sugar or carbohydrate of animal origin. Lactose is a disaccharide that consists of β-D-galactose and β-D-glucose fragments bonded through a β(1⟶4) glycosidic linkage.

An enzyme, lactase, is essential for digestion of lactose, and a majority of adults in this country do not have lactase, which digests milk sugar, or lactose. Thus, it is very difficult for them to digest milk and may contribute to gaseousness, cramping, and diarrhea.

E. Maltose

Systemic name: ***4-O-α -D-glucopyranosyl-D-glucose***

Molecular formula: $\mathbf{C_{12}H_{22}O_{11}}$



Maltose

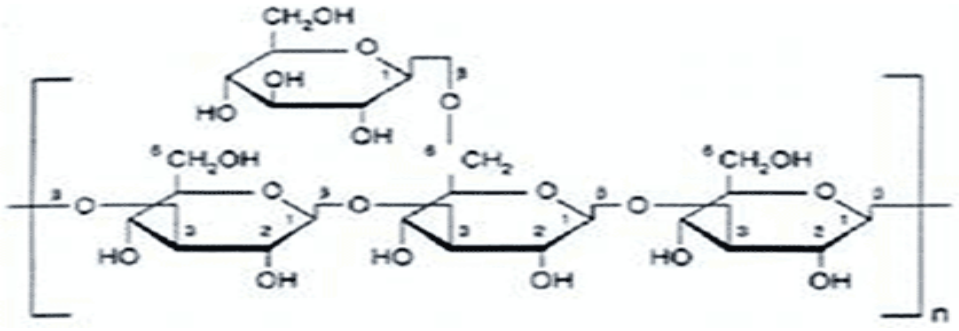
Maltose, or malt sugar, is a disaccharide formed from two units of glucose joined with an α(1⟶4) linkage. It is the second member of an important biochemical series of glucose chains. The addition of another glucose unit yields maltotriose; further additions will produce dextrins (also called maltodextrins) and eventually starch.

Maltose can be broken down into two glucose molecules by hydrolysis. In living organisms, the enzyme maltase can achieve this very rapidly. In the laboratory, heating with a strong acid for several minutes will produce the same result. The production of maltose from germinating cereals, such as barley, is an important part of the brewing process. When barley is malted, it is brought into a condition in which the concentration of maltose-producing amylases has been maximized. Mashing is the process by which these amylases convert the cereal's starches into maltose. Metabolism of maltose by yeast during fermentation then leads to the production of ethanol and carbon dioxide.

10.5 Polysaccharides

Polysaccharides are relatively complex carbohydrates. They are polymers made up of many monosaccharides joined together by glycosidic bonds. They are, therefore, very large, often branched, macromolecules. They tend to be amorphous, insoluble in water, and have no sweet taste. When all the monosaccharides in a polysaccharide are of the same type, the polysaccharide is called a homopolysaccharide and when more than one type of monosaccharide is present, they are called heteropolysaccharides. Examples include storage polysaccharides such as starch and glycogen and structural polysaccharides such as cellulose, and chitin. Xylan a hemicellulose is a heteropolysaccharide. Polysaccharides have a general formula of $C_n(H_2O)_{n-1}$ where n can be any number between 200 and 2500. Considering that the repeating units in the polymer backbone are often six-carbon

monosaccharides, the general formula can also be represented as $(C_6H_{105}O_n)$ where n={40...3000}.



Polysaccharide

Carbohydrate composed of ten or more monosaccharide units joined together by glycosidic linkages are classified as polysaccharides. Most of the carbohydrates found in nature occur as polysaccharides, polymers of high molecular weight; which on hydrolysis yield monosaccharides or products related to monosaccharides, most frequently D-glucose. Others monosaccharides obtained are D-mannose. D- and L-galactose, L-arabinose, D-glucuronic acid, D- and L-galactose, L-arabinose. D-glucuronic acid, D-glucosamine, etc. Polysaccharides, also called glycans, differ from each other in the identity of their recurring monosaccharide units, in the length of their chains, in the types of bonds linking the units, and in the degree of branching. Polysaccharides can be classified-as homopolysaccharidcs and heleropolyscicchariде (Fig. 23) depending on the variety of sugar moieties joined to the sugar chain. Some are linear polymers and others are branched. Some typical polysaccharides are starches, glycogens celluloses, agar, gum chitin, etc.

1. Homopolysaccharides

A homopolysaccharide is made up of a single kind of mono-saccharide. Starches, glycogens, and celluloses, which are made up of only glucose residues, are example of homopolysaccharides.

i) **Starch** The starches occur widespread as reserve carbohydrate in tubers such as potatoes, in many fruits, grains and seeds. In the grains, the starch is arranged in concentric layers. When starch grains are treated with boiling water, the substance in the center

passes into solution, but the greater part of the grain is not soluble. This insoluble portion swells as it absorbs water and the whole mass becomes starch paste. Both the soluble portion and the insoluble portion are heterogeneous mixtures. The soluble fraction is referred to as amylose, and the insoluble fraction as amylopectin. Most starches contain 80-90 per cent amylopectin and 10—20 per cent amylose. Amylose and amylopectin can be separated by taking advantage of the difference in solubility in water. Both amylose and amylopectin are polymers of glucose and upon hydrolysis with acid they give D-glucose as the product.

ii) ***Structure of amylose***: Amylose is an unbranched long chain polymer in which the glucose residues are linked through α-1, 4-glycosidic linkages. The amylose structure may be ragarded as a repeated maltose structure with a free sugar group (acetal group) at one end. This is also known as the reducing end (nth residue), whereas, the opposite end (first residue) is referred to as the non-reducing end. Any particular preparation of amylose usually consists of a mixture of populations of molecules, which differ widely in chain length (number of glucose residues per chain)

Amylose

Structure of amylopectin: Amylopectin is also made of chains of glucose residues, but the chains are highly branched. The glucose residue situated at the branching point is substituted not only on carbon 4 but also on carbon 6 (Fig.). Both amylose and amylopectin give characteristic colour reactions with iodine.

Amylose produces a blue-black colour, whereas, amylopectin gives a purple colour.

Saccharification of starch by amylases: Amylases are enzymes of plant and animal origin and they hydrolyse starch. There are two kinds of amylases, alpha-amylases and beta-amylases. Alpha-amylases are endo enzymes, act on amylose and amylopectin in a random fashion. Initially more central linkages are cleaved and smaller polysaccharide chains are formed. As the reaction proceeds, these are further hydrolysed to maltose and glucose.

α-amylases hydrolyse amylose and amylopectin in an orderly fashion. It acts from one end of the polymer and cleaves off two glucose residues at a time, as a maltose unit. As the reaction proceeds, amylose is completely hydrolysed to maltose. However, with the amylopectin, the reaction stops as a branch point is approached. The terminal parts of the branches are digested away as maltose units in an orderly fashion and the central core is left behind as the enzyme is blocked at 1-6 glycosidic linkages or branch points. The polysaccharide fragment that remains after such incomplete hydrolysis is called a dextrin.

Amylopectin

Dextrins formed from amylopectin by β-amylase are highly branched and give a red colour with iodine. Dextrins of relatively small molecular size do not give a colour with iodine. The colour produced by reaction with iodine is used as an indication of the degree of branching of starch. Starch is readily hydrolysed by dilute mineral acid with ultimate formation of glucose in quantitative yield. The course of hydrolysis may be followed by the gradual change in colour produced by iodine: blue-black-purple-red-colourless.

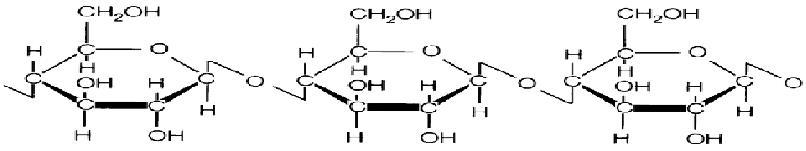
ii) Cellulose

Cellulose is the most abundant organic compound in nature and it is the chief constituent of the fibrous parts of plants. The purest form of cellulose is usually obtained from cotton. Cellulose is a polymer made up of glucose residues. Upon hydrolysis, cellulose yields D-glucose as the product. Cellulose molecules are not branched and consist essentially of long chains with glucose residues linked in repeating sequence of cellobiose structures. The glucose residues are linked together through β-l, 4-glycosidic linkages. The celluloses obtained from different sources differ in molecular size though they are all made up of glucose. Cellulose is found in plants as microfibrils (2-20 nm diameter and 100 - 40 000 nm long). These form the structurally strong framework in the cell walls.

***Structural unit*:** Cellulose is a linear polymer of β-(14)-D-glucopyranose units in $^{4}C_{1}$ conformation (Fig.). The fully equatorial conformation of β-linked glucopyranose residues stabilizes the chair structure, minimizing its flexibility (for example, relative to the slightly more flexible α-linked glucopyranose residues in amylose). Cellulose preparations may contain trace amounts (~0.3%) of arabinoxylans

***Molecular structure*:** Cellulose is an insoluble molecule consisting of between 2000 - 14000 residues with some preparations being somewhat shorter. It forms crystals (cellulose Iα) where intra-molecular (O3-HO5' and O6H-O2') and intra-strand (O6-HO3') hydrogen bonds holds the network flat allowing the more hydrophobic ribbon faces to stack. Each residue is oriented 180° to the next. Although individual strand of cellulose are intrinsically no less hydrophilic, or no more hydrophobic, than some other soluble polysaccharides (such as amylose) this tendency to form crystals utilizing extensive intra- and intermolecular hydrogen bonding makes it completely insoluble in normal aqueous solutions. It is thought that water molecules catalyze the formation of the natural cellulose crystals by helping to align the chains through hydrogen-bonded bridging. Part of a cellulose preparation is amorphous between these crystalline sections. The overall structure is of aggregated particles with extensive pores capable of holding relatively large amounts of water by capillarity. The natural crystal is made up from metastable Cellulose I with all the cellulose strands parallel and no inter-sheet hydrogen bonding. This cellulose I (natural cellulose) contains two coexisting phases

cellulose Iα (triclinic) and cellulose Iβ (monoclinic) in varying proportions dependent on its origin (Fig.).



Cellulose

Function **–** Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form biofilms.

iii) Glycogen

Glycogen is the reserve carbohydrate in the animals and it is found in significant amounts in the liver and muscle. Glycogen is made up of D-glucose residues. Upon hydrolysis, it yields D-glucose as the product. Glycogen is a highly branched chain polysaccharide and it resembles amylopectin in structure. Thus glucose residues are linked together through α-l,4-glycosidic linkages except at the branch points. The branch is linked to the main chain through α-l,6-glycosidic linkages. It is very similar to the structure of amylopectin. The average molecular weights of glycogen preparations vary from 270,000 to 100,000,000. A single preparation usually consists of a mixture of populations of molecules that differ in molecular weight (Fig. 28). In the structure of glycogen, O represents glucose residues. The arrows indicate the α-1⟶6 glycosidic linkage. All the other glycosidic linkage are α-1,4 . The asterisks indicate the non—reducing end groups and r.e. strands for reducing end group.

Fig. : Glycogen

In a wide range of organisms, excess glucose is stored not as monomer but converted to polymeric forms for storage—glycogen in vertebrates and many microorganisms, starch in plants. With two minor differences, glycogen has almost the same structure as amylopectin (a constituent of starch). The glycogen molecule is roughly twice as large as amylopectin, and branching frequency—that also controls the mobilization of stored polysaccharide. Glycogen has roughly twice as many branches (branching occurs on an average after every 8-12 residues unlike amylopectin where it is after every 24-30 residues). There is an advantage to

branched polysaccharides such as amylopectin and glycogen. During times of shortage, enzymes attack one end of the polymer chain and cut off glucose molecules, one at a time. More the branches, more the points at which the enzyme attacks the polysaccharide. Thus, a highly branched polysaccharide is better suited for the rapid release of glucose than a linear polymer.

In vertebrates, glycogen is found primarily in the liver and skeletal muscle but can also be made by the brain, uterus, and the vagina. However, muscle glycogen is not generally available to other tissues, because muscle lacks the enzyme glucose-6-phosphatase. Glycogen may represent up to 10% of the weight of liver and 1% to 2% of the weight of muscle. Stores of glycogen in the liver are considered the main buffer of blood glucose levels. If this much glucose was dissolved in the cytosol of a hepatocyte, its concentration would be about 0.4 M, enough to dominate the osmotic properties of the cell. When stored as a long polymer (glycogen), however, the same mass of glucose has a concentration of only 0.01 μM. Glycogen is stored in large cytosolic granules. The elementary particle of glycogen, the β particle, about 21 nm in diameter, consists of up to 55,000 glucose residues with about 2,000 nonreducing ends. The major site of daily glucose consumption (75%) is the brain via aerobic pathways. Most of the remainder of it is utilized by erythrocytes, skeletal muscle, and heart muscle. Due to disbalance in glucose utilization iabetics may experience Glycogen degradation and synthesis are relatively simple biochemical processes. Glycogen synthesis differs from glycogen breakdown. Unlike breakdown, synthesis is endergonic, meaning that glycogen is not synthesized without the input of energy. Energy for glycogen synthesis comes from UTP, which reacts with glucose-1-phosphate, forming UDP-glucose, in reaction catalysed by UDP-glucose pyrophosphorylase. Glycogen is synthesized from monomers of UDP-glucose by the enzyme Glycogen synthase, which progressively lengthens the glycogen chain. As glycogen synthase can only lengthen an existing chain, the protein glycogenin is needed to initiate the synthesis of glycogen.

Glycogen degradation consists of three steps: (1) the release of glucose 1-phosphate from glycogen, (2) the remodeling of the glycogen substrate to permit further degradation, and (3) the conversion of glucose 1-phosphate into glucose 6-phosphate for further metabolism. It is cleaved from the nonreducing ends of the chain by the enzyme glycogen phosphorylase to produce monomers of glucose-1-

phosphate that is then converted to glucose 6-phosphate. A special debranching enzyme is needed to remove the α (1-6) branches in branched glycogen and reshape the chain into linear polymer. Debranching enzyme has two independent active sites, consisting of residues in different segments of a single polypeptide chain, that catalyze α(1-6) glucosidase and transferase (transglycosylase) reactions.

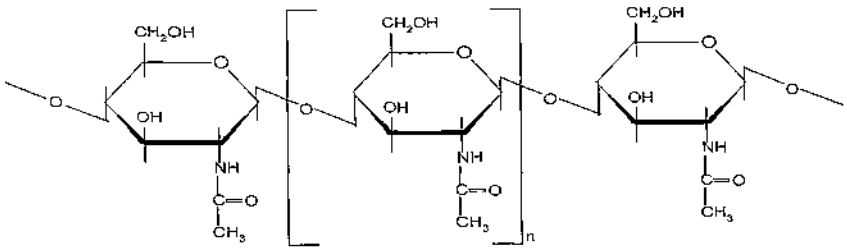
The transferase of the debranching enzyme transfers three glucose residues from a 4-residue limit branch to the end of another branch, diminishing the limit branch to a single glucose residue. The α(1-6) glucosidase moiety of the debranching enzyme then catalyzes hydrolysis of the α(1-6) linkage, yielding free glucose. This is a minor fraction of glucose released from glycogen. The major product of glycogen breakdown is glucose-1-phosphate, arising from phosphorylase activity, which is subsequently converted, to glucose-6-phosphate. The G6P monomers produced have three possible fates:

- G6P can continue on the glycolysis pathway and be used as fuel.
- G6P can enter the pentose phosphate pathway via the enzyme glucose-6-phosphate dehydrogenase to produce NADPH and 5-carbon sugars.
- In the liver and kidney, G6P can be dephosphorylated back to glucose by the enzyme glucose 6-phosphatase. This is the final step in the gluconeogenesis pathway.

v) Chitin

Chitin is a linear homopolysacchande composed of N-acetyl- D-glucosamine residues in β-linkage. The only chemical difference from cellulose is the replacement of a hydroxyl group a: C-2 with an acetylated amino group. Chitin forms extended fibers similar to those of cellulose, and structure of glycogen. Chitin like cellulose is indigestible by vertebrate animals. It is the main component of the cell walls of fungi, the exoskeletons of arthropods, such as crustaceans (like the crab, lobster and shrimp) and the insects, including ants, beetles and butterflies, the radula of mollusks and the beaks of the cephalopods, including squid and octopuses. Chitin is probably the second most abundant polysaccharide next to cellulose, in nature (Fig. 29).

Chitin is used in water purification, and as an additive to thicken and stabilize foods and pharmaceuticals. It also acts as a binder in dyes, fabrics, and adhesives. Industrial separation membranes and ion-exchange resins can be made from chitin. Processes to size and strengthen paper employ chitin. Its properties as a flexible and strong material make it favorable as surgical thread. Its biodegradability means it wears away with time as the wound heals. Moreover, the polysaccharide has some unusual properties that accelerate healing of wounds in humans. Most recent studies point out that chitin is a good inductor for defense mechanisms in plants. It is being tested as a fertilizer that can help plants develop healthy immune responses, and have a much better yield and life expectancy.



Chitin

10.6 Summary

This chapter introduces the major classes of carbohydrates and glycoconjugates, and provides a few examples of their many structural and functional roles. Students are also able to recognize the Polysaccharides consist of long chains having hundreds or thousands of monosaccharide units. Some polysaccharides, such as cellulose, occur in linear chains, whereas others, such as glycogen, have branched chains. The most abundant polysaccharides, starch and cellulose made by plants, consist of recurring units of D-glucose, but they differ in the type of glycosidic linkage.

10.7 Self Learning Exercise

Section A

1 Mention any cru disachaidis.

2 Write down the commern empirical formula of corbohydrats.

3 What are 2 major role of monosachorids?

4 Which mnonosacharide serues a structural role in bacterial cell wall

5 Name the polyschasid that is good.

6 Inclutor for defeuse

4 Mechanism in plants.

Section B

1. Write down the structure and functions of these derivatives of monosaccharides
   a. Myoinositol
   b. N-acetyl meuramic acid
   c. Sialic acid

Section c

1 Give a brief account on conformation of monosaccharides.

2. Describe the various examples of disaccharides.
3. Write a note on starch and glycogen.
4. Describe the structure of bacterial cell wall.

Answer of Section A

1 Lactose /Sucrole/Mathcle

1 $(CH_2O)_n$

2 (i) full molecules

(ii) building bleks for muclicacels

3 Peptiogly can

4 Chitin

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Unit-11 Carbohydrates II

Structure of Unit

11.0. Objective

On completion of this unit you will able to understand

- The structure and function of various derivatives of polysaccharides.
- The role of glycolipids and glycoproteins in cells.
- The role of carbohydrates in biological recognition.
- The various metabolic pathways of glucose in our body.

11.1 Introduction

Carbohydrates are of great importance in biology. The unique reaction, which makes life possible on Earth, namely the assimilation of the green plants, produces sugar, from which originate, not only all carbohydrates but, indirectly, also all other components of living organisms.

Carbohydrates comprise a comprehensive group of naturally occurring substances, which include innumerable sugars and sugar derivatives, as well as high-molecular weight carbohydrates (polysaccharides) like starch and cellulose in plants and glycogen in animals. A polysaccharide molecule is composed of a large number of sugar or sugar-like units. This unit let you understand the functions of such

diversity in different derivatives of carbohydrates like chondroitin sulfate and related glycosaminoglycans are a major goal of glycobiology.

This chapter is created in view of giving an idea about sugars (monosaccharides to polysaccharides; their derivatives, their important reactions, structures, function and biological importance. Efforts have made to explain the chemistry and organization of biomolecules in terms of blood sugars and the complete metabolism is also included.

11.2 Polysaccharides acides Glycosaminoglycans (GAGs) or mucopolysaccharides

Structure: Glycosaminoglycans (GAGs) or mucopolysaccharides are long unbranched anionic polysaccharides consisting of a repeating disaccharide unit. Members of the glycosaminoglycan family vary in the type of hexosamine, hexose or hexuronic acid unit (e.g. glucuronic acid, iduronic acid, galactose, galactosamine, glucosamine). They also vary in the geometry of the glycosidic linkage. They are synthesized in either endoplasmic reticulum and/or Golgi.

A glycosaminoglycans unit consists of an N-acetyl-hexosamine and a hexose or hexuronic acid, either or both of which may be sulfated. The combination of the sulfate group and the carboxylate groups of the uronic acid residues gives them a very high density of negative charge.

Function: This family of carbohydrates is essential or important for the life of vertebrates and an assortment of lower animals. It is present on the cell surface and in the extracellular matrix of animals. GAGs form an important component of connective tissues. GAG chains may be covalently linked to a protein to form proteoglycans.

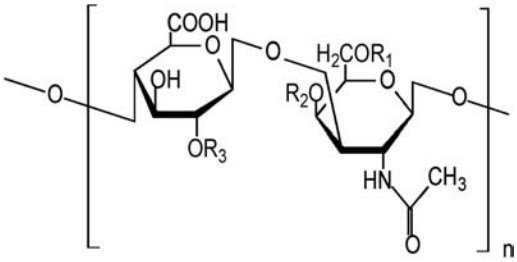
Examples of GAGs:

Name	**Sugar 1**	**Sugar 2**	**Linkage**	**Unique features**
Chondroitin sulphate	N-acetylgalactosamine	Glucuronic acid	β (1$\rightarrow$3)	Most prevalent GAG

Dermatan sulphate	Iduronic acid	N_Acetylgalactosamine	β (1⟶3)	Only one with iduronic acid
Keratan sulphate	Galactose	(varies)	β (1⟶4)	Very variable
Heparin	Glucuronic acid	Glucosamine	α (1⟶4)	Only one intracellular; high negative charge density
Heparan sulphate	Glucuronic acid	Glucosamine	α (1⟶4)	Similar to heparin but extracellular
Hyaluronan	Glucuronic acid	N-Acetylglucosamine	β (1⟶3)	Only bacterial one, only one without sulfur

i) Chondroitin sulfate

Chondroitin sulfate is a sulfated glycosaminoglycan (GAG) composed of a chain of alternating sugars (N-acetylgalactosamine and glucuronic acid). It is usually found attached to proteins as part of a proteoglycan. A chondroitin chain can have over 100 individual sugars, each of which can be sulfated in variable positions and quantities. Chondroitin sulfate is an important structural component of cartilage and provides much of its resistance to compression. Chondroitin sulfate chains are unbranched polysaccharides of variable length containing two alternating monosaccharides: D-glucuronic acid (GlcA) and N-acetyl-D-galactosamine (GalNac). Some GlcA residues are epimerized into L-iduronic acid (IdoA); the resulting disaccharide is then referred to as dermatan sulfate.



Chondroitin sulfate

Protein attachment: Chondroitin sulfate chains are linked to hydroxyl groups on serine residues of certain proteins. Exactly how proteins are selected for attachment of glycosaminoglycans is not understood. Empirically, glycosylated serines are often followed by a glycine and have neighboring acidic residues, but this motif does not always predict glycosylation.

The attachment of the GAG chain begins with four monosaccharides in a fixed pattern: Xyl - Gal - Gal - GlcA. Each sugar is attached by a specific enzyme, allowing for multiple levels of control over GAG synthesis. Xylose begins to be attached to proteins in the endoplasmic reticulum, while the rest of the sugars are attached in the Golgi apparatus.

Sulfation: Each monosaccharide may be left unsulfated, sulfated once, or sulfated twice. Most commonly the hydroxyls of the 4 and 6 positions of the N-acetyl-galactosamine are sulfated. Sulfation is mediated by specific sulfotransferases.

Functions: Chondroitin's functions largely depend on the properties of the overall proteoglycan of which it is a part. These functions can be broadly divided into structural and regulatory roles.

However, this division is not absolute and some proteoglycans have both structural and regulatory roles.

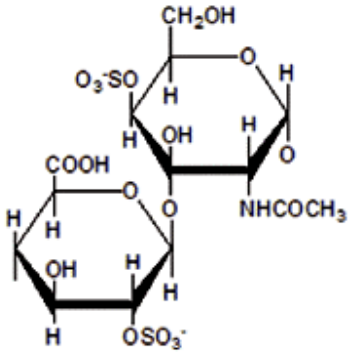
Structural functions: Chondroitin sulfate is a major component of extracellular matrix, and is important in maintaining the structural integrity of the tissue. This function is typical of the large aggregating proteoglycans: aggrecan, versican, brevican, and neurocan. As part of aggrecan, chondroitin sulfate is a major component of cartilage. The tightly packed and highly charged sulfate groups of chondroitin sulfate generate electrostatic repulsion that provides much of the resistance of cartilage to compression. Loss of chondroitin sulfate from the cartilage is a major cause of osteoarthritis.

Regulatory functions: Chondroitin sulfate readily interacts with proteins in the extracellular matrix due to its negative charges. These interactions are important for regulating a diverse array of cellular activities. In the nervous system, chondroitin sulfate proteoglycans regulate the growth and development of the nervous system as well as the nervous system response to injury.

Medical use: Chondroitin is an ingredient found commonly in dietary supplements used as an alternative medicine to treat osteoarthritis. It is commonly sold together with glucosamine.

ii) Dermatan sulfate

Dermatan sulfate is a glycosaminoglycan (formerly called a mucopolysaccharide) found mostly in skin, but also in blood vessels, heart valves, tendons, and lungs.

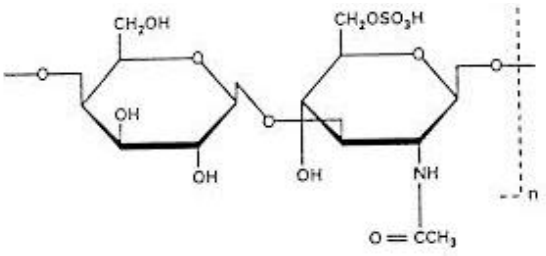


Dermatan sulphate

Function: Dermatan sulfate may have roles in coagulation, cardiovascular disease, carcinogenesis, infection, wound repair, and fibrosis. Dermatan sulfate accumulates abnormally in several of the mucopolysaccharidosis disorders.

iii) Keratan sulfate

Keratan sulfate is any of several sulfated glycosaminoglycans that have been found especially in the cornea, cartilage, and bone. It is a large, highly hydrated structural carbohydrates molecule, which in joints can act as a cushion. There are two main types. Type I is found in the cornea, and Type II is found in cartilage.

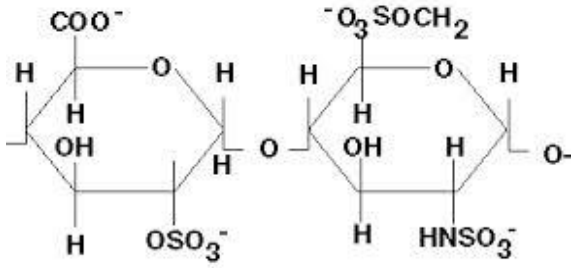


Repeating units of Keratan sulphate

iv) Heparin

Heparin is a member of the glycosaminoglycan family of carbohydrates (which includes the closely related molecule heparan sulfate). It is widely used as an injectable anticoagulant and has the highest negative charge density of any known biological molecule. It can also be used to form an inner anticoagulant surface on various experimental and medical devices such as test tubes and renal dialysis machines.

Structure: Native heparin is a polymer with a molecular weight ranging from 3 kDa to 40 kDa although the average molecular weight of most commercial heparin preparations is in the range of 12 kDa to 15 kDa. It is a member of the glycosaminoglycan family of carbohydrates (which includes the closely related molecule heparan sulfate) and consists of a variably sulfated repeating disaccharide unit. The most common disaccharide unit is composed of a 2-O-sulfated iduronic acid and 6-O-sulfated, N-sulfated glucosamine, IdoA(2S)-GlcNS(6S). Under physiological conditions the ester and amide sulfate groups are deprotonated and attract positively charged counterions to form a heparin salt. It is in this form that heparin is usually administered as an anticoagulant.



Heparin

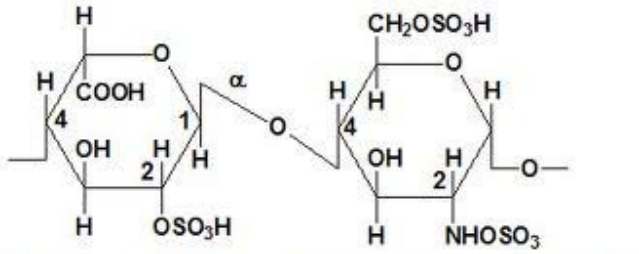
Mechanism of action: Heparin is a naturally occurring anticoagulant produced by basophils and mast cells. Heparin binds to the enzyme inhibitor antithrombin III (AT-III) causing a conformational changes which results in its active site being exposed. The activated AT-III then inactivates thrombin and other proteases involved in blood clotting, most notably factor Xa.

Heparin's exact physiological role is still unclear, because blood anti-coagulation is mostly achieved by endothelial cell-derived heparan sulfate proteoglycans. Heparin is usually stored within the secretory granules of mast cells and only released into the vasculature at sites of tissue injury. It has been proposed that rather than anticoagulation the main purpose of heparin is in a defensive mechanism at sites of tissue injury against invading bacteria and other foreign materials.

v) Heparan sulfate

Heparan sulfate (HS) is a linear polysaccharide found in all animal tissues. It occurs as a proteoglycan (PG) in which two or three HS chains are attached in close proximity to cell suface or extracellular matrix proteins. It is in this form that HS binds to a variety of protein ligands and regulates a wide variety of biological activities, including developmental processes, angiogenesis, blood coagulation and tumour metastasis.

Heparan sulfate structure: Heparan sulfate is a member of the glycosaminoglycan family of carbohydrates and is very closely related in structure to heparin. Both consist of a variably sulfated repeating disaccharide unit. The most common disaccharide unit within heparan sulfate is composed of a glucuronic (GlcA) linked to N-acetyl glucosamine (GlcNAc) typically making up around 50% of the total disaccharide units. It has been suggested that a GAG should qualify as heparin only if its content of N-sulfate groups largely exceeds that of N-acetyl groups and the concentration of O-sulfate groups exceeds those of N-sulfate. Under physiological conditions the ester and amide sulfate groups are deprotonated and attract positively charged counterions to form a salt. It is in this form that HS is thought to exist at the cell surface.



L-iduronate-2-sulfate *N*-sulfo-D-glucosamine-6-sulfate

Heparan sulfate is initially synthesized on a membrane-embedded core protein as a polymer of alternating glucuronate and N-acetylglucosamine residues. Later, in

segments of the polymer, glucuronate residues may be converted to the sulfated sugar iduronic acid, while N-acetylglucosamine residues may be deacetylated and/or sulfated. Some cell surface heparan sulfate glycosaminoglycans remain covalently linked to core proteins embedded in the plasma membrane. Proteins involved in signaling and adhesion at the cell surface recognize and bind segments of heparan sulfate chains having particular patterns of sulfation.

vi) Hyaluronan

Hyaluronan (also called hyaluronic acid or hyaluronate) is a non-sulfated glycosaminoglycan distributed widely throughout connective, epithelial, and neural tissues. Hyaluronan is a polymer of disaccharides themselves composed of D-glucuronic acid and D-N-acetylglucosamine, linked together via alternating β-1,4 and β-1,3 glycosidic bonds. Hyaluronan can be 25,000 disaccharide repeats in length. Polymers of hyaluronan can range in size from 5,000 to 20,000,000 Da *in vivo*. The average molecular weight in human synovial fluid is 3−4,000,000 Da and hyaluronan purified from human umbilical cord is 3,140,000 Da.

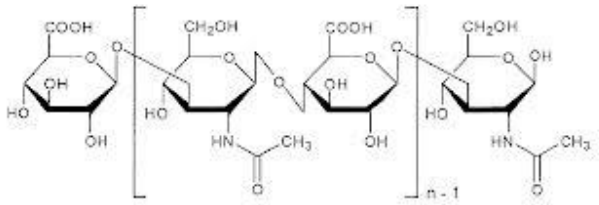
Functions: Until the late 1970s, hyaluronan was described as a "goo" molecule, a ubiquitous carbohydrate polymer that is part of the extracellular matrix. For example, hyaluronan is a major component of the synovial fluid and was found to increase the viscosity of the fluid. Along with lubricin, it is one of the fluid's main lubricating components. Hyaluronan is an important component of articular cartilage, where it is present as a coat around each cell (chondrocyte). When aggrecan monomers bind to hyaluronan in the presence of link protein, large highly negatively charged aggregates form. These aggregates imbibe water and are responsible for the resilience of cartilage (its resistance to compression). The molecular weight (size) of hyaluronan in cartilage decreases with age however the amount increases.

Hyaluronan is also a major component of skin, where it is involved in tissue repair. When skin is excessively exposed to UV-B rays, it becomes inflamed (sunburn) and the cells in the dermis stop producing as much hyaluronan and increase the rate of its degradation. Hyaluronan degradation products also accumulate in the skin after UV exposure.

It is one of the chief components of the extracellular matrix, contributes significantly to cell proliferation and migration, and may also be involved in the

progression of some malignant tumors. The average 70 kg man has roughly 15 grams of hyaluronan in his body, one third of which is turned over (degraded and synthesised) every day.

While it is abundant in extracellular matrices, hyaluronan also contributes to tissue hydrodynamics, movement and proliferation of cells, and participates in a number of cell surface receptor interactions, notably those including its primary receptor, CD44. CD44 participates in cell adhesion interactions required by tumor cells.



Hyaluronan

11.3 Derivatives with proteins of Carbohydrate

These are sugars which combine with proteins in different ways to create glycoproteins, proteoglycans etc.

a. Glycoproteins

A glycoprotein is a biomolecule composed of a protein and a carbohydrate (an oligosaccharide). The carbohydrate is attached to the protein in a co-translational or post-translational modification. This process is known as glycosylation. The addition of sugar chains can happen either at asparagines (N-glycosylation); or at hydroxylysine, hydroxyproline, serine, or threonine (O-glycosylation). Monosaccharides commonly found in eukaryotic glycoproteins include glucose, N-acetylglucosamine, galactose, N-acetylgalactosamine, mannose, fucose, xylose and N-acetylneuraminic acid (also known as sialic acid). In proteins that have segments extending extracellularly, the extracellular segments are often glycosylated.

Principals of glycosylations:

a) Glycoproteins have carbohydrate attached to them and this attachment is a covalent linkage to:

- The hydroxyl (-OH) group of the R group of serine or threonine - called "O-linked" in both cases.
- The amino group (-NH_2) in the R group of asparagine - called "N-linked".

b) The carbohydrate consists of short, usually branched, chains of

- Simple sugars (e.g., glucose, galactose)
- Amino sugars (sugars with an amino group, e.g., N-acetylglucosamine), and
- Acidic sugars (sugars with a carboxyl group, e.g., sialic acid)

Sugars are very hydrophilic due to to their many -OH groups. Their presence makes glycoproteins far more hydrophilic than they would be otherwise and essential for the proper folding of the protein into its tertiary structure. Most of the proteins exposed to the watery surroundings at the surface of cells are glycoproteins. Soluble glycoproteins often show a high viscosity, for example, in egg white and blood plasma.

Types of Glycoproteins

Broadly, they can be classified into two types according to the site of glycosylation.

A) In **N-glycosylation** the addition of sugar chains can happen at the amide nitrogen on the side chain of the asparagines.

N-linked glycosylation is important for the folding of some eukaryotic proteins. The *N*-linked glycosylation process occurs in eukaryotes and widely in archaea, but very rarely in bacteriaeukaryotesglucosemannosedolichol. For *N*-linked oligosaccharides, a 14-sugar precursor is first added to the asparagine in the polypeptide chain of the target protein. The structure of this precursor is common to most , and contains 3 , 9 , and 2 *N*-acetylglucosamine molecules. A complex set of reactions attaches this branched chain to a carrier molecule called, and then it is transferred to the appropriate point on the polypeptide chain as it is translocated into the ER lumen.

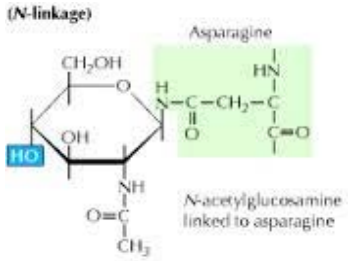


Fig. 11.1 : Overview of the major types of vertebrate N-linked glycan glycosylation

There are two major types of *N*-linked saccharides: high-mannose oligosaccharides, in essence, just two *N*-acetylglucosamines with many mannose residues, and complex oligosaccharides, containing almost any number of the other types of saccharides, including more than the original two *N*-acetylglucosamines.

The oligosaccharide chain is attached by oligosaccharyltransferase to asparagine occurring in the tripeptide SerThr Cysamino acid Pro*sequon*sequence Asn-X-, Asn-X-or Asn-X-, where X could be any except . This sequence is known as a glycosylation. After attachment, once the protein is correctly folded, the three glucose residues are removed from the chain and the protein is available for export from the ER. The glycoprotein thus formed is then transported to the Golgi where removal of further mannose residues may take place.

B) In **O-glycosylation**, the addition of sugar chains can happen on the hydroxyl oxygen on the side chain of hydroxylysine, hydroxyproline, serine or threonine. It can again be of the following types depending on the sugar moiety being attached:

a) O-N-acetylgalactosamine (O-GalNAc)- O-linked glycosylation occurs at a later stage during protein processing, probably in the Golgi apparatus. This is the addition of N-acetyl-galactosamine to serine or threonine by the enzyme UDP-N-acetyl-D-galactosamine:polypeptide, N-acetylgalactosaminyltransferase, followed by other carbohydrates. This process is important for certain types of proteins such as, which involves the addition of glycosaminoglycan chains to an initially unglycosylated "proteoglycan core protein." These additions are usually serine O-linked glycoproteins, which seem to have one of two main functions. One function involves secretion to form components of the extracellular matrix, adhering one cell to another by interactions between the large sugar complexes of proteoglycans. The other main function is to act as a component of mucosal

secretions, and it is the high concentration of carbohydrates that tends to give mucus its "slimy" feel. Proteins that circulate in the blood are not normally O-glycosylated, with the exception of IgA1 and IgD (two types of antibody) and C1-inhibitor.

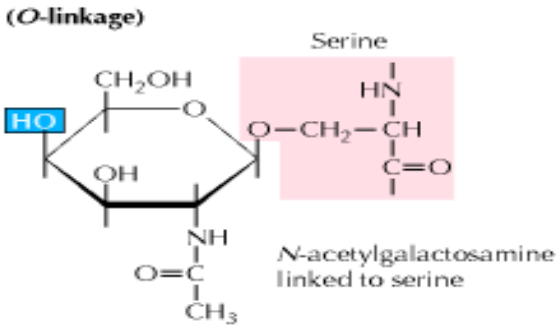


Fig. 11.2 : Overview of the major O-linked glycan types glycosylation

b) O-fucose - O-fucose is added between the second and third conserved cysteines of EGF-like repeats in the Notch protein, and possibly other substrates by GDP-fucose protein O-fucosyltransferase 1, and to Thrombospondin repeats by GDP-fucose protein O- fucosyltransferase 2. In the case of EGF-like repeats, the O-fucose may be further elongated to a tetrasaccharide by sequential addition of N-acetylglucoasamine (GlcNAc), galactose and sialic acids, and for Thrombospondin repeats, may be elongated to a disaccharide by the addition of glucose. Both of these fucosyltransferases have been localized to the endoplasmic reticulum, which is unusual for glycosyltransferases, most of which function in the Golgi apparatus.

c) O-glucose - O-glucose is added between the first and second conserved cysteines of EGF-like repeats in the Notch protein, and possibly other substrates by an unidentified O-glucosyltransferase.

d) O-N-acetylglucosamine (O-GlcNAc) - O-GlcNAc is added to serines or threonines by O-GlcNAc transferase. O-GlcNAc appears to occur on serines and threonines that would otherwise be phosphorylated by serine/threonine kinases. This is an incredibly important finding because phosphorylation/dephosphorylation has become a scientific paradigm for the regulation of signaling within cells. A massive amount of cancer research is focused on phosphorylation. Ignoring the involvement of this form of glycosylation, which clearly appears to act in concert with phosphorylation, means that a lot of current research is missing at least half of the picture. O-GlcNAc addition and removal also appear to be key regulators of the

pathways that are deregulated in diabetes mellitus. The gene encoding the O-GlcNAc removal enzyme has been linked to non-insulin dependent diabetes mellitus. It is the terminal step in a nutrient-sensing hexosamine signaling pathway.

e) GPI anchor - A special form of glycosylation is the GPI anchor. This form of glycosylation functions to attach a protein to a hydrophobic lipid anchor, via a glycan chain.

f) C-mannosylation – A mannose sugar is added to tryptophan residues in Thrombospondin repeats. This is an unusual modification both because the sugar is linked to a carbon rather than a reactive atom like a nitrogen or oxygen and because the sugar is linked to a tryptophan residue rather than an asparagines or serine/threonine.

Functions of Glycoproteins

In vivo, glycan moieties of glycoproteins has been known to play important roles in - maintenance of protein conformation and solubility, - proteolytic processing and stabilization of the polypeptide, - mediation of biological activity, - intracellular sorting and externalization of glycoproteins, and – embryonic development and differentiation. Glycosylation on protein residues confers on them a host of physiological functions, which are vital for maintenance of life processes. Some of these are enlisted below:

Structural: Glycoproteins are found throughout matrices. They act as receptors on cell surfaces that bring other cells and proteins (collagen) together giving strength and support to a matrix (Ivatt). Proteoglycan-linking glycoproteins cross links proteoglycan molecules and is involved in the formation of the ordered structure within cartilage tissue. In nerve tissue glycoproteins are abundant in gray matter and appear to be associated with synaptosomes, axons, and microsomes. Prothrombin, thrombin, and fibrinogen are all glycoproteins that play an intricate role in the blood clotting mechanism (Gottschalk). In certain bacteria the slime layer that surrounds the outermost components of cell walls are made up of glycoproteins of high molecular weight. In addition to forming these s-layers, glycoproteins also function as bacterial flagella. These are made up of bundles of glycoproteins protruding from the cell's surface. Their rotation provides propulsion. In plants, glycoproteins have roles in cell wall formation, tissue differentiation, embryogenesis, and sexual adhesion (certain algal species).

Protection: High molecular weight polymers called mucins are found on internal epithelial surfaces. They form a highly viscous gel that protects epithelium form chemical, physical, and microbial disturbances. Examples of mucin sites are the human digestive tract, urinary tract, and respiratory tracts. "Cervical mucin" is a glycoprotein found in the cervix of animals that regulates access of spermatozoa to the upper reproductive tract. Mucins are also found on the outer body surfaces of fish to protect the skin. Mucins also acts as a lubricant. Human lacrimal glands produce a glycoprotein, which protects the corneal epithelium from desiccation and foreign particles. Human sweat glands secrete glycoproteins, which protect the skin from the other excretory products that could harm the skin.

Reproduction: Glycoproteins found on the surface of spermatozoa appear to increase a sperm cell's attraction for the egg by altering the electrophoretic mobility of the plasma membrane. Actual binding of the sperm cell to the egg is mediated by glycoproteins serving as receptors on the surface of each the two membranes. The zona pellucida is an envelope made of glycoprotein that surrounds the egg and prevents polyspermy from occurring after the first sperm cell has penetrated the egg's plasma membrane. Hen ovalbumin is a glycoprotein found in egg white that serves as a food storage unit for the embryo.

Adhesion: Glycoproteins serve to adhere cells to cells and cells to substratum. Cell-cell adhesion is the basis for the development of functional tissues in the body. The interactions between cells are mediated by the glycoproteins on those cell's surfaces. In different domains of the body, different glycoproteins act to unite cells. For example, nerve cells recognize and bind to one another via the glycoprotein N-CAM (nerve cell adhesion molecule). N-CAM is also found on muscle cells indicating a role in the formation of myoneural junctions. With cell-substratum adhesion, glycoproteins serve as cell surface receptors for certain adhesion ligands that mediate and coordinate the interaction of cells. Substrates with the appropriate receptor will bind to the cell related to that receptor. For example, a substrate containing the glycoprotein fibronectin will be recognized and adhered to by fibroblasts. The fibroblasts will then secrete adhesion molecules and continue to spread, producing a pericellular matrix.

Hormones: There are many glycoproteins that function as hormones such as human chorionic gonadotropin (HCG), which is present in human pregnancy urine. Another example is erythropoietin, which regulates erythrocyte production.

Enzymes: Glycoprotein enzymes are of three types. These are oxidoreductases, transferases, and hydrolases. Majority of fungal enzymes are glycosylated.

Carriers: Glycoproteins can bind to certain molecules and serve as vehicles of transport. They can bind to vitamins, hormones, cations, and other substances.

Vision: In bovine visual pigment a glycoprotein forms the outer membranes of retinal rods.

Immunological: The interaction of blood group substances with antibodies is determined by the glycoproteins on erythrocytes. Adding or removing just one monosaccharide from a blood group structure, the antigenicity and therefore a person's blood type can be altered. Many immunoglobulins are actually glycoproteins. Soluble immune mediators such as helper, suppressor, and activator cell have been shown to bind to glycoproteins found on the surface of their target cells. B and T cells contain surface glycoproteins that attract bacteria to these sites and bind them. In much the same manner, glycoproteins can direct phagocytosis. Because the HIV virus recognizes the receptor protein CD4, it binds to helper T cells that contain it.

Table 11.1 : Functions of glycoproteins

Function	**Glycoproteins**
Structural molecule	Collagens
Lubricant and protective agent	Mucins
Transport molecule	Transferrin, ceruloplasmin
Immunologic molecule	Immunoglobins histocompatibility antigens
Hormone	Chorionic gonadotropin thyroid-stimulating hormone (TSH)
Enzyme	Various, e.g. alkaline phosphatase, cellulases, xylanases, amylases
Cell attachment-recognition site	Various proteins involved in cell-cell (sperm-oocyte), virus-cell, bacterium-cell,

	and hormone cell interactions
Interact with specific carbohydrates	Lectins, selectins (cell adhesion lectins), antibodies
Receptor	Various proteins involved in hormone and drug action
Affect folding of certain proteins	Calnexin, Calreticuluin
Regulation of development	Notch and its analogs, key proteins in development
Homostasis and thrmbosis	Specific glycoproteins on the surface membranes of platelets

Other specialized functions

As an antifreeze: The blood serums of Antarctic fishes freeze at -2°C, which is approximately 1°C below the melting points of their serums. This thermal hysteresis is due to the influence of some serum glycoproteins designated as antifreeze glycoproteins. They were first discovered by Arthur L. DeVries in the 1960's The temperatures of freezing and melting of aqueous solutions of the purified glycoproteins suggest that this thermal hysteresis results from the adsorption of the glycoprotein molecule onto the surface of ice crystals. Antifreeze proteins are found in some fish, insects and plants. They bind to ice crystals and prevent them from growing to a size where they would damage the host. Specific hydrogen bonds form on the surface where protein meets ice and inhibits crystal growth. The antifreeze molecules accumulate at the interface between ice and water, not at the interface between ice and a vacuum. So it is hypothesised that a hydrophobic reaction between the protein and the neighboring water prevents the water from forming ice crystals.

As an anticancer agent: Normal Gc protein (also called vitamin D binding protein), an abundant glyco-protein found in human blood serum, becomes the molecular switch to activate macrophages when it is converted to its active form, called Gc macrophage activating factor (Gc-MAF). Gc protein is normally activated by conversion to Gc-MAF with the help of the B and T cells (bone

marrow-made and thymus gland-made white blood cells). Cancer cells secrete an enzyme known as alpha-N-acetylgalactosaminidase (also called Nagalase) that completely blocks conversion of Gc protein to Gc-MAF, preventing tumor-cell killing by the macrophages. This is the way cancer cells escape detection and destruction, by disengaging the human immune system. This also leaves cancer patients prone to infections and many then succumb to pneumonia or other infections. The once-weekly injection of minute amounts of Gc-MAF, just 100 nanograms (billionths of a gram), activate macrophages and allow the immune system to pursue cancer cells with vigor, sufficient to produce total long-term cures in humans.

In protein folding: Glycoproteins also play important roles in mediating proper folding of proteins in the ER, which accounts for the observations that glycan addition to proteins in the ER is a cotranslational event. When inhibitors of ER glycosylation are added to cells, protein misfolding and aggregation are observed. The extent of misfolding depends on the particular protein and particular glycosylation sites with the protein. The polar CHO residues help promote solubility of folding intermediates, similar to the effects of many chaperone proteins. Some of the typical sugars found frequently in eukaryotic glycoproteins which assist in protein folding as also imparts solubility to the proteins include the following.

Sugar	**Type**	**Abbreviation**
Galactose	Hexose	Gal
Glucose	Hexose	Glc
Mannose	Hexose	Man
N-Acetylneuraminic acid	Sialic acid (nine C atoms)	NeuAc
Fucose	Deoxyhexose	Fuc
N-Acetylgalactosamine	Aminohexase	GalNAc
N-Acetylglucosamine	Aminohexase	GlcNac
Xylose	Pentose	Xyl

Synthesis & Regulation

Regulation and control of glycoproteins is not as straightforward as some might think. To understand regulation in glycoproteins, the enzymes that are involved in the biosynthesis pathway of these molecules are monitored. Control of glycoproteins can be seen through biosynthesis and degradation.

Synthesis: The protein part of the glycoprotein is formed at the ribosomes, where all proteins are synthesized on template represented by RNA and DNA. As a result, its structure can change only through the mutation of the genetic material of the cell. On the other hand, the carbohydrate component of a glycoprotein is not a product of the ribosome; it is synthesized somewhere in the cytoplasm, the exact site of synthesis has not been established. Since it is not directly genetically controlled, the oligosaccharide part shows a much greater variation.

In contrast with O-linked glycoproteins, where oligosaccharide assemble occurs on the polypeptide chain, N-linked glycoproteins assemble their oligosaccharide portions on a lipid linked intermediate, dolichol phosphate. The first step in oligosaccharide synthesis is the formation of that intermediate. In subsequent steps, sugars, the first being always N-acetylglucosamine (GlcNAc), are chain-like connected to dolichol phosphate. One more GlcNAc and three more mannose sugars are linked to the first GlcNAc to form the typical core of N-linked glycoproteins. Addition of any other sugar can be in any possible combination, according to the desired resulting functions. The specificity of the enzymes is very important in the synthesis process. Every sugar added, is catalyzed by a different enzyme. These group of enzymes are called glycosyltransferases. The first addition of GlcNAc to dolichol phosphate is catalyzed by the specific enzyme that cleave peptide bonds, and glycosidases (e.g example), enzymes that remove sugars one at a time from the end of an oligosaccharide chain. Both of these groups are contained in lysozomes. The lysosome attaches to a phagocyte, which has engulfed a substance that needs to be broken down, and releases its enzymes in it. Next, these enzymes begin their catalytic action. In degradation, ad in synthesis, the enzymes involved are very specific. After the glycoprotein is broken down, its amino acid and sugar components are either metabolized or can be used in the formation of another glycoprotein. Enzymatic degradation can provide much information about the structure of the oligosaccharide chains, as well as about the carbohydrate peptide linkage. For example, if a glycoprotein is treated with

mannosidase (removes mannose), and mannose is released, one can conclude that mannose residues were located at the periphery of the molecule since glycosidases remove sugars from the end of the oligosaccharide chain. Regulation and control is the organism's ultimate tool to monitor and adjust the production or degradation of different molecules.

11.4 Blood group substances

ABO Blood group system

The International Society of Blood Transfusion currently recognizes 29 blood group systems (including the ABO and Rh systems). ABO blood types are also present in some animals, for example; apes such as chimpanzees, bonobos and gorillas.

Carbohydrates form the most important part of blood group system in human blood transfusion. The associated anti-A antibodies and anti-B antibodies are usually IgM antibodies, which are usually produced in the first years of life by sensitization to environmental substances such as food, bacteria and viruses. The corresponding blood group carbohydrate structures, designated ABH, are found at the termini of oligosaccharide chains on glycoproteins and glycolipids on the surface of RBC & endothelial & most epithelial cells. The immunodominant monosaccharide that determines blood group A, is a terminal α-1,3-linked N-acetylgalactosamine (GalNAc), whereas the corresponding monosaccharide of blood group B specificity is an α-1,3-linked galactose. Group O cells lack chains, which instead are terminated with α-1,2-linked-fucose. The ABO blood group system is widely credited to have been discovered by the Austrian scientist Karl Landsteiner, who found three different blood types A, B, and O in 1900; Czech serologist Jan Janský independently pioneered the classification of human blood into four groups. Decastrello and Sturli discovered the fourth type, AB, in 1902. Ludwik Hirszfeld and E. von Dungern discovered the heritability of ABO blood groups in 1910-11, with Felix Bernstein demonstrating the correct blood group inheritance pattern of multiple allelesatonelocus in 1924.

Chemical nature & Structure: The antigens, which determine blood types belong to glycoproteins and glycolipids. There are three types of blood-group antigens: O, A, and B. They differ only slightly in the composition of carbohydrates. The A

antigen and the B antigen are derived from a common precursor known as the H antigen (or H substance). The H antigen is a carbohydrate sequence with carbohydrates linked mainly to protein (with a minor fraction attached to ceramide moiety). The majority of the ABO determinants are expressed on the ends of long polylactosamine chains attached mainly to Band 3 protein (1), the anion exchange protein of the red cell membrane, and a minority of the epitopes is expressed on neutral glycosphingolipids (1). In blood group O, the H antigen remains unchanged and consists of a chain of beta-D-galactose, beta-D-N-Acetylglucosamine, beta-D-galactose, and 2-linked, alpha-L-fucose, the chain being attached to the protein or ceramide. H antigens can be changed into A or B antigens by enzymes coded by the blood group A or B genes, which are sugar (glycosyl) tranferases. Type A has an extra alpha-N-Acetyl-D-galactosamine bonded to the D-galactose at the end, while type B has an extra alpha-D-galactose bonded to the D-galactose at the end.

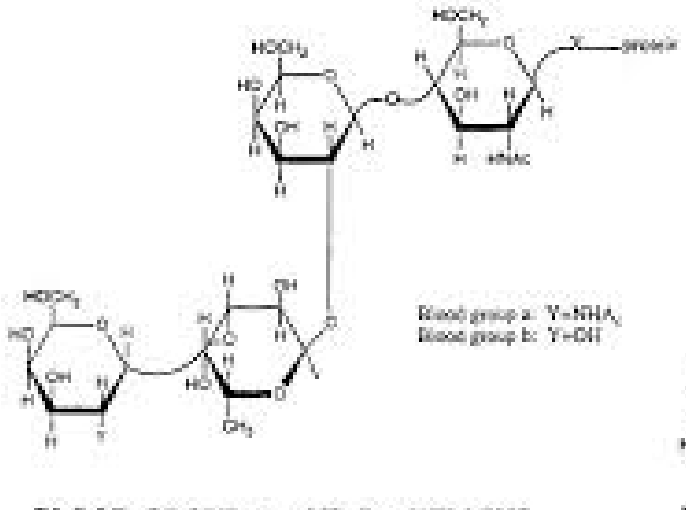
- Individuals with Type A blood can receive blood from donors of type A and type O blood.
- Individuals with type B blood can receive blood from donors of type B and type O blood.
- Individuals with type AB blood can receive blood from donors of type A, type B, type AB, or type O blood. Type AB blood is referred to as the universal recipient.
- Individuals with of O blood can receive blood from donors of only type O.

- Individuals of type A, B, AB and O blood can receive blood from donors of type O blood. Type O blood is called the universal donor. Antibodies are not formed against the H antigen except by those with the Bombay phenotype.

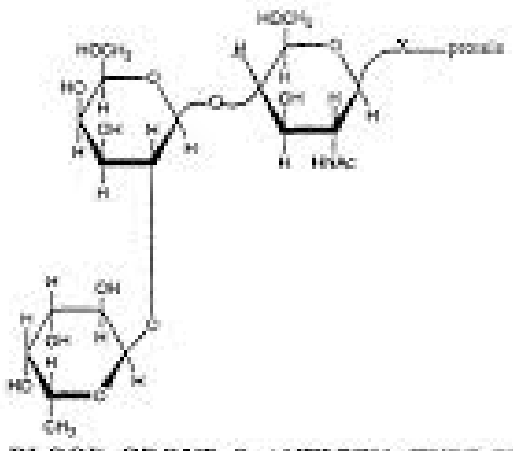
In ABH secretors, ABH antigens are secreted by most mucus-producing cells of the body interfacing with the environment, including lung, skin, liver, pancreas, stomach, intestines, ovaries and prostate.

Blood-group antigens

All humans contain enzymes, which catalyze the synthesis of the O antigen. Humans with A-type blood also contain an additional enzyme (called A-type enzyme here), which adds N-acetylgalactosamine to the O antigen. Humans with B-type blood contain another enzyme (called B-type enzyme here), which adds galactose to the O antigen. Humans with AB-type blood contain both A-type and B-type enzymes while humans with O-type blood lack both types of enzymes.



BLOOD GROUP A AND B ANTIGENS



BLOOD GROUP O ANTIGEN, TYPE II

The Rh System

Rh antigens are transmembrane proteins with loops exposed at the surface of red blood cells. They appear to be used for the transport of carbon dioxide and/or ammonia across the plasma membrane. They are named for the rhesus monkey in which they were first discovered. There are a number of Rh antigens. Red cells that are "Rh positive" are designated as D. About 15% of the population have no RhD antigens and thus are "Rh negative". The major importance of the Rh system for

human health is to avoid the danger of RhD incompatibility between mother and fetus.

During birth, there is often a leakage of the baby's red blood cells into the mother's circulation. If the baby is Rh positive (having inherited the trait from its father) and the mother Rh-negative, these red cells will cause her to develop antibodies against the Rh D antigen. The antibodies, usually of the IgG class, do not cause any problems for that child, but can cross the placenta and attack the red cells of a subsequent Rh+ fetus. This destroys the red cells producing anemia and jaundice. The disease, called erythroblastosis fetalis or hemolytic disease of the newborn may be so severe as to kill the fetus or even the newborn infant. It is an example of an antibody-mediated cytotoxicity disorder.

11.5 Role of sugars in biological recognition

Glycosaminoglycans as polymers of derivatives of carbohydrates are of critical importance in intercellular communication in organisms. This ubiquitous class of linear polyanions interact with a wide variety of proteins, including growth factors and chemokines, which regulate important physiological processes. The presence of glycosaminoglycans on cell membranes and in the extracellular matrix also has resulted in their exploitation by infectious pathogens to gain access and entry into animal cells. Other carbohydrate polymers lubricate skeletal joints and participate in recognition and adhesion between cells.

More complex carbohydrate polymers covalently attached to proteins or lipids act as signals that determine the intracellular location or metabolic fate of these hybrid molecules, called glycoconjugates. Glycoconjugates carry various important functions of cell. Glycoproteins act as receptors and integral membrane proteins in membranes, cytoskeletal proteins in cytoplasm, extracellular proteins such as antibodies, hormones, collagen (found outside the cell), enzymes (RNase, DNase, lipases, cholinesterase, phosphatase, pepsinogen, glycosyltransferases) etc. Functions and locations of glycolipids within the cell are diverse—take for example: GAGs: submaxillary secretions, human gastric mucin, RBC membrane sialoglycoprotein, membrane protein, secretory proteins without enzymatic functions, immunoglobins, enzymes.

The Carbohydrate recognition domain (CRD) is a protein domain of approximately 130 amino acids includes a number of invariant cysteine residues. The C-lectin

domain is a carbohydrate binding domain that contains a number of invariant cysteine residues, which form disulfide bonds, and that requires calcium ions for binding. The S-lectin domain is a carbohydrate binding domain that contains cysteine residues as free thiols, contains a number of invariant amino acid positions, and does not require divalent cations for binding. The distinction goes back to work by Drickamer classified animal lectins into C and S classes.

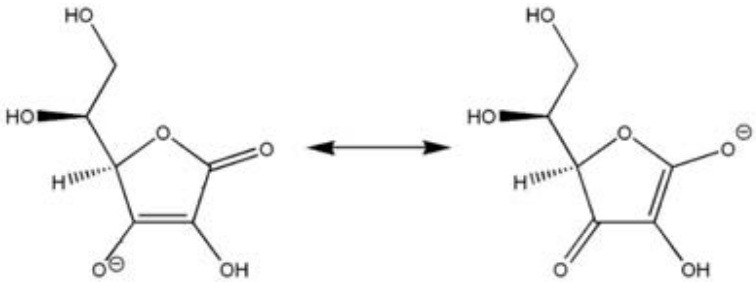
Carbohydrate recognition domains are found in a large number of proteins. Their major function is the recognition of oligosaccharides at the cell surface through the mediation of calcium. These domains can function independently of the rest of the protein containing them and thus have been employed also for the purification of fusion proteins.

Different types of carbohydrate recognition domains arranged in a number of combinations, in three dimensions, increase the affinity of proteins for specific carbohydrates and carbohydrate structures existing in a variety of different conformations.

11.6 Ascorbic acid

Ascorbic acid is a naturally occurring organic compound with antioxidant properties. It is a white solid, but impure samples can appear yellowish. It dissolves well in water to give mildly acidic solutions. Ascorbic acid is one form ("vitamer") of vitamin C. It was originally called L-hexuronic acid, but, when it was found to have vitamin C activity in animals ("vitamin C" being defined as a vitamin activity, not then a specific substance), the suggestion was made to rename L-hexuronic acid.

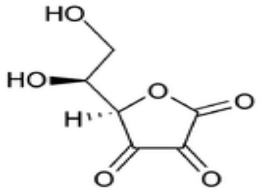
Structure and functions:



Canonical structures for the ascorbate anion

Ascorbic acid is classed as a reductone. The ascorbate anion is stabilized by electron delocalization, as shown above in terms of resonance between two canonical forms. For this reason, ascorbic acid is much more acidic than would be expected if the compound contained only isolated hydroxyl groups.

Antioxidant mechanism



End-product of oxidation of ascorbic acid

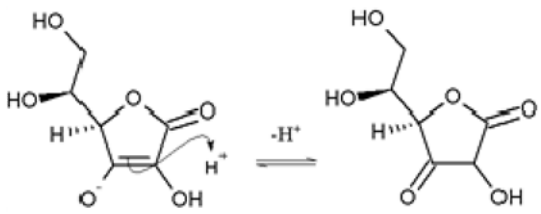
The ascorbate ion is the predominant species at typical biological pH values. It is a mild reducing agent and antioxidant. It is oxidized with loss of one electron to form a radical cation and then with loss of a second electron to form dehydroascorbic acid. It typically reacts with oxidants of the reactive oxygen species, such as the hydroxyl radical. Such radicals are damaging to animals and plants at the molecular level due to their possible interaction with nucleic acids, proteins, and lipids. Sometimes these radicals initiate chain reactions. Ascorbate can terminate these chain radical reactions by electron transfer. Ascorbic acid is special because it can transfer a single electron, owing to the resonance-stabilized nature of its own radical ion called, semidehydroascorbate. The net reaction is:

$$RO\bullet + C_6H_7O_6^- \longrightarrow ROH + C_6H_6O_6^{\bullet -}$$

The oxidized forms of ascorbate are relatively unreactive and do not cause cellular damage.

However, being a good electron donor, excess ascorbate in the presence of free metal ions can not only promote but also initiate free radical reactions, thus making it a potentially dangerous pro-oxidative compound in certain metabolic contexts.

Reactions



Nucleophilic attack of ascorbic enol on proton to give 1,3-diketone

11.7 Carbohydrate metabolism

Carbohydrate metabolism denotes the various biochemical processes responsible for the formation, breakdown and interconversion of carbohydrates in livingorganisms.

The most important carbohydrate is glucose, a simple sugar (monosaccharide) that is metabolized by nearly all known organisms. Glucose and other carbohydrates are part of a wide variety of metabolic pathways across species: plants synthesize carbohydrates from carbon dioxide and water by photosynthesis storing the absorbed energy internally, often in the form of starch or lipids. Plant components are consumed by animals and fungi, and used as fuel for cellular respiration. Oxidation of one gram of carbohydrate yields approximately 4 kcal of energy and from lipids about 9 kcal. Energy obtained from metabolism (e.g. oxidation of glucose) is usually stored temporarily within cells in the form of ATP. Organisms capable of aerobic respiration metabolize glucose and oxygen to release energy with carbon dioxide and water as byproducts.

Carbohydrates can be chemically divided into complex and simple. Simple carbohydrates consist of single or double sugar units (monosaccharides and disaccharides, respectively). Sucrose or table sugar (a disaccharide) is a common example of a simple carbohydrate. Complex carbohydrates contain three or more sugar units linked in a chain. They are digested by enzymes to release the simple sugars. Starch, for example, is a polymer of glucose units and is typically broken down to glucose. Simple and complex carbohydrates are digested at similar rates, so the distinction is not very useful for distinguishing nutritional quality. Cellulose is also a polymer of glucose but it cannot be digested by most organisms. Some bacteria that produce enzymes for cellulose live inside the gut of some mammals such as cows, and when cows eat plants, the cellulose is broken down by the bacteria and some of it is released into the gut.

All carbohydrates share a general formula of approximately $C_nH_{2n}O_n$; glucose is $C_6H_{12}O_6$. Monosaccharides may be chemically bonded together to form

disaccharides such as sucrose and longer polysaccharides such as starch and cellulose.

a. Kreb's Cycle

The citric acid cycle also known as the tricarboxylic acid cycle (TCA cycle), or the Krebs cycle, is a series of chemical reactions used by all aerobic organisms to generate energy through the oxidation of acetate derived from carbohydrates, fats and proteins into carbon dioxide and chemical energy in the form of adenosine triphosphate (ATP). In addition, the cycle provides precursors of certain amino acids as well as the reducing agentNADH that is used in numerous other biochemical reactions. Its central importance to many biochemical pathways suggests that it was one of the earliest established components of cellular metabolism and may have originated abiogenically.

The name of this metabolic pathway is derived from citric acid (a type of tricarboxylic acid) that is consumed and then regenerated by this sequence of reactions to complete the cycle. In addition, the cycle consumes acetate (in the form of acetyl-CoA) and water, reduces NAD^+ to NADH, and produces carbon dioxide as a waste byproduct. The NADH generated by the TCA cycle is fed into the oxidative phosphorylation (electron transport) pathway. The net result of these two closely linked pathways is the oxidation of nutrients to produce usable chemical energy in the form of ATP.

In eukaryotic cells, the citric acid cycle occurs in the matrix of the mitochondrion. In prokaryotic cells, such as bacteria which lack mitochondria, the TCA reaction sequence is performed in the cytosol with the proton gradient for ATP production being across the cell's surface (plasma membrane) rather than the inner membrane of the mitochondrion.

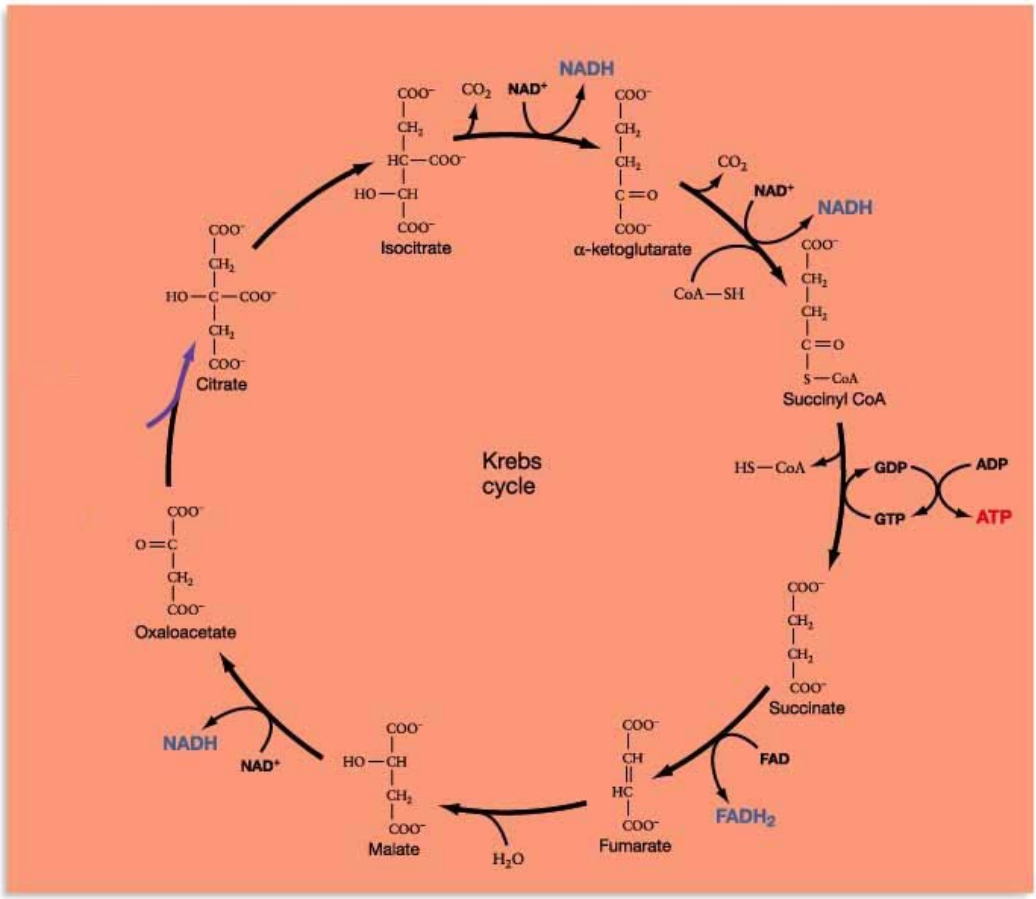


Fig. 11.5 : Kreb's cycle

The citric acid cycle is a key component of the metabolic pathway by which all aerobic organisms generate energy. Through catabolism of sugars, fats, and proteins, two-carbon organic product acetate in the form of acetyl-CoA is produced. Acetyl-CoA along with two equivalents of water (H_2O) is consumed by the citric acid cycle producing two equivalents of carbon dioxide (CO_2) and one equivalent of HS-CoA. In addition, one complete turn of the cycle converts three equivalents of nicotinamide adenine dinucleotide (NAD^+) into three equivalents of reduced NAD^+ (NADH), one equivalent of ubiquinone (Q) into one equivalent of reduced ubiquinone (QH_2), and one equivalent each of guanosine diphosphate (GDP) and inorganic phosphate (P_i) into one equivalent of guanosine triphosphate (GTP). The NADH and QH_2 generated by the citric acid cycle are in turn used by the oxidative phosphorylation pathway to generate energy-rich adenosine triphosphate (ATP).

One of the primary sources of acetyl-CoA is sugars that are broken down by glycolysis to produce pyruvate that in turn is decarboxylated by the enzyme pyruvate dehydrogenase generating acetyl-CoA according to the following reaction scheme:

- $CH_3C(=O)C(=O)O^-$ (pyruvate) + HSCoA + $NAD^+ \longrightarrow CH_3C(=O)SCoA$ (acetyl-CoA) + NADH + CO_2

The product of this reaction, acetyl-CoA, is the starting point for the citric acid cycle. Below is a schematic outline of the cycle:

- The citric acid cycle begins with the transfer of a two-carbon acetyl group from acetyl-CoA to the four-carbon acceptor compound (oxaloacetate) to form a six-carbon compound (citrate).
- The citrate then goes through a series of chemical transformations, losing two carboxyl groups as CO_2. The carbons lost as CO_2 originate from what was oxaloacetate, not directly from acetyl-CoA. The carbons donated by acetyl-CoA become part of the oxaloacetate carbon backbone after the first turn of the citric acid cycle. Loss of the acetyl-CoA-donated carbons as CO_2 requires several turns of the citric acid cycle. However, because of the role of the citric acid cycle in anabolism, they may not be lost, since many TCA cycle intermediates are also used as precursors for the biosynthesis of other molecules.
- Most of the energy made available by the oxidative steps of the cycle is transferred as energy-rich electrons to NAD^+, forming NADH. For each acetyl group that enters the citric acid cycle, three molecules of NADH are produced.
- Electrons are also transferred to the electron acceptor Q, forming QH_2.
- At the end of each cycle, the four-carbon oxaloacetate has been regenerated, and the cycle continues.

Differents Steps of Kreb's cycle:

Two carbon atoms are oxidized to CO_2, the energy from these reactions being transferred to other metabolic processes by GTP (or ATP), and as electrons in NADH and QH_2. The NADH generated in the TCA cycle may later donate its electrons in oxidative phosphorylation to drive ATP synthesis; $FADH_2$ is

covalently attached to succinate dehydrogenase, an enzyme functioning both in the TCA cycle and the mitochondrial electron transport chain in oxidative phosphorylation. $FADH_2$, therefore, facilitates transfer of electrons to coenzyme Q, which is the final electron acceptor of the reaction catalyzed by the Succinate:ubiquinone oxidoreductase complex, also acting as an intermediate in the electron transport chain.

Mitochondria in animals, including humans, possess two succinyl-CoA synthetases: one that produces GTP from GDP, and another that produces ATP from ADP. Plants have the type that produces ATP (ADP-forming succinyl-CoA synthetase). Several of the enzymes in the cycle may be loosely associated in a multienzyme protein complex within the mitochondrial matrix.

The GTP that is formed by GDP-forming succinyl-CoA synthetase may be utilized by nucleoside-diphosphate kinase to form ATP (the catalyzed reaction is GTP + ADP ⟶ GDP + ATP).

Products

Products of the first turn of the cycle are: one GTP (or ATP), three NADH, one QH_2, two CO_2.

Because two acetyl-CoA molecules are produced from each glucose molecule, two cycles are required per glucose molecule. Therefore, at the end of two cycles, the products are: two GTP, six NADH, two QH_2, and four CO_2

The total number of ATP obtained after complete oxidation of one glucose in glycolysis, citric acid cycle, and oxidative phosphorylation is estimated to be between 30 and 38.

b. Glycolysis

Glycolysis literally means "splitting sugars." In glycolysis, glucose (a six carbon sugar) is split into two molecules of a three-carbon sugar. Glycolysis yields two molecules of ATP (free energy containing molecule), two molecules of pyruvic acid and two "high energy" electron carrying molecules of NADH. Glycolysis can occur with or without oxygen. In the presence of oxygen, glycolysis is the first stage of cellular respiration. Without oxygen, glycolysis allows cells to make small amounts of ATP. This process is called fermentation.

Step-1

The enzyme hexokinase phosphorylates (adds a phosphate group to) glucose in the cell's cytoplasm. In the process, a phosphate group from ATP is transferred to glucose producing glucose 6-phosphate.

Glucose ($C_6H_{12}O_6$) + hexokinase + ATP ⟶ ADP + Glucose 6-phosphate ($C_6H_{11}O_6P_1$)

Step-2

The enzyme phosphoglucoisomerase converts glucose 6-phosphate into its isomer fructose 6 phosphate. Isomers have the same molecular formula, but the atoms of each molecule are arranged differently.

Glucose 6-phosphate ($C_6H_{11}O_6P_1$) + Phosphoglucoisomerase ⟶ Fructose 6-phosphate ($C_6H_{11}O_6P_1$)

Step-3

The enzyme phosphofructokinase uses another ATP molecule to transfer a phosphate group to fructose 6-phosphate to form fructose1,6-bisphosphate.

Fructose 6-phosphate ($C_6H_{11}O_6P_1$) + phosphofructokinase + ATP ⟶ ADP + Fructose 1, 6-bisphosphate ($C_6H_{10}O_6P_2$)

Step-4

The enzyme aldolase splits fructose 1, 6-bisphosphate into two sugars that are isomers of each other. These two sugars are dihydroxyacetone phosphate and glyceraldehyde phosphate.

Fructose 1, 6-bisphosphate ($C_6H_{10}O_6P_2$) + aldolase ⟶ Dihydroxyacetone phosphate ($C_3H_5O_3P_1$) + Glyceraldehyde phosphate ($C_3H_5O_3P_1$)

Step-5

The enzyme triose phosphate isomerase rapidly inter-converts the molecules dihydroxyacetone phosphate and glyceraldehyde phosphate. Glyceraldehyde phosphate is removed as soon as it is formed to be used in the next step of glycolysis.

Dihydroxyacetone phosphate ($C_3H_5O_3P_1$) ⟶ Glyceraldehyde phosphate ($C_3H_5O_3P_1$)

Net result for steps 4 and 5: Fructose 1, 6-bisphosphate ($C_6H_{10}O_6P_2$) ↔ 2 molecules of Glyceraldehyde phosphate ($C_3H_5O_3P_1$)

Step-6

The enzyme triose phosphate dehydrogenase serves two functions in this step. First the enzyme transfers a hydrogen (H^-) from glyceraldehyde phosphate to the oxidizing agent nicotinamide adenine dinucleotide (NAD^+) to form NADH. Next triose phosphate dehydrogenase adds a phosphate (P) from the cytosol to the oxidized glyceraldehyde phosphate to form 1, 3-bisphosphoglycerate. This occurs for both molecules of glyceraldehyde phosphate produced in step 5.

A. Triose phosphate dehydrogenase + 2 H^- + 2 NAD^+⟶ 2 NADH + 2 H^+

B. Triose phosphate dehydrogenase + 2 P + 2 glyceraldehyde phosphate ($C_3H_5O_3P_1$) ⟶ 2 molecules of 1,3-bisphosphoglycerate ($C_3H_4O_4P_2$)

Step-7

The enzyme phosphoglycerokinase transfers a P from 1,3-bisphosphoglycerate to a molecule of ADP to form ATP. This happens for each molecule of 1,3-bisphosphoglycerate. The process yields two 3-phosphoglycerate molecules and two ATP molecules.

2 molecules of 1,3-bisphoshoglycerate ($C_3H_4O_4P_2$) + phosphoglycerokinase + 2 ADP ⟶ 2 molecules of 3-phosphoglycerate ($C_3H_5O_4P_1$) + 2 ATP

Step-8

The enzyme phosphoglyceromutase relocates the P from 3-phosphoglycerate from the third carbon to the second carbon to form 2-phosphoglycerate.

2 molecules of 3-Phosphoglycerate ($C_3H_5O_4P_1$) + phosphoglyceromutase ⟶ 2 molecules of 2-Phosphoglycerate ($C_3H_5O_4P_1$)

Step-9

The enzyme enolase removes a molecule of water from 2-phosphoglycerate to form phosphoenolpyruvic acid (PEP). This happens for each molecule of 2-phosphoglycerate.

2 molecules of 2-Phosphoglycerate ($C_3H_5O_4P_1$) + enolase ⟶ 2 molecules of phosphoenolpyruvic acid (PEP) ($C_3H_3O_3P_1$)

Step-10

The enzyme pyruvate kinase transfers a P from PEP to ADP to form pyruvic acid and ATP. This happens for each molecule of PEP. This reaction yields 2 molecules of pyruvic acid and 2 ATP molecules.

2 molecules of PEP ($C_3H_3O_3P_1$) + pyruvate kinase + 2 ADP ⟶ 2 molecules of pyruvic acid ($C_3H_4O_3$) + 2 ATP

In summary, a single glucose molecule in glycolysis produces a total of 2 molecules of pyruvic acid, 2 molecules of ATP, 2 molecules of NADH and 2 molecules of water.
Although 2 ATP molecules are used in steps 1-3, 2 ATP molecules are generated in step 7 and 2 more in step 10. This gives a total of 4 ATP molecules produced. If you subtract the 2 ATP molecules used in steps 1-3 from the 4 generated at the end of step 10, you end up with a net total of 2 ATP molecules produced.

Glycogenesis,Glycogenolysis and Gluconeogenesis

Biosynthesis of Glycogen:

The goal of glycolysis, glycogenolysis, and the citric acid cycle is to conserve energy as ATP from the catabolism of carbohydrates. If the cells have sufficient supplies of ATP, then these pathways and cycles are inhibited. Under these conditions of excess ATP, the liver will attempt to convert a variety of excess molecules into glucose and/or glycogen.

c. Glycogenesis:

Glycogenesis is the formation of glycogen from glucose. Glycogen is synthesized depending on the demand for glucose and ATP (energy). If both are present in

relatively high amounts, then the excess of insulin promotes the glucose conversion into glycogen for storage in liver and muscle cells. In the synthesis of glycogen, one ATP is required per glucose incorporated into the polymeric branched structure of glycogen. actually, glucose-6-phosphate is the cross-roads compound. Glucose-6-phosphate is synthesized directly from glucose or as the end product of gluconeogenesis.

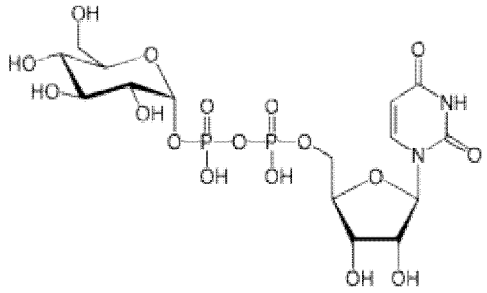


Fig. UDP-Glucose

Steps of Glycogenesis:

Glucose is converted into glucose-6-phosphate by the action of glucokinase or hexokinase.

1. Glucose-6-phosphate is converted into glucose-1-phosphate by the action of Phosphoglucomutase, passing through an obligatory intermediate step of glucose-1, 6-bisphosphate. Phosphoglucomutase is an enzyme that transfers a phosphate group on a glucose monomer from the 1' to the 6' position in the forward direction or the 6' to the 1' position in the reverse direction. To be specific, it facilitates the interconversion of glucose 1-phosphate and glucose 6-phosphate.Phosphoglucomutase also acts in the opposite fashion when a large concentration of glucose-6-phosphate is present. In this case, it is the 1-carbon that is phosphorylated and the 6-carbon that is dephosphorylated. The resulting glucose-1-phosphate is then changed into UDP-glucose in a number of intermediate steps. If activated by insulin, glycogen synthase will proceed to clip the glucose from the UDP-glucose complex and on to the glycogen molecule.

2. Glucose-1-phosphate is converted into UDP-glucose by the action of Uridyl Transferase (also called UDP-glucose pyrophosphorylase) and pyrophosphate is formed, which is hydrolyzed by pyrophosphatase into 2 molecules of Pi.
3. UTP—glucose-1-phosphate uridylyltransferase also known as glucose-1-phosphate uridylyltransferase (or UDP–glucose pyrophosphorylase) is an enzyme associated with glycogenesis. It synthesizes UDP-glucose from glucose-1-phosphate and UTP; i.e., glucose-1-phosphate + UTP -- UDP-glucose + pyrophosphate.

d. Glycogenolysis:

In glycogenolysis, glycogen stored in the liver and muscles, is converted first to glucose-1- phosphate and then into glucose-6-phosphate. Two hormones which control glycogenolysis are a peptide, glucagon from the pancreas and epinephrine from the adrenal glands.

Glucagon is released from the pancreas in response to low blood glucose and epinephrine is released in response to a threat or stress. Both hormones act upon enzymes to stimulate glycogen phosphorylase to begin glycogenolysis and inhibit glycogen synthetase (to stop glycogenesis).

Glycogen is a highly branched polymeric structure containing glucose as the basic monomer. First individual glucose molecules are hydrolyzed from the chain, followed by the addition of a phosphate group at C-1. In the next step the phosphate is moved to the C-6 position to give glucose 6-phosphate, a cross road compound.

Glucose-6-phosphate is the first step of the glycolysis pathway if glycogen is the carbohydrate source and further energy is needed. If energy is not immediately needed, the glucose-6-phosphate is converted to glucose for distribution in the blood to various cells such as brain cells.

Mechanism of Glycogenolysis

The overall reaction for the breakdown of glycogen to glucose-1-phosphate is:

$$\text{glycogen}_{(\text{n residues})} + P_i \rightleftharpoons \text{glycogen}_{(\text{n-1 residues})} + \text{glucose-1-phosphate}$$

Here, glycogen phosphorylase cleaves the bond linking a terminal glucose residue to a glycogen branch by substitution of a phosphoryl group for the α[1⟶4] linkage. Glucose-1-phosphate is converted to glucose-6-phosphate by the enzyme phosphoglucomutase. Glucose residues are phosphorolysed from branches of glycogen until four residues before a glucose that is branched with a α[1⟶6] linkage. Glycogen debranching enzyme then transfers three of the remaining four glucose units to the end of another glycogen branch. This exposes the α[1⟶6] branching point, which is hydrolysed by α[1⟶6] glucosidase, removing the final glucose residue of the branch as a molecule of glucose and eliminating the branch. This is the only case in which a glycogen metabolite is not glucose-1-phosphate. The glucose is subsequently phosphorylated to glucose-6-phosphate by hexokinase.

Biosynthesis of Glucose:

e. Gluconeogenesis: Gluconeogenesis is the process of synthesizing glucose from non-carbohydrate sources. The starting point of gluconeogenesis is pyruvic acid, although oxaloacetic acid and dihydroxyacetone phosphate also provide entry points. Lactic acid, some amino acids from protein and glycerol from fat can be converted into glucose. Gluconeogenesis is similar but not the exact reverse of glycolysis, some of the steps are the identical in reverse direction and three of them are new ones. Without going into detail, the general gluconeogenesis sequence is given in the graphic on the left.

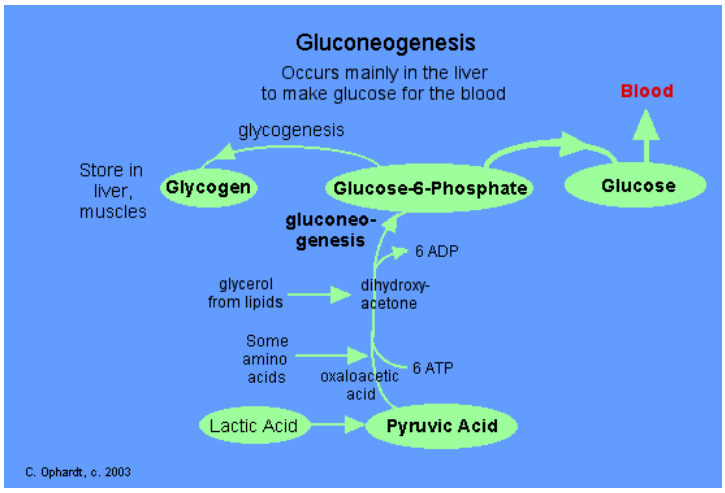


Fig 11.4 : Gluconcogensis

Notice that oxaloacetic acid is synthesized from pyruvic acid in the first step. Oxaloacetic acid is also the first compound to react with acetyl CoA in the citric acid cycle. The concentration of acetyl CoA and ATP determines the fate of oxaloacetic acid. If the concentration of acetyl CoA is low and concentration of ATP is high then gluconeogenesis proceeds. Also notice that ATP is required for a biosynthesis sequence of gluconeogenesis.

Gluconeogenesis occurs mainly in the liver with a small amount also occurring in the cortex of the kidney. Very little gluconeogenesis occurs in the brain, skeletal muscles, heart muscles or other body tissue. In fact, these organs have a high demand for glucose. Therefore, gluconeogenesis is constantly occurring in the liver to maintain the glucose level in the blood to meet these demands.

Gluconeogenesis is a pathway consisting of a series of eleven enzyme-catalyzed reactions. The pathway may begin in the mitochondria or cytoplasm, this being dependent on the substrate being used. Many of the reactions are the reversible steps found in glycolysis.

- Gluconeogenesis begins in the mitochondria with the formation of oxaloacetate by the carboxylation of pyruvate. This reaction also requires one molecule of ATP, and is catalyzed by pyruvate carboxylase. This enzyme is stimulated by high levels of acetyl-CoA (produced in β-oxidation in the liver) and inhibited by high levels of ADP.

- Oxaloacetate is reduced to malate using NADH, a step required for its transportation out of the mitochondria.
- Malate is oxidized to oxaloacetate using NAD^+ in the cytosol, where the remaining steps of gluconeogenesis take place.
- Oxaloacetate is decarboxylated and then phosphorylated to form phosphoenolpyruvate using the enzyme phosphoenolpyruvate carboxykinase. A molecule of GTP is hydrolyzed to GDP during this reaction.
- The next steps in the reaction are the same as reversed glycolysis. However, fructose-1,6-bisphosphatase converts fructose-1,6-bisphosphate to fructose 6-phosphate, using one water molecule and releasing one phosphate. This is also the rate-limiting step of gluconeogenesis.
- Glucose-6-phosphate is formed from fructose 6-phosphate by phosphoglucoisomerase. Glucose-6-phosphate can be used in other metabolic pathways or dephosphorylated to free glucose. Whereas free glucose can easily diffuse in and out of the cell, the phosphorylated form (glucose-6-phosphate) is locked in the cell, a mechanism by which intracellular glucose levels are controlled by cells.
- The final reaction of gluconeogenesis, the formation of glucose, occurs in the lumen of the endoplasmic reticulum, where glucose-6-phosphate is hydrolyzed by glucose-6-phosphatase to produce glucose. Glucose is shuttled into the cytoplasm by glucose transporters located in the endoplasmic reticulum's membrane.

e. Pentose Phosphate Pathway

The pentose phosphate pathway is the major source for the NADPH required for anabolic processes. There are three distinct phases each of which has a distinct outcome. Depending on the needs of the organism the metabolites of that outcome can be fed into many other pathways. Gluconeogenesis is directly connected to the pentose phosphate pathway. As the need for glucose-6-phosphate (the beginning metabolite in the pentose phosphate pathway) increases so does the activity of gluconeogenesis.

Introduction

The main molecule in the body that makes anabolic processes possible is NADPH. Because of the structure of this molecule it readily donates hydrogen ions to metabolites thus reducing them and making them available for energy harvest at a later time. The PPP is the main source of synthesis for NADPH. The pentose phosphate pathway (PPP) is also responsible for the production of Ribose-5-phosphate which is an important part of nucleic acids. Finally the PPP can also be used to produce glyceraldehyde-3-phosphate which can then be fed into the TCA and ETC cycles allowing for the harvest of energy. Depending on the needs of the cell certain enzymes can be regulated and thus increasing or decreasing the production of desired metabolites. The enzymes reasonable for catalyzing the steps of the PPP are found most abundantly in the liver (the major site of gluconeogenesis) more specifically in the cytosol. The cytosol is where fatty acid synthesis takes place which is a NADPH dependent process.

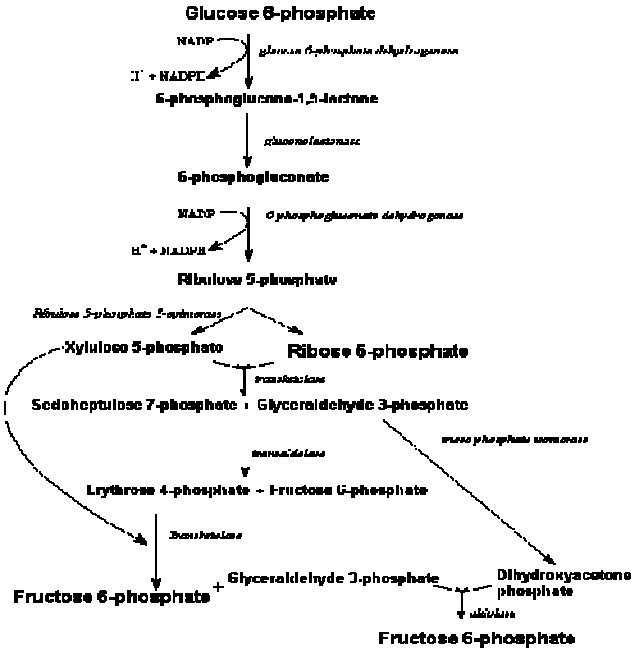


Fig. 11.5 Pentose Phosphate Pathway

Oxidation Phase

- The beginning molecule for the PPP is glucose-6-P which is the second intermediate metabolite in glycolysis. Glucose-6-P is oxidized in the presence of glucose-6-P dehydrogenase and $NADP^+$. This step is irreversible and is highly regulated. NADPH and fatty acyl-CoA are strong negative inhibitors to this enzyme. The purpose of this is to decrease production of NADPH when concentrations are high or the synthesis of fatty acids is no longer necessary.
- The metabolic product of this step is gluconolactone which is hydrolytrically unstable. Gluconolactonase causes gluconolactone to undergo a ring opening hydrolysis. The product of this reaction is the more stable sugar acid, 6-phospho-D-gluconate.
- 6-phospho-D-gluconate is oxidized by $NADP^+$ in the presence of 6-phosphogluconate dehydrogenase which yields ribulose-5-phosphate.

- The oxidation phase of the PPP is solely responsible for the production of the NADPH to be used in anabolic processes.

Isomerization Phase

- Ribulose-5-phosphate can then be isomerized by phosphopentose isomerase to produce ribose-5-phosphate. Ribose-5-phosphate is one of the main building blocks of nucleic acids and the PPP is the primary source of production of ribose-5-phosphate.
- If production of ribose-5-phosphate exceeds the needs of required ribose-5-phosphate in the organism, then phosphopentose epimerase catalyzes a chiralty rearrangement about the center carbon creating xylulose-5-phosphate.
- The products of these two reactions can then be rearranged to produce many different length carbon chains. These different length carbon chains have a variety of metabolic fates.

Rearrangement Phase

- There are two main classes of enzymes responsible for the rearrangement and synthesis of the different length carbon chain molecules. These are transketolase and transaldolase.
- Transketolase is responsible for the cleaving of a two carbon unit from xylulose-5-P and adding that two carbon unit to ribose-5-P thus resulting in glyceraldehyde-3-P and sedoheptulose-7-P.
- Transketolase is also responsible for the cleaving of a two carbon unit from xylulose-5-P and adding that two carbon unit to erythrose-4-P resulting in glyceraldehyde-3-P and fructose-6-P.
- Transaldolase is responsible for cleaving the three carbon unit from sedoheptulose-7-P and adding that three carbon unit to glyceraldehyde-3-P thus resulting in erythrose-4-P and fructose-6-P.
- The end results of the rearrangement phase is a variety of different length sugars which can be fed into many other metabolic processes. For example,

fructose-6-P is a key intermediate of glycolysis as well as glyceraldehyde-3-P.

11.8 Summary

Carbohydrates are of great importance in biology. The unique reaction, which makes life possible on the earth, namely the assimilation of the green plants, produces sugar, from which originate, not only all carbohydrates but, directly or indirectly, all other components of living organisms. The carbohydrates are a major source of metabolic energy, both for plants and for animals that depend on plants for food. Aside from the sugars and starch that meet this vital nutritional role, carbohydrates also serve as a structural material (cellulose), a component of the energy transport compound ATP, recognition sites on cell surfaces, and one of three essential components of DNA and RNA. Importance of carbohydrates in our body can be considered under above described headings.

11.9 Self Learning Excersice

Section A

1 What is the common medical use of heparin?
2 How many types of blood group antigen an brown.
3 Write down one example of an antibody meditie ytotoxicity discorder.
4 What is gliconeogenesis?
5 What are the @ main products of pentose phosphate pathary?

Section B

1 Write a short note on the conformation of mucopolysaccharides.
2 Describe the role of sugars in biological recognition.
3 With the suitable examples meation functions of glycoprotins
4 Write down process of glycol genolysis.
5 Diagramatically reprisents kreb's cycle.

Section C

1. Write a short note on the conformation of mucopoly-saccharides.
2. How the glycoproteins and glycolipids are formed? Name the different types of glycoproteins and glycolipids.
3. Describe the role of sugars in biological recognition.

4. Describe the role of carbohydrates as Blood group substances.
5. Where the Kreb's cycle is regulated? Make the diagram of Kreb's cycle.
6. Differentiate between ,glycolysis, glycogenesis glycogenolysis, and gluconeogenesis,
7. What is pentose phosphate pathway and how it is regulated?

Answer for Section A

1 Anticoagulaut

2 B A, B,O

3 erythroblastosis fetalis

4 Sybtgusus of glucose from non-corbohydrote precurrors

5 NABPH2 rivose-5-phosphats

11.10 References and Suggested readings

1. Morrison, R.T. & Boyd, R.N. (1992) *Organic Chemistry*, 6th edn, Benjamin Cummings, San Francisco. Chapters 34 and 35 cover the structure, stereochemistry, nomenclature, and chemical reactions of carbohydrates.
2. Pigman, W. & Horton, D. (Eds) (1970, 1972, 1980) the *Carbohydrates: Chemistry and Biochemistry, Vols IA, IB, IIA, and IIB,* Academic Press, Inc., New York. Comprehensive treatise on carbohydrate chemistry.
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Unit-12 : Lipids

Structure of Units:

12.0 Objectives

After learning about lipids you will be able to

- Know about the function of lipids in our body.
- Distinguish in various types of lipids and their role in our body and diseases.
- Understand the membrane structure and arrangement of lipids and proteins in cell membrane.
- Understand the metabolism of lipids inside the body.

12.1 Introduction

As we all know that Lipids are hydrophobic or amphipathic small molecules that may originate entirely or in part by carbanion-based condensations of thioesters (fatty acids, polyketides, etc.) and/or by carbocation-based condensations of isoprene units (prenols, sterols, etc.).

The most common lipid classes in nature consist of fatty acids linked by an ester bond to the trihydric alcohol - glycerol, or to other alcohols such as cholesterol, or by amide bonds or amines. In addition, they may contain alkyl moieties other than fatty acids, phosphoric acid, organic bases, carbohydrates and many more components, which can be released by various hydrolytic procedures. Fatty acids consist of the elements carbon (C), hydrogen (H) and oxygen (O) arranged as a carbon chain skeleton with a carboxyl group (-COOH) at one end. Saturated fatty acids (SFAs) have all the hydrogen that the carbon atoms can hold, and therefore, have no double bonds between the carbons. Monounsaturated fatty acids (MUFAs) have only one double bond. Polyunsaturated fatty acids (PUFAs) have more than one double bond.

The numbers at the beginning of the scientific names indicate the locations of the double bonds. By convention, the carbon of the carboxyl group is carbon number one. Greek numeric prefixes such as di, tri, tetra, penta, hexa, etc., are used as multipliers and to describe the length of carbon chains containing more than four atoms. Thus, "9,12-octadecadienoic acid" indicates that there is an 18-carbon chain (octa deca) with two double bonds (di en) located at carbons 9 and 12, with carbon 1 constituting a carboxyl group (oic acid). The structural formula corresponds to:

$CH_3CH_2CH_2CH_2CH_2CH=CHCH_2CH=CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$

9,12-octadecadienoic acid (Linoleic Acid)

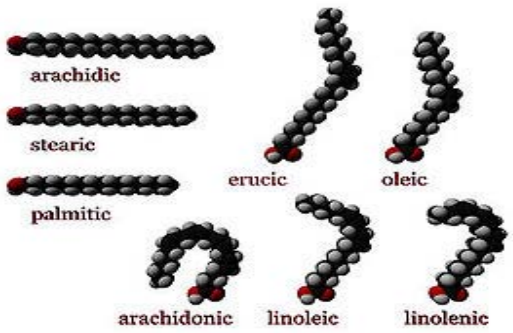
This would be abbreviated as:

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$

Fatty acids are frequently represented by a notation such as C18:2 that indicate that the fatty acid consists of an 18-carbon chain and 2 double bonds. Although this could refer to any of several possible fatty acid isomers with this chemical composition, it implies the naturally-occurring fatty acid with these characteristics, i.e., linoleic acid.

12.2 Fatty acids

A fatty acid is a carboxylic acid with a long aliphatic tail (chain), which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28. Fatty acids are usually derived from triglycerides or phospholipids. When they are not attached to other molecules, they are known as "free" fatty acids. Fatty acids are important sources of fuel because, when metabolized, they yield large quantities of ATP. Many cell types can use either glucose or fatty acids for this purpose. In particular, heart and skeletal muscle prefer fatty acids. Despite long-standing assertions to the contrary, the brain can use fatty acids as a source of fuel in addition to glucose and ketone bodies.



12.1 : Three-dimensional representations of several fatty acids

Fatty acids that have carbon–carbon double bonds are known as unsaturated. Fatty acids without double bonds are known as saturated. They differ in length as well.

Length of free fatty acid chains

Fatty acid chains differ by length, often categorized as short to very long.

- Short-chain fatty acids (SCFA) are fatty acids with aliphatic tails of fewer than six carbons (i.e. butyric acid).
- Medium-chain fatty acids (MCFA) are fatty acids with aliphatic tails of 6–12 carbons, which can form medium-chain triglycerides.

- Long-chain fatty acids (LCFA) are fatty acids with aliphatic tails 13 to 21 carbons.
- Very long chain fatty acids (VLCFA) are fatty acids with aliphatic tails longer than 22 carbons.

Cis and Trans configuration

a. Cis configuration

- A cis configuration means that adjacent hydrogen atoms are on the same side of the double bond.
- The rigidity of the double bond freezes its conformation and, in the case of the cis isomer, causes the chain to bend and restricts the conformational freedom of the fatty acid.
- The more double bonds the chain has in the cis configuration, the less flexibility it has.
- When a chain has many cis bonds, it becomes quite curved in its most accessible conformations. For example, oleic acid, with one double bond, has a "kink" in it, whereas linoleic acid, with two double bonds, has a more pronounced bend. Alpha-linolenic acid, with three double bonds, favors a hooked shape.

b. Trans configuration

- A trans configuration, by contrast, means that the next two hydrogen atoms are bound to opposite sides of the double bond. As a result, they do not cause the chain to bend much, and their shape is similar to straight saturated fatty acids.
- In most naturally occurring unsaturated fatty acids, each double bond has three n carbon atoms after it, for some n, and all are cis bonds. Most fatty acids in the trans configuration (trans fats) are not found in nature and are the result of human processing (e.g., hydrogenation).
- The differences in geometry between the various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids, play an important role in biological processes, and in the construction of biological structures (such as cell membranes).

Types of fatty acids

a. Unsaturated fatty acids

Unsaturated fatty acids have one or more double bonds between carbon atoms. (Pairs of carbon atoms connected by double bonds can be saturated by adding hydrogen atoms to them, converting the double bonds to single bonds. Therefore, the double bonds are called unsaturated.)

The two carbon atoms in the chain that are bound next to either side of the double bond can occur in a cis or trans configuration. Ex. Oleic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, Elaidic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, Vaccenic acid $CH_3(CH_2)_5CH=CH(CH_2)_9COOH$, Linoleic acid $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$ etc.

b. Essential fatty acids

Fatty acids that are required by the human body but cannot be made in sufficient quantity from other substrates, and therefore must be obtained from food, are called essential fatty acids. There are two series of essential fatty acids: one has a double bond, three carbon atoms removed from the methyl end; the other has a double bond six carbon atoms removed from the methyl end. Humans lack the ability to introduce double bonds in fatty acids beyond carbons 9 and 10, as counted from the carboxylic acid side. Two essential fatty acids are linoleic acid (LA) and alpha-linolenic acid (ALA). They are widely distributed in plant oils. The human body has a limited ability to convert ALA into the longer-chain n-3 fatty acids eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), which can also be obtained from fish.

c. Saturated fatty acids

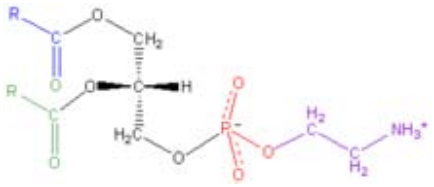
Saturated fatty acids are long-chain carboxylic acids that usually have between 12 and 24 carbon atoms and have no double bonds. Thus, saturated fatty acids are saturated with hydrogen (since double bonds reduce the number of hydrogens on each carbon). Because saturated fatty acids have only single bonds, each carbon atom within the chain has 2 hydrogen atoms (except for the omega carbon at the end that has 3 hydrogens). Ex. Lauric acid $CH_3(CH_2)_{10}COOH$, Myristic acid

$CH_3(CH_2)_{12}COOH$, Palmitic acid $CH_3(CH_2)_{14}COOH$, Stearic acid $CH_3(CH_2)_{16}COOH$, Arachidic acid $CH_3(CH_2)_{18}COOH$ etc.

12.3 Structure and functions of various derivatives of lipids

a. Glycerophospholipids

Glycerophospholipids, usually referred to as phospholipids, are ubiquitous in nature and are key components of the lipid bilayer of cells, as well as being involved in metabolism and cell signaling. Neural tissue (including the brain) contains relatively high amounts of glycerophospholipids, and alterations in their composition has been implicated in various neurological disorders. Glycerophospholipids may be subdivided into distinct classes, based on the nature of the polar headgroup at the *sn*-3 position of the glycerol backbone in eukaryotes and eubacteria, or the *sn*-1 position in the case of archaebacteria.

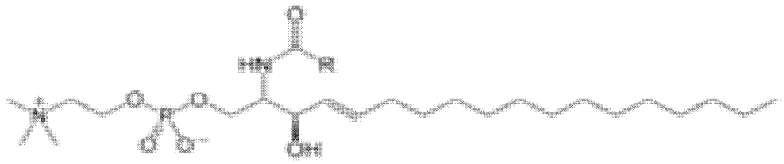


Phosphatidylethanolamine

Examples of glycerophospholipids found in biological membranes are phosphatidylcholine (also known as PC, GPCho or lecithin), phosphatidylethanolamine (PE or GPEtn) and phosphatidylserine (PS or GPSer). In addition to serving as a primary component of cellular membranes and binding sites for intra- and intercellular proteins, some glycerophospholipids in eukaryotic cells, such as phosphatidylinositols and phosphatidic acids are either precursors of or, themselves, membrane-derived second messengers. Typically, one or both of these hydroxyl groups are acylated with long-chain fatty acids, but there are also alkyl-linked and 1Z-alkenyl-linked (plasmalogen) glycerophospholipids, as well as dialkylether variants in archaebacteria.

b. Sphingolipids

Sphingolipids are a complicated family of compounds that share a common structural feature, a sphingoid base backbone that is synthesized *de novo* from the amino acid serine and a long-chain fatty acyl CoA, then converted into ceramides, phosphosphingolipids, glycosphingolipids and other compounds. The major sphingoid base of mammals is commonly referred to as sphingosine. Ceramides (N-acyl-sphingoid bases) are a major subclass of sphingoid base derivatives with an amide-linked fatty acid. The fatty acids are typically saturated or mono-unsaturated with chain lengths from 16 to 26 carbon atoms.



Sphingomyelin

The major phosphosphingolipids of mammals are sphingomyelins (ceramide phosphocholines), whereas insects contain mainly ceramide phosphoethanolamines and fungi have phytoceramide phosphoinositols and mannose-containing headgroups. The glycosphingolipids are a diverse family of molecules composed of one or more sugar residues linked via a glycosidic bond to the sphingoid base. Examples of these are the simple and complex glycosphingolipids such as cerebrosides and gangliosides.

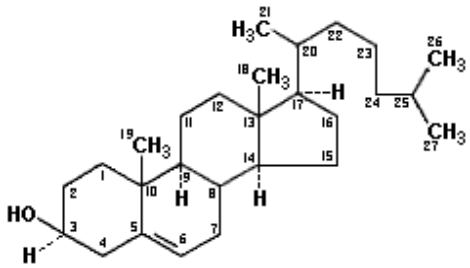
c. Sterol lipids

Sterol lipids, such as cholesterol and its derivatives, are an important component of membrane lipids, along with the glycerophospholipids and sphingomyelins. The steroids, all derived from the same fused four-ring core structure, have different biological roles as hormones and signaling molecules. The eighteen-carbon (C18) steroids include the estrogen family whereas the C19 steroids comprise the androgens such as testosterone and androsterone. The C21 subclass includes the progestogens as well as the glucocorticoids and mineralocorticoids. The secosteroids, comprising various forms of vitamin D, are characterized by cleavage of the B ring of the core structure. Other examples of sterols are the bile acids and their conjugates, which in mammals are oxidized derivatives of cholesterol and are synthesized in the liver. The plant equivalents are the phytosterols, such as β-

sitosterol, stigmasterol, and brassicasterol; the latter compound is also used as a biomarker for algal growth. The predominant sterol in fungal cell membranes is ergosterol.

Cholesterol

The general structure of cholesterol consists of two six-membered rings side-by-side and sharing one side in common, a third six-membered ring off the top corner of the right ring, and a five-membered ring attached to the right side of that. The central core of this molecule, consisting of four fused rings, is shared by all steroids, including estrogen (estradiol), progesterone, corticosteroids such as cortisol (cortisone), aldosterone, testosterone, and Vitamin D. In the various types of steroids, various other groups/molecules are attached around the edges. Know how to draw the four rings that make up the central structure.



Cholesterol

Our bodies make about 2 g of cholesterol per day, and that makes up about 85% of blood cholesterol, while only about 15% comes from dietary sources.

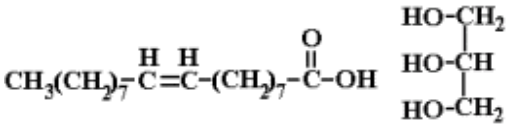
Functions of Cholesterol

- Cholesterol is an essential structural component of cell membranes and of the myelin sheaths that insulate the axons of nerve cells.
- Cholesterol is also a precursor of steroid hormones and of the bile acids necessary for digestion. The liver produces approximately 70% of the cholesterol used by the body, and the other 30% comes from the diet.
- Cholesterol is the precursor to our sex hormones and Vitamin D. Vitamin D is formed by the action of UV light in sunlight on cholesterol molecules that have "risen" to near the surface of the skin. Our cell membranes

contain a lot of cholesterol (in between the phospholipids) to help keep them “fluid” even when our cells are exposed to cooler temperatures.

d. **Triglycerides**

Triglycerides are the main constituents of vegetable oils and animal fats. Triglycerides have lower densities than water (they float on water), and at normal room temperatures may be solid or liquid. When solid, they are called "fats" or "butters" and when liquid they are called "oils". A triglyceride, also called triacylglycerol (TAG), is a chemical compound formed from one molecule of glycerol and three fatty acids.



Oleic Acid Glycerol or Glycerin

Glycerol is a trihydric alcohol (containing three -OH hydroxyl groups) that can combine with up to three fatty acids to form monoglycerides, diglycerides, and triglycerides. Fatty acids may combine with any of the three hydroxyl groups to create a wide diversity of compounds. Monoglycerides, diglycerides, and triglycerides are classified as esters which are compounds created by the reaction between acids and alcohols that release water (H_2O) as a by-product.

Function:

- One of the very important functions of triglycerides is contribute to the structure of membranes by the formation of a lipid bilayer.
- The membranes serve as a barrier to keep separate the inside of a cell and the outside of a cell. The triglycerides and the phospholipids help to achieve this by having the polar head of the molecule facing the inside of the cell as well as the outside of the cell and then the nonpolar fatty acid portions of the molecules tend to dissolve into one another and form a mix that is resistant to water, thus keeping the solution of the inside of the cell inside restricting the flow of water and things to the outside of the cell and vice versa.

e. Prostaglandins Thromboxanes & Leukotrienes

The members of this group of structurally related natural hormones have an extraordinary range of biological effects. They can lower gastric secretions, stimulate uterine contractions, lower blood pressure, influence blood clotting and induce asthma-like allergic responses. Because their genesis in body tissues is tied to the metabolism of the essential fatty acid arachadonic acid (5,8,11,14-eicosatetraenoic acid) they are classified as eicosanoids. Many properties of the common drug aspirin result from its effect on the cascade of reactions associated with these hormones.

The metabolic pathways by which arachidonic acid is converted to the various eicosanoids are complex and will not be discussed here. A rough outline of some of the transformations that take place is provided below.

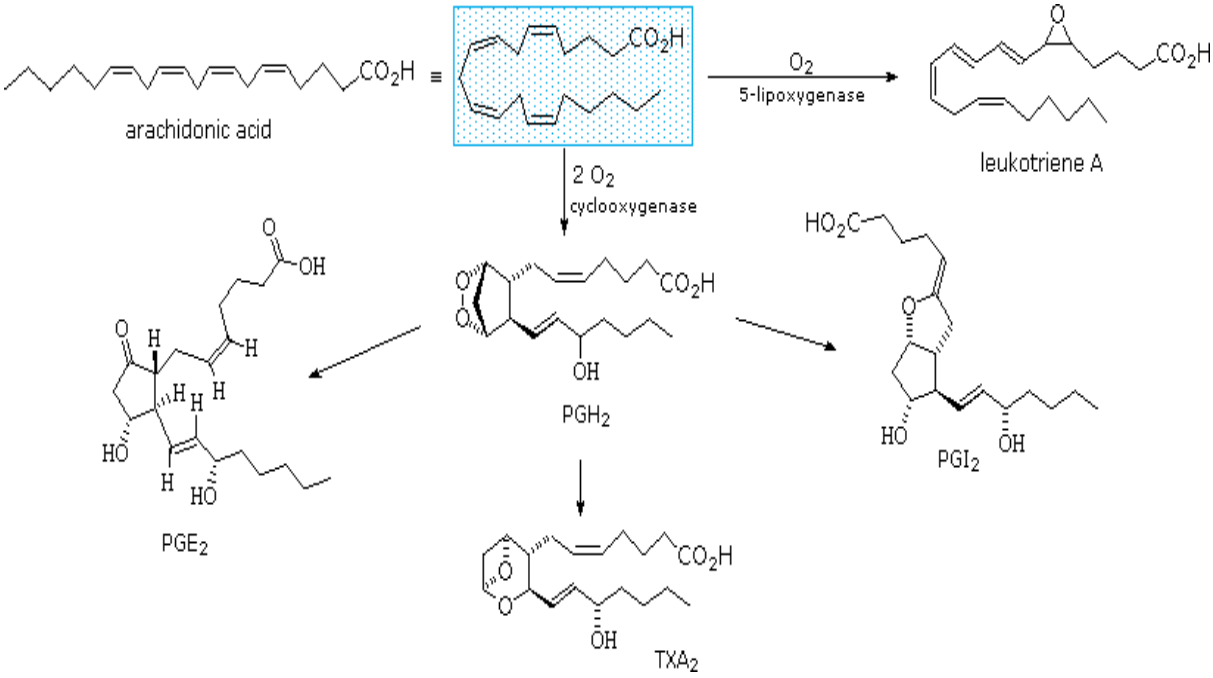


Fig 12.2

Leukotriene A is a precursor to other leukotriene derivatives by epoxide opening reactions. The prostaglandins are given systematic names that reflect their structure. The initially formed peroxide PGH_2 is a common intermediate to other prostaglandins, as well as thromboxanes such as TXA_2.

f. Bile acids

Bile acids are steroidacids found predominantly in the bile of mammals. Bile salts are bile acids compounded with a cation, usually sodium. In humans, the salts of

taurocholic acid and glycocholic acid (derivatives of cholic acid) represent approximately eighty percent of all bile salts. Bile acids, glycine and taurine conjugates, and 7-alpha-dehydroxylated derivatives (deoxycholic acid and lithocholic acid) are all found in human intestinal bile. An increase in bile flow is exhibited with an increased secretion of bile acids. The main function of bile acid is to facilitate the formation of micelles, which promotes processing of dietary fat.

Bile acids: Synthesis and function

In humans, bile acid synthesis begins when liver cells synthesize the two primary bile acids, cholic acid and chenodeoxycholic acid, via the cytochrome P450-mediated oxidation of cholesterol. Approximately 600 mg of bile salts are synthesized daily to replace bile acids lost in the feces. In humans, the rate-limiting step is the addition of a hydroxyl group on position 7 of the steroid nucleus by the enzyme cholesterol 7 alpha-hydroxylase. This enzyme is down-regulated by cholic acid and up-regulated by cholesterol.

When these two bile acids are secreted into the lumen of the intestine, intestinal bacteria dehydroxylate a portion of each of them to form the secondary bile acids, deoxycholic acid and lithocholic acid. (Cholic acid becomes deoxycholic acid. Chenodeoxycholic acid becomes lithocholic acid.) All four of these bile acids can be taken back up into the blood stream, return to the liver, and be re-secreted in a process known as enterohepatic circulation.

Prior to secreting any of the four bile acids, the liver cells may also conjugate them with one of two amino acids, glycine or taurine, to form a total of 8 possible conjugated bile acids. These conjugated bile acids are usually referred to as bile saltsbecause of their physiologically-important acid-base properties. The pKa of the unconjugated bile acids are between 5 and 6.5,[4] and the pH of the duodenum ranges between 3 and 5, so when unconjugated bile acids are in the duodenum, they are almost always protonated (HA form), which makes them relatively insoluble in water. Conjugating bile acids with amino acids lowers the pKa of the bile-acid/amino-acid conjugate to between 1 and 4. Thus conjugated bile acids are almost always in their deprotonated (A-) form in the duodenum, which makes them much more water soluble and much more able to fulfill their physiologic function of emulsifying fats.

One way this added solubility aids in bile salt function is by preventing passive re-absorption once secreted into the small intestine. As a result, the concentration of bile acids/salts in the small intestine can stay high enough to form micelles and solubilize lipids. "Critical micellar concentration" refers to both an intrinsic property of the bile acid itself and amount of bile acid necessary to function in the spontaneous and dynamic formation of micelles.

Bile acids also serve other functions, including eliminating cholesterol from the body, driving the flow of bile to eliminate catabolites from the liver, emulsifying lipids and fat-soluble vitamins in the intestine to form micelles that can be transported via the lacteal system, and aiding in the reduction of the bacteria flora found in the small intestine and biliary tract.

12.4 Lipoproteins- composition and function, role in atherosclerosis

Lipoproteins are clusters of proteins and lipids all tangled up together. These act as a means of carrying lipids, including cholesterol, around in our blood. There are two main categories of lipoproteins distinguished by how compact/dense they are.

1. LDL or low density lipoprotein is the “bad guy,” being associated with deposition of “cholesterol” on the walls of someone’s arteries.

2. HDL or high density lipoprotein is the “good guy,” being associated with carrying “cholesterol” out of the blood system, and is more dense/more compact than LDL.

Lipoproteins as Good cholesterol (HDL) and Bad cholesterol (LDL)

Lipoproteins are small spherules that transport fats in the body and consist of protein, cholesterol, triglycerides, and phospholipids. The terms "good" and "bad" cholesterol refer to High Density Lipoproteins (HDL) and Low Density Lipoproteins (LDL), respectively. High levels of LDL are associated with coronary atherosclerosis, whereas high levels of HDL appear to protect against diseases.

Classification of Lipoproteins

There are five main classes of lipoproteins:

- Chylomicrons
- Very Low Density Lipoproteins (VLDL)

- Intermediate Density Lipoproteins (IDL)
- Low Density Lipoproteins (LDL)
- High Density Lipoproteins (HDL)

Lipoprotein particles range in size from 10 to 1000 nanometers. The largest lipoproteins are about one tenth the size of a red blood cell. The density of lipoproteins increases in proportion to their ratio of proteins to lipids. In general, as the density of a lipoproteins increases, the size of the particles decreases. The outer layer of a lipoprotein consists of a water-soluble (hydrophilic) layer of apolipoproteins, phospholipids and cholesterol. The center of a lipoprotein is composed of cholesteryl esters, triglycerides, fatty acids and fat-soluble vitamins like Vitamin E.

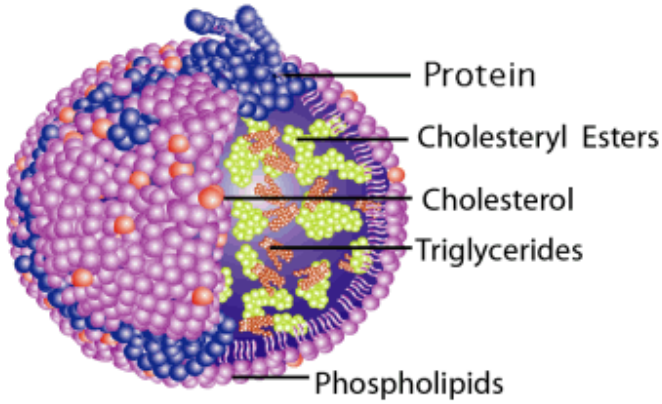


Fig 12.3 Structure of Lipoproteins

apolipoprotein	a protein that binds to lipids
cholesteryl ester	a compound of cholesterol and a fatty acid
triglyceride	a compound of glycerol and three fatty acids, an ordinary fat molecule
phospholipid	a compound of glycerol, two fatty acids, and choline phospate, an emulsifier like lecithin

1. Chylomicrons

Chylomicrons are the largest and least dense of the lipoproteins. These 1000-nanometer particles originate in the intestinal mucosa. Their function is to transport dietary triglycerides and cholesterol absorbed by the intestinal epithelial cells. Chylomicrons contain about 1-2% protein, 85-88% triglycerides, ~8% phospholipids, ~3% cholesteryl esters and ~1% cholesterol. The high triglyceride content of chylomicrons gives them a density of less than 0.95.

The lymphatic system transports chylomicrons to the plasma where they acquire additional apolipoproteins from HDL. Triglycerides contained in chylomicrons are hydrolyzed in the tissues and the particle remnants are processed by the liver.

2. Very Low Density Lipoproteins (VLDL)

Very low density lipoproteins are approximately 25-90 nanometers in size, and have a density of ~0.98. VLDL contains 5-12% protein, 50-55% triglycerides, 18-20% phospholipids, 12-15% cholesteryl esters and 8-10% cholesterol. VLDL also acquires several apolipoproteins from plasma HDL and is a source of triglycerides for the cells.

3. Intermediate Density Lipoproteins (IDL)

Intermediate density lipoproteins are smaller than VLDL, approximately 40 nanometers, and have a density of ~1.0. IDLs are composed of 10-12% protein, 24-30% triglycerides, 25-27% phospholipids, 32-35% cholesteryl esters and 8-10% cholesterol. IDLs are derived from VLDL by triglyceride depletion and therefore contain the same apolipoproteins as VLDL. IDL becomes LDL as its triglycerides are transferred to the cells.

4. Low Density Lipoproteins (LDL) - "Bad" Cholesterol

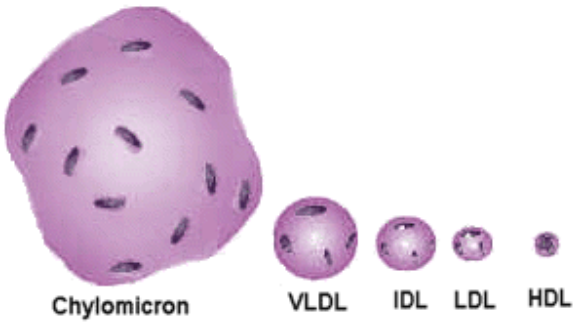
Low density lipoproteins are smaller than IDL, approximately 26 nanometers, and have a density of ~1.04. LDL contains 20-22% protein, 10-15% triglycerides, 20-28% phospholipids, 37-48% cholesteryl esters, and 8-10% cholesterol. One of the protein components of LDL is apolipoprotein B100 which serves to bind the lipoprotein particles to LDL-specific receptors on the surface of many cells. LDL particles bound to the surface of a cell are engulfed and the cholesterol in the LDL particles is used as a structural component of cell membranes or converted to steroid hormones. Apoprotein B is the major protein in all lipoproteins, except high density lipoprotein (HDL).

LDL and HDL transport both dietary and endogenous cholesterol in the plasma, but LDL is the main transporter of cholesterol and cholesteryl esters and makes up more than half of the total lipoprotein in plasma.

5. High Density Lipoproteins (HDL) - "Good" Cholesterol

High density lipoproteins are the smallest of the lipoproteins. HDL particles have a size of 6-12.5 nanometers and a density of ~1.12. HDL contains approximately 55% protein, 3-15% triglycerides, 26-46% phospholipids, 15-30% cholesteryl esters, and 2-10% cholesterol. HDL contains a large number of different proteins including apolipoproteins such as apo-AI (apolipoprotein A1), apo-CI, apo-CII, apo-D, and apo-E. The HDL proteins serve in lipid metabolism, complement regulation, and participate as proteinase inhibitors and acute phase response to support the immune system against inflammation and parasitic diseases.

HDL is produced in the liver and intestine and acts like a scavenger of cholesterol. HDL can bind to cholesterol in cell membranes by using the apo-AI protein to mediate the formation of cholesteryl esters. The apo-D protein in HDL then activates the transfer of cholesteryl esters to VLDL and LDL. HDL also transfers apo-CII and apo-E proteins to chylomicrons and other low density lipoproteins. In the liver, the apo-E protein is used to recognize and absorb the remants of lipoproteins so that excess cholesterol can be removed and converted to bile acids that are excreted into the duodenum (small intestine) through the bile duct.



12.4 Relative Sizes of Lipoproteins

Lipoproteins and their role in atherosclerosis

Lipoproteins are macromolecular assemblies composed of lipids and proteins at variable ratios, densities and sizes. Their role is to transport water-insoluble lipids in the blood. On the basis of their buoyant density lipoproteins are divided into 5

major classes: chylomicrons, very low density lipoproteins (VLDL), intermediate density lipoproteins (IDL), low density lipoproteins (LDL) and high density lipoproteins (HDL). LDL and HDL are known as the “bad” and “good” cholesterol, respectively. Thus, elevated levels of LDL are linked to premature development of atherosclerosis and coronary heart disease, while high levels of HDL appear to be protective.

A crucial step in the pathogenesis of atherosclerosis is believed to be the oxidative modification of low density lipoprotein (LDL). The oxidation of LDL is a free radical driven lipid peroxidation process and the aldehyde products of lipid hydroperoxide breakdown are responsible for the modification of the LDL apoprotein. Aldehyde-modified apoB protein has altered receptor affinity, causing it to be scavenged by macrophages in an uncontrolled manner with the development of foam cells and the initiation of the atherosclerotic lesion. The aldehydic products of lipid peroxidation may also be involved in other aspects of the development of the lesion. The oxidation of LDL may be prevented by its endogenous antioxidant compounds, most prominent of which is α-tocopherol. Consequently, an improved antioxidant status may offer possibilities for the prevention of this major disease.

12.5 Lipid aggregates

a. Micelles

A micelle or micella (plural micelles or micellae) is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre. This phase is caused by the packing behavior of single-tail lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a normal-phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle).

Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers, are also possible. The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellisation and forms part of the Phase behaviour of many lipids according to their polymorphism.

Functions of micelles

- Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. Bile salts formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (e.g., lecithin) and lipid-soluble vitamins (A, D, E, and K) within the micelle by the small intestine.
- Micelles are used for targeted drug delivery.

b. Liposome

A liposome is an artificially-prepared spherical vesicle composed of a lipid bilayer. The liposome can be used as a vehicle for administration of nutrients and pharmaceutical drugs. Liposomes can be prepared by disrupting biological membranes (such as by sonication). Liposomes are often composed of phosphatidylcholine-enriched phospholipids and may also contain mixed lipid chains with surfactant properties such as eggphosphatidylethanolamine. A liposome design may employ surface ligands for attaching to unhealthy tissue.

Types of liposomes

The major types of liposomes are the multilamellar vesicle (MLV), the small unilamellar vesicle (SUV), the large unilamellar vesicle (LUV), and the cochleate vesicle.

Structure of liposomes

A liposome encapsulates a region of aqueous solution inside a hydrophobic membrane; dissolved hydrophilicsolutes cannot readily pass through the lipids. Hydrophobic chemicals can be dissolved into the membrane, and in this way liposome can carry both hydrophobic molecules and hydrophilic molecules. To deliver the molecules to sites of action, the lipid bilayer can fuse with other

bilayers such as the cell membrane, thus delivering the liposome contents. By making liposomes in a solution of DNA or drugs (which would normally be unable to diffuse through the membrane) they can be (indiscriminately) delivered past the lipid bilayer. A liposome does not necessarily have lipophobic contents, such as water, although it usually does.

Uses of liposomes

- Liposomes are used as models for artificial cells. Liposomes can also be designed to deliver drugs in other ways. Liposomes that contain low (or high) pH can be constructed such that dissolved aqueous drugs will be charged in solution (i.e., the pH is outside the drug's pI range). As the pH naturally neutralizes within the liposome (protons can pass through some membranes), the drug will also be neutralized, allowing it to freely pass through a membrane. These liposomes work to deliver drug by diffusion rather than by direct cell fusion.

- A similar approach can be exploited in the biodetoxification of drugs by injecting empty liposomes with a transmembrane pH gradient. In this case the vesicles act as sinks to scavenge the drug in the blood circulation and prevent its toxic effect.

- Another strategy for liposome drug delivery is gene and drug delivery applications in target endocytosis events. Liposomes can be made in a particular size range that makes them viable targets for natural macrophagephagocytosis. These liposomes may be digested while in the macrophage's phagosome, thus releasing its drug. Liposomes can also be decorated with opsonins and ligands to activate endocytosis in other cell types.

- The use of liposomes for transformation or transfection of DNA into a host cell is known as lipofection.

- Liposomes can be used as carriers for the delivery of dyes to textiles, pesticides to plants, enzymes and nutritional supplements to foods, and cosmetics to the skin.

- Liposomes are also used as outer shells of some microbubble contrast agents used in contrast-enhanced ultrasound.

12.6 Lipids in Biological Membranes

A biological membrane is a form of lipid bilayer. The formation of lipid bilayers is an energetically preferred process when the glycerophospholipids described above are in an aqueous environment. This is known as the hydrophobic effect. In an aqueous system, the polar heads of lipids align towards the polar, aqueous environment, while the hydrophobic tails minimize their contact with water and tend to cluster together, forming a vesicle; depending on the concentration of the lipid, this biophysical interaction may result in the formation of micelles, liposomes, or lipid bilayers. Other aggregations are also observed and form part of the polymorphism of amphiphile (lipid) behavior. Phase behavior is an area of study within biophysics and is the subject of current academic research. Micelles and bilayers form in the polar medium by a process known as the hydrophobic effect. When dissolving a lipophilic or amphiphilic substance in a polar environment, the polar molecules (i.e., water in an aqueous solution) become more ordered around the dissolved lipophilic substance, since the polar molecules cannot form hydrogen bonds to the lipophilic areas of the amphiphile. So in an aqueous environment, the water molecules form an ordered "clathrate" cage around the dissolved lipophilic molecule.

Eukaryotic cells are compartmentalized into membrane-bound organelles that carry out different biological functions. The glycerophospholipids are the main structural component of biological membranes, such as the cellular plasma membrane and the intracellular membranes of organelles; in animal cells the plasma membrane physically separates the intracellular components from the extracellular environment.

The glycerophospholipids are amphipathic molecules (containing both hydrophobic and hydrophilic regions) that contain a glycerol core linked to two fatty acid-derived "tails" by ester linkages and to one "head" group by a phosphate ester linkage. While glycerophospholipids are the major component of biological membranes, other non-glyceride lipid components such as sphingomyelin and sterols (mainly cholesterol in animal cell membranes) are also found in biological

membranes. In plants and algae, the galactosyldiacylglycerols, and sulfoquinovosyldiacylglycerol, which lack a phosphate group, are important components of membranes of chloroplasts and related organelles and are the most abundant lipids in photosynthetic tissues, including those of higher plants, algae and certain bacteria.

Bilayers have been found to exhibit high levels of birefringence, which can be used to probe the degree of order (or disruption) within the bilayer using techniques such as dual polarization interferometry and Circular dichroism.

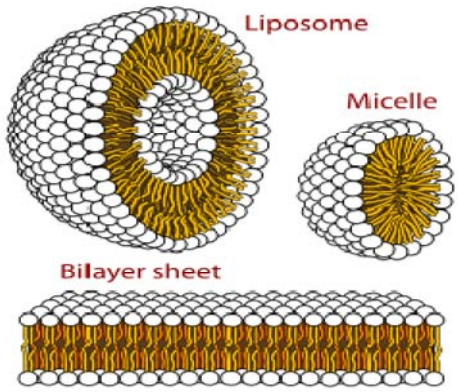


Fig 12.5

Cross-section view of the structures that can be formed by phospholipids in aqueous solutions (Note that, unlike this illustration, micelles are usually formed by single-chain lipids, since it is tough to fit two chains into this shape)

12.7 The Fluid-Mosaic Model of the Plasma Membrane

The fluid-mosaic model describes the plasmamembrane of animal cells. It has the following structure:

- The plasma membrane that surrounds these cells has two layers (a bilayer) of phospholipids (fats with phosphorous attached).
- Each phospholipid molecule has a head that is attracted to water (hydrophilic: hydro = water; philic = loving) and a tail that repels water (hydrophobic: hydro = water; phobic = fearing). Both layers of the plasma membrane have the hydrophilic heads pointing toward the outside; the hydrophobic tails form the inside of the bilayer.

- Because cells reside in a watery solution (extracellular fluid), and they contain a watery solution inside of them (cytoplasm), the plasma membrane forms a circle around each cell so that the water-loving heads are in contact with the fluid, and the water-fearing tails are protected on the inside.

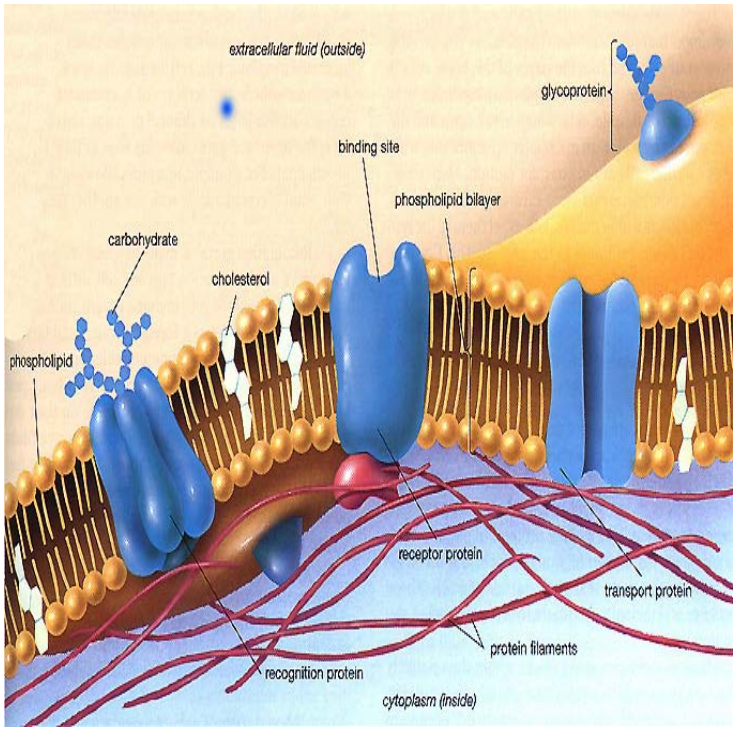


Fig 12.6 The fluid-mosaic model of plasma membranes.

- Proteins and substances such as cholesterol become embedded in the bilayer, giving the membrane the look of a mosaic. Because the plasma membrane has the consistency of vegetable oil at body temperature, the proteins and other substances are able to move across it. That's why the plasma membrane is described using the fluid-mosaic model.

- The molecules that are embedded in the plasma membrane also intentionally embedded. For example, the cholesterol that is stuck in there makes the membrane more stable and prevents it from solidifying when your body temperature is low. (It keeps you from literally freezing when you're "freezing.") Carbohydrate chains attach to the outer surface of the plasma membrane on each cell. These carbohydrates are specific to every person, and they supply characteristics such as your blood type.

12.8 Lipid metabolism: The Beta - oxidation

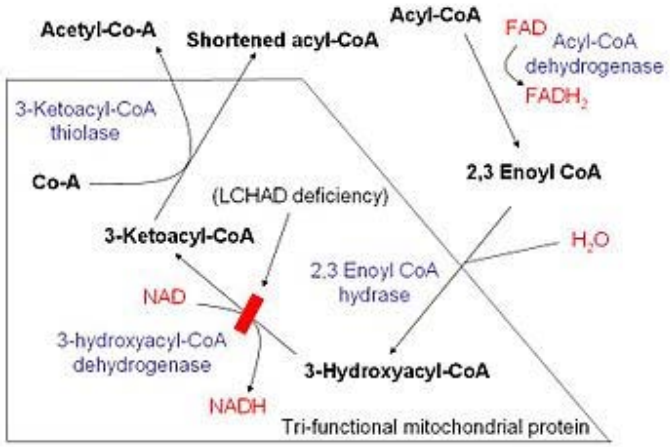


Fig 12.7 (Schematic demonstrating mitochondrialfatty acid beta-oxidation and effects of long-chain 3-hydroxyacyl-coenzyme A dehydrogenase deficiency, LCHAD deficiency)

Beta-oxidation is the process by which fatty acid molecules are broken down in the mitochondria to generate acetyl-coA, which enters the citric acid cycle, and NADH and FADH2, which are used by the electron transport chain. Fatty Acid Catabolism involves three stages. The first stage of fatty acid catabolism is Beta-Oxidation. The second stage is acetyl CoA oxidation to carbon dioxide. The third stage is electron transfer from electron carriers to the electron transfer chain.

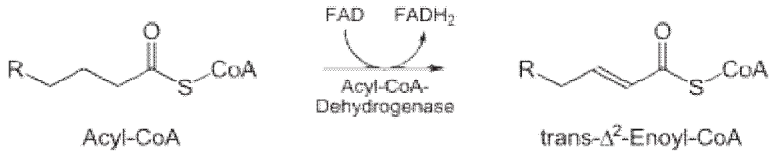
Priming the fatty acid to for oxidation: Carnitine Shuttle

1. Acyl CoA is transferred to the hydroxyl group of carnitine by carnitine palmitoyltransferase I (palmitoyltransferase) located on the outer mitochondrial membrane
2. Acylcarnitine is shuttled inside by a carnitine-acylcarnitine translocase
3. Acylcarnitine is converted back to acyl CoA by carnitine acyltransferase II (palmitoyltransferase) located on the inner mitochondrial membrane. The liberated carnitine returns to the cytosol.

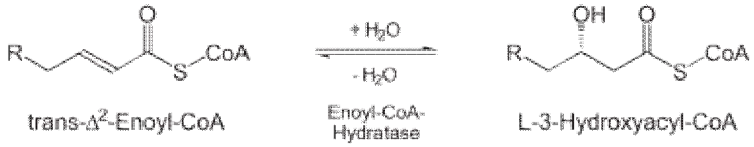
Once the fatty acid is inside the mitochondrial matrix, Beta Oxidation can begin. It has 4 steps.

Step 1 Dehydrogenation: Long chain fatty acid is dehydrogenated to create a trans double bond between C2 and C3. This is catalyzed by the fatty acyl CoA

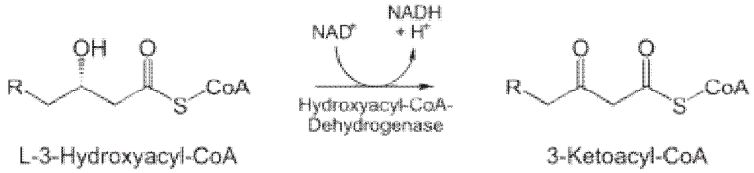
dehydrogenase to produce trans-delta 2-enoyl CoA. It uses FAD as an electron acceptor and it is reduced to FADH2.



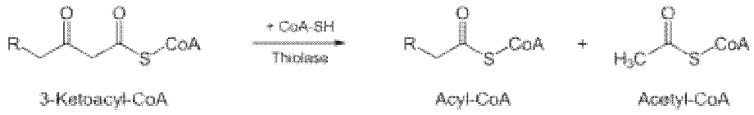
Step 2 Hydration: Trans-delta2-enoyl CoA is hydrated at the double bond to produce L-B-hydroxyacyl CoA. This is catalyzed by enoyl CoA hydratase.



Step 3 Oxidation by NAD^+: L-B-hydroxyacyl CoA is dehydrogenated again to create B-ketoacyl CoA by B-hydroxyacyl CoA dehydrogenase. This enzyme uses NAD as an electron acceptor.



Step 4 Thiolysis: Thiolysis occurs between C2 and C3 (alpha and beta carbons) of B-ketoacyl CoA. Thiolase enzyme catalyzes the reaction when a new molecule of coenzyme A breaks the bond by nucleophilic attack on C2. This releases the first two carbon units, as acetyl CoA, and an fatty acyl CoA without the two first carbons. The process continues until all of the carbons in the fatty acid are turned into acetyl CoA.



This process continues until the entire chain is cleaved into acetyl CoA units. The final cycle produces two separate acetyl CoAs, instead of one acyl CoA and one acetyl CoA. For every cycle, the Acyl CoA unit is shortened by two carbon atoms. Concomitantly, one molecule of $FADH_2$, NADH and acetyl CoA are formed. Fatty acids are oxidized by most of the tissues in the body. However, some tissues such as the adrenal medulla do not use fatty acids for their energy requirements and instead use carbohydrates.

Activation and transport

Free fatty acids cannot penetrate the plasma membrane due to their negative charge. Once in the cytosol, activation of the fatty acid is catalyzed by long fatty acyl CoA synthetase. A fatty acid reacts with ATP to give a fatty acyl adenylate, plus inorganic pyrophosphate, which then reacts with free coenzyme A to give a fatty acyl-CoA ester plus AMP. If the fatty acyl-CoA has a long chain (10 or more carbons) then it is reacted with carnitine to form acylcarnitine, which is transported across the inner mitochondrial membrane by a Carnitine-acylcarnitine translocase. If the fatty acyl-CoA contains a short chain (less than 10 carbons) it can simply diffuse through the inner mitochondrial membrane.

Even-numbered saturated fatty acids

Once inside the mitochondria, each cycle of β-oxidation, liberating a two carbon unit (acetyl-CoA), occurs in a sequence of four reactions:

Odd-numbered saturated fatty acids

In general, fatty acids with an odd number of carbons are found in the lipids of plants and some marine organisms. Many ruminant animals form a large amount of 3-carbon propionate during the fermentation of carbohydrates in the rumen.

Chains with an odd-number of carbons are oxidized in the same manner as even-numbered chains, but the final products are propionyl-CoA and acetyl-CoA.

Propionyl-CoA is first carboxylated using a bicarbonateion into D-stereoisomer of methylmalonyl-CoA, in a reaction that involves a biotinco-factor, ATP, and the enzyme propionyl-CoA carboxylase. The bicarbonate ion's carbon is added to the middle carbon of propionyl-CoA, forming a D-methylmalonyl-CoA. However, the D conformation is enzymatically converted into the L conformation by methylmalonyl-CoA epimerase, then it undergoes intramolecular rearrangement, which is catalyzed by methylmalonyl-CoA mutase (requiring B_{12} as a coenzyme) to form succinyl-CoA. The succinyl-CoA formed can then enter the citric acid cycle.

However, whereas acetyl-CoA enters the citric acid cycle by condensing with an existing molecule of oxaloacetate, succinyl-CoA enters the cycle as a principal in its own right. Thus the succinate just adds to the population of circulating molecules in the cycle and undergoes no net metabolization while in it. When this

infusion of citric acid cycle intermediates exceeds cataplerotic demand (such as for aspartate or glutamate synthesis), some of them can be extracted to the gluconeogenesis pathway, in the liver and kidneys, through phosphoenolpyruvate carboxykinase, and converted to free glucose.

Unsaturated fatty acids

β-Oxidation of unsaturated fatty acids poses a problem since the location of a cis bond can prevent the formation of a trans-Δ^2 bond. These situations are handled by an additional two enzymes, Enoyl CoA isomerase or 2,4 Dienoyl CoA reductase.

Whatever the conformation of the hydrocarbon chain, β-oxidation occurs normally until the acyl CoA (because of the presence of a double bond) is not an appropriate substrate for acyl CoA dehydrogenase, or enoyl CoA hydratase:

- If the acyl CoA contains a cis-Δ^3 bond, then cis-Δ^3-Enoyl CoA isomerase will convert the bond to a trans-Δ^2 bond, which is a regular substrate.
- If the acyl CoA contains a cis-Δ^4 double bond, then its dehydrogenation yields a 2,4-dienoyl intermediate, which is not a substrate for enoyl CoA hydratase. However, the enzyme 2,4 Dienoyl CoA reductase reduces the intermediate, using NADPH, into trans-Δ^3-enoyl CoA. As in the above case, this compound is converted into a suitable intermediate by 3,2-Enoyl CoA isomerase.

To summarize:

- Odd-numbered double bonds are handled by the isomerase.
- Even-numbered double bonds by the reductase (which creates an odd-numbered double bond)

Oxidation in peroxisomes

Fatty acid oxidation also occurs in peroxisomes, when the fatty acid chains are too long to be handled by the mitochondria. However, the oxidation ceases at octanoyl-CoA. It is believed that very long chain (greater than C-22) fatty acids undergo initial oxidation in peroxisomes which is followed by mitochondrial oxidation.

One significant difference is that oxidation in peroxisomes is not coupled to ATP synthesis. Instead, the high-potential electrons are transferred to O_2, which yields H_2O_2. The enzyme catalase, found exclusively in peroxisomes, converts the hydrogen peroxide into water and oxygen.

Peroxisomal β-oxidation also requires enzymes specific to the peroxisome and to very long fatty acids. There are three key differences between the enzymes used for mitochondrial and peroxisomal β-oxidation:

1. β-oxidation in the peroxisome requires the use of a peroxisomal carnitine acyltransferase (instead of carnitine acyltransferase I and II used by the mitochondria) for transport of the activated acyl group into the mitochondria for further breakdown.
2. The first oxidation step in the peroxisome is catalyzed by the enzyme acyl-CoA oxidase.
3. The β-ketothiolase used in peroxisomal β-oxidation has an altered substrate specificity, different from the mitochondrial β-ketothiolase.

Peroxisomal oxidation is induced by high-fat diet and administration of hypolipidemic drugs like clofibrate.

Energy yield

The ATP yield for every oxidation cycle is theoretically at maximum yield 17, as NADH produces 3 ATP, FADH2 produces 2 and a full rotation of the Citric Acid Cycle produces 12. In practice it's closer to 14 ATP for a full oxidation cycle as in practice the theoretical yield isn't attained, it's generally closer to 2.5 ATP per NADH molecule produced, 1.5 for each FADH2 Molecule produced and this equates to 10 per cycle of the TCA (according to the P/O ratio), broken down as follows:

Source	ATP	Total
1 $FADH_2$	x 1.5 ATP =	1.5 ATP (Theoretically 2 ATP)
1 NADH	x 2.5 ATP =	2.5 ATP (Theoretically 3 ATP)
1 acetyl CoA	x 10 ATP =	10 ATP (Theoretically 12 ATP)

TOTAL = 14 ATP

For an even-numbered saturated fat (C_{2n}), n - 1 oxidations are necessary, and the final process yields an additional acetyl CoA. In addition, two equivalents of ATP are lost during the activation of the fatty acid. Therefore, the total ATP yield can be stated as:

(n - 1) * 14 + 10 - 2 = total ATP

For instance, the ATP yield of palmitate (C_{16}, $n = 8$) is:

(8 - 1) * 14 + 10 - 2 = 106 ATP

Represented in table form:

Source	**ATP**	**Total**
7 $FADH_2$	x 1.5 ATP	= 10.5 ATP
7 NADH	x 2.5 ATP	= 17.5 ATP
8 acetyl CoA	x 10 ATP	= 80 ATP
Activation		= -2 ATP
NET		= 106 ATP

For sources that use the larger ATP production numbers described above, the total would be 129 ATP ={(8-1)*17+12-2} equivalents per palmitate. Beta-oxidation of unsaturated fatty acids changes the ATP yield due to the requirement of two possible additional enzymes. The energy yield of the complete oxidation of the fatty acid palmitate is 106 ATP. Unsaturated and odd-chain fatty acids require additional enzymatic steps for degradation.

12.9 Summary

The lipids are a large and diverse group of naturally occurring organic compounds that are related by their solubility in nonpolar organic solvents (e.g. ether, chloroform, acetone & benzene) and general insolubility in water. There is great structural variety among the lipids, which is demonstrated in the above sections of the present unit. The facts of Beta oxidation is also described in this unit to aware

the students about the metabolic process by which fatty acids are broken down in the mitochondria and/or in peroxisomes to generate acetyl-CoA. That is, how the two-carbon fragments are removed sequentially from the carboxyl end of the acid after steps of dehydrogenation, hydration, and oxidation to form a beta-keto acid, which is split by thiolysis. The acetyl-CoA is then ultimately converted into ATP, CO_2, and H_2O using the citric acid cycle and the electron transport chain. Hence the Krebs Cycle can start at acetyl-CoA when fat is being broken down for energy if there is little or no glucose available.

12.10 Self Learning Exersice

Section A

I. HDLs are synthesized in:

a blood b Liver

c Intestine d pancreas

2. Triacylglycerolsare:

a soluble in water

b insoluble in water

c soluble in water at elevated temperature

d partially soluble in water

3. Micelles of fatty acids in water are organized such that the __ a faces the solvent and the b are directed toward the interior.

4. Fatty acids break down of eukaryotes occurs in

5. How many A TPs are formed during complete oxidation of palmitate?

Section B

1. What is the structural difference between cis- and trans-fatty acids?

2. Which are the largest and which is the smallest of the lipoprotein family?

3. Mention biological functions of lipid aggregates.

4. What is the chemical difference between a saturated and an unsaturated fat?

Section C

1. Describe different types of fatty acids. Differentiate cis and trans configuration of fatty acids.
2. What are sphingomylins? Demonstrate with suitable diagram.
3. Differentiate between 'Good' and 'Bad' cholesterol. Write abot different types of lipoproteins.
4. What is atherosclerosis? Write about the probable reason of this disease.
5. Describe the structure of micelles and their functions.
6. Construct the Fluid mosaic model of membrane structure.
7. Write the steps of β-oxidation of fatty acids and the energy yield.

Answer Key

I.b

2. b

3. a=carboxylic acid groups, hydrocarbon chains heads;

b= hydrophilic heads, hydrophobic tails

4. Mitochondria

5.106

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Unit - 13 : Amino Acids, Peptides And Proteins

Structure of Unit:

13.0 Objective

After studying this unit you should be able to:

- Understand the structure and classification of amino acids; scheme of classification,
- Structure of peptides and protin, peptide bond formation, nomenclature and biological uses of peptides and bonding involve in their structure.
- Explain the primary and secondary structure of proteins and forces responsible for holding secondary structure of protein.

- Understand the α-Helix structure and β-Pleated sheet structure of secondary protein and bonding pattern available in these structure
- Explain the triple helix structure of collagen.

13.1 Introduction

Amino acids are the building blocks of proteins and simple proteins contain only conjugated proteins. More than 200 amino acids have been isolated and identified but twenty amino acids are specified by the genetic code and are utilized by ribosomes. Generally these are classifying as-essential, semi-essential and non-essential amino acids.

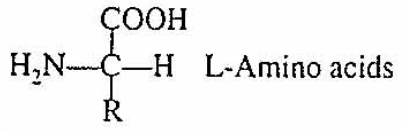
Peptide is composed of two or more amino acids joined through peptide bonds and the term peptide bond is applied to the amide link between amino acid residues and classified as dipeptide, tripeptides, tetrapeptides or olypeptide. Protein has four basic structural levels of organization on the basis of degree of complexity of their molecule and these are known as primary, secondary, tertiary and quaternary. The primary, secondary and tertiary can exist in molecules composed of a single polypeptide chain and fourth (quaternary) involves interactions of polypeptides within a multi-chained protein molecule.

The most probable component of the secondary structure of proteins may be either α-helix or β-helix. The β-helix is a rod like structure, tightly coiled polypeptide main chain forms the inner part of the rod, side chains extend outward in a helical array and this α-helix is stabilized by hydrogen bonds between the NH and CO groups of the main chain. β-Pleated sheet structure of secondary protein is repetitive, minimum energy or stable conformation and formation depends on intermolecular and intramolecular hydrogen bonds. Collagen is the most abundant proteinof mammals and makes up 25-33% of all the body protein. It is a rod-shaped molecule, about 3,000 A° (= 300 nm) long and only 15A° (=1.5 nm) in diameter. The amino acid sequence of collagen is remarkably regular: nearly every third residue is glycine. Proline is also present to a much greater extent than in most other proteins.

13.2 Amino acids

The amino acids are compound containing an amino group and acidic function. Amino acids are the building blocks of proteins and simple proteins contain only

conjugated proteins. The α -Amino acids have the following general structure:



The carbon atom that attached to carboxylic group is called an alpha (α -) carbon. More than 200 amino acids have been isolated and identified but only 25 are obtained upon hydrolysis of typical proteins.

Twenty amino acids are specified by the genetic code and are utilized by ribosomes. But some additional amino acids are isolated from some proteins and these are modifications of the amino acids specified by the genetic code.

13.3 Classification and nomenclature of Amino Acids

These may be named analogously to the hydroxy acids with the amino group designated as □, □, □, □, etc. to indicate its position on the chain of the carboxylic acid called by its common name. In IUPAC system these are named as amino derivatives of the corresponding acid, with the position of the amino group defined by an appropriate number as □-C is C-2, the □-C is C-3, etc.

Out of 25 only 20 amino acids are of general occurrence usually found in all proteins but 10 out of 25 are essential amino acids. Out of 25, 23 amino acids are □-amino acids and remaining two (proline and hydroxyproline) are imino acids. Generally the amino acids are classifying as**-essential, semi-essential and non-essential amino acids**.

There are eight (valine, leucine, isoleucine, threonine, methionine, phenylalanine, tryptophan and lysine) essential amino acids that owe special importance to human beings and adequate amounts of these required to maintain the proper nitrogen balance. The semi-essential amino acids are synthesized partially by the body but not at the rate to meet the requirement of the body but non-essential amino acids are synthesised by the body and these derived from carbon skeletons of lipids and carbohydrates metabolism or from the transformation of essential amino acids.

There are 3 main schemes for classifying amino acids:

Scheme I: On the basis of charge amino acids may be classified as neutral, basic

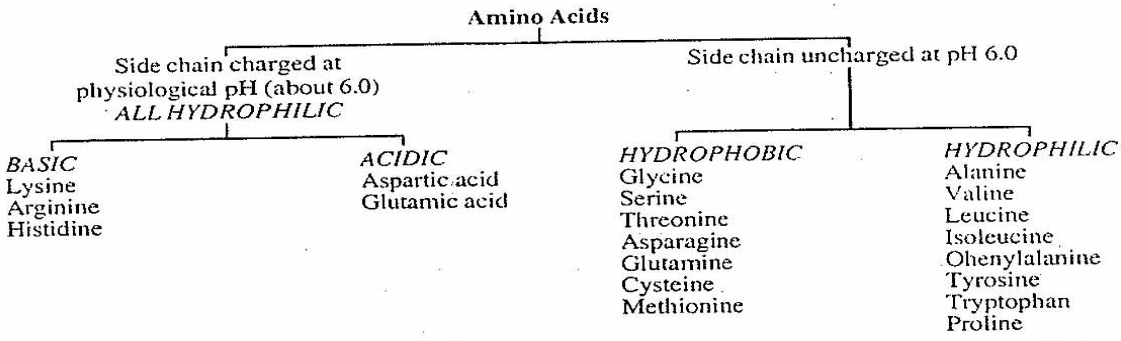
or acidic.

(a) Neutral amino acids- contain one amino-group and one carboxylic group,

(b) Acidic amino acids- contain one amino group and two carboxylic groups and (c) Basic amino acids contain two amino groups and one carboxylic group.

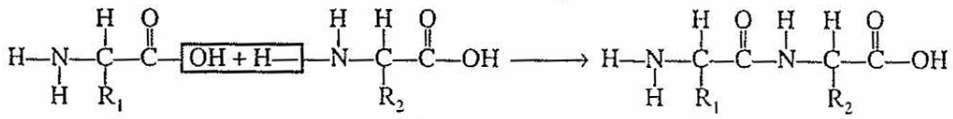
Scheme II: It is based on structure of side chain and according to this side chain amino acids classified into seven groups.

Scheme III: On the basis of the affinity of their side chains for water, amino acids are classified as hydrophilic or hydrophobic. In hydrophilic amino acids the side chains have high affinity for water.



13.4 Structure of peptides

A peptide is composed of two or more amino acids joined through peptide bonds and the term peptide bond is applied to the amide link between amino acid residues. When two amino acids combine to form a dipeptide, a water molecule is removed from the α -carboxyl group of one amino acid and the a-amino group of the other.



The tripeptides are formed by the linkages of three amino acids, tetrapeptides by the linkage of four amino acids and so on. When many amino acids are joined together, the compound is called. Infrared strides have been extensively used to characterize peptide linkage in peptides. Recently X-ray used to study of dipeptides that the entire peptide linkage is flat, carboxyl carbon, nitrogen and the four atoms attached to them lie in the same plane. The carbon nitrogen bond distance has been found to be 132 pm or 1.32A° indicating that carbon-nitrogen

bond has about 50% double bond character.

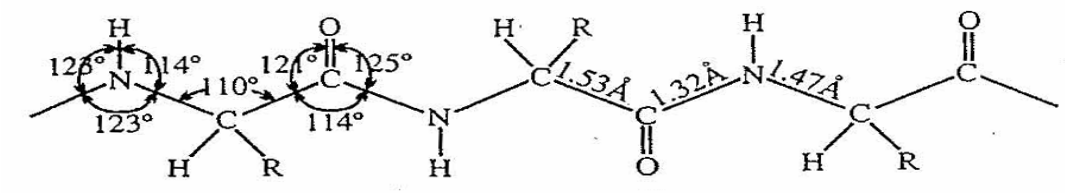


Fig. 13.1: Geometry of peptides linkage

There is no sharp dividing line between a polypeptide and a protein but molecular weight of 10,000 is generally accepted as an arbitrary dividing line means below a molecular weight of 10,000 the compound is considered to be a polypeptide and above 10,000 considered beinga protein. It is accepted that a polypeptide chain contains many units of only one amino acid whereas proteins of the body usually contain a combination of many amino acids and often modified derivatives of these as well.

There are many naturally occurring peptides which owe high biological significance. These include hormones, growth factors and bacterial products.

Table 13.1: Polypeptides of biological significance

Peptides	**Biological Significance**	**No of amino acid residues**
Adreno-corticotropic hormone	Stimulates adrenal cortex	39
Bacitracin	Antibiotic	12
Glucagon	Increases sugar in blood	29
Glutathione	Biological reducing agent	3
Gramicidin A	Antibiotic	10
Melanocyte hormone	Stimulates pigment cell	18
Vasopressin	Water balance hormone	9

13.5 Characteristics, classification, structure and nomenclature of proteins

The proteins are now defined as complex nitrogeneous substances that are found in the protoplasm of cells or these are biopolymers containing large number of amino acids joined to each other by peptide bonds. Depending upon the source most proteins contain 46-55 percent carbon, 6-9 percent hydrogen, 12-30 percent hydrogen, 10-32 percent nitrogen, and 0.2-0.3 percent sulphur and other elements like iron (haemoglobin), phosphorus (nucleoproteins), iodine, copper, manganese and zinc. Biologically proteins comprise of the structural building blocks and functional machinery of living organism or serve as the basis of protoplasm. Some of these are listed as follows:

(a) Proteins constitute the chief structural units of protoplasm and certain proteins are responsible for the control of expression of hereditary information transcription to final translation into new polypeptide chains.

(b) Proteins present in diet serve as the primary source of amino acids participate diverse and necessary processes as respiration, muscular contraction active transport of cellular constituents, electrical transmission etc.

(c) These act as hormonal regulators, storage depots for certain molecules, antibodies complex proteins and weapon for defence of organism.

Proteins are good buffers and play an important role in the control of pH in biological systems.

(d) Viruses are composed of proteins and nucleic acids

These proteins also have some biological functions like e**nzymes** (proteins act as catalysts for biological reactions having specificity, highly efficient), **antibodies** (defence line against foreign organism eg. Gamaglobulins of blood), t**ransport agents (**haemoglobiln), s**tructural materials (**kertain in skin, hair, nails, horm and feathers, myosin in muscles and collagen in tendons), f**ood reserves (o**valbumin of egg, casein of milk) and m**otion proteins (**involved in mechanical movement of muscles as myosin and actin).

Characteristics of proteins: the characteristics of proteins are as follows-

Molecular weight- these are macromolecules constructed by the repetition of one or more structural elements called the monomers (of 20 amino acids). These are linked together to form chains of varying lengths.

Protein has the characteristics of denaturation, changes in conformation or unfolding of the protein molecule i.e. the secondary and tertiary structures of proteins are completely lost in denaturation without any break in the primary structure. An interesting example of irreversible or uncontrolled denaturation is the boiling of an egg during which there occurs the destroying of tertiary structure of protein in an irreversible manner to form a disorganised mass of polypeptide chains (Fig. 2.11).

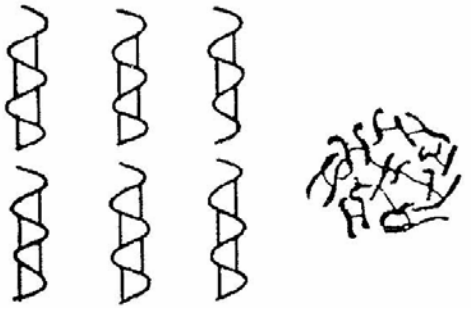
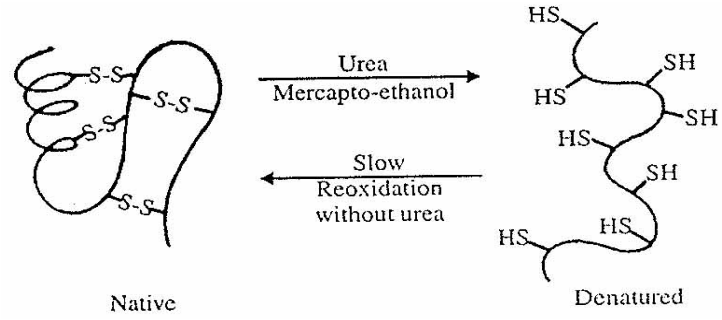


Fig. 13.4: Egg albumin before cooking and after cooking.

Other example of chemical treatment of protein with urea that breaks the disulphide links. The denaturated protein on slow reoxidation without the urea is again changed into the original tertiary structure shown below.



Coagulation of Proteins- the proteins are precipitated (or coagulated) in solutions alkaline to the isoelectirc pH by positive ions such as Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{2+}, Ca^{2+} and Pb^{2+}.

Salting in and out of Proteins- the solubility of many proteins is increased in the presence of small concentrations of various neutral salts that s referred salting in proteins.

Colour Reactions for protein are Biuret test, Millon, xanthoproteic and ninhydrin reactions as well as the Hopkin-Cole reactions (Glyoxylic acid test) are specific tests for various amino acids.

Classification of Proteins: There are several arbitrary classifications of the proteins in use and some of these are as follows:

I. According to Solubility: proteins may be divided into two groups:

1. Fibrous Proteins and 2. Globular Proteins

Table 13.2: Differences between globular and fibrous proteins

Globular Proteins	Fibrous Proteins
(1) They have folded ball-like structures.	Their molecules have long threadlike structures.
(2) They may have three-dimensional shapes.	They have helical or sheet structures.
(3) They are soluble in water, acids, bases and salts.	They are insoluble in water, but soluble in strong acids and bases.
(4) They involve weak inter-molecular hydrogen bonding.	They involve comparatively stronger inter-molecular forces of attraction.
(5) Examples: Egg. albumin, casein (of milk), insulin, myoglobin (of skeletal muscle), haemoglobin (of cells), thyroglobin, etc.	Examples: Keratin, collagen, fibroin, myosin, hair, hoofs, skin, silk, wool, etc.

II. On the Basis of increasing complexity in structures

Proteins may be divided into three main groups as simple, conjugated and derived proteins.

1. Simple Proteins

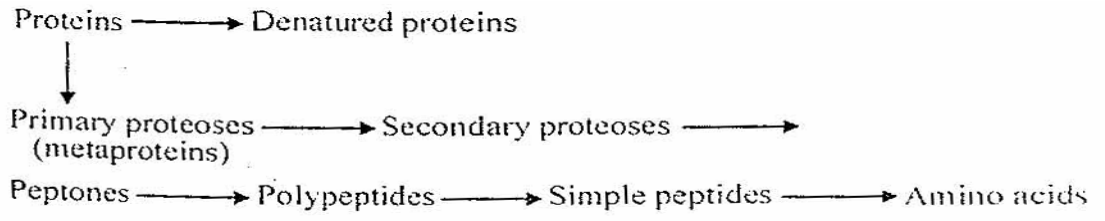
(a) Albumins, (b) Globulins (c) Glutelins, (d) Prolamins, (e) Albuminoids (Scleroproteins)- Albuminoids are further subdivided into two types **(i) Collagens and (ii) Elastins, (f) Basic Proteins-** strongly basic and further divided into two subclasses- **(i) histones and(ii) protamines**

2. Conjugated Proteins

(a) Nucleoproteins, (b) Chromoproteins, (c) Glycoproteins, (d) Phosphoproteins, (e) Lipoproteins and (f) Metalloproteins

3. Derived Proteins

When proteins are hydrolysed by acids, alkalis or enzymes, the degradation products obtained from them are called derived proteins. The derived proteins are further classified on the basis of progressive cleavage as proteins, primary proteoses, secondary proteoses, peptones, polypeptides, simple peptides and amino acids.



Protein has four basic structural levels of organization on the basis of degree of complexity of their molecule and these are known as primary, secondary, tertiary and quaternary or in mathematical term depicted as 1°, 2°, 3° and 4° respectively. The primary, secondary and tertiary can exist in molecules composed of a single polypeptide chain, whereas the fourth (quaternary) involves interactions of polypeptides within a multi-chained protein molecule. The basic primary structure of a protein is relatively simple and consists of one or more linear chains of a number of amino acid units and often assumes a helical shape to produce the secondary structure. This structure in turn, may fold in certain specific patterns and produce the twisted three-dimensional or tertiary structure of the protein molecule. Certain other proteins are made up of subunits of similar or dissimilar types of polypeptide chains interact with other in specific form and give rise quaternary structure of protein.

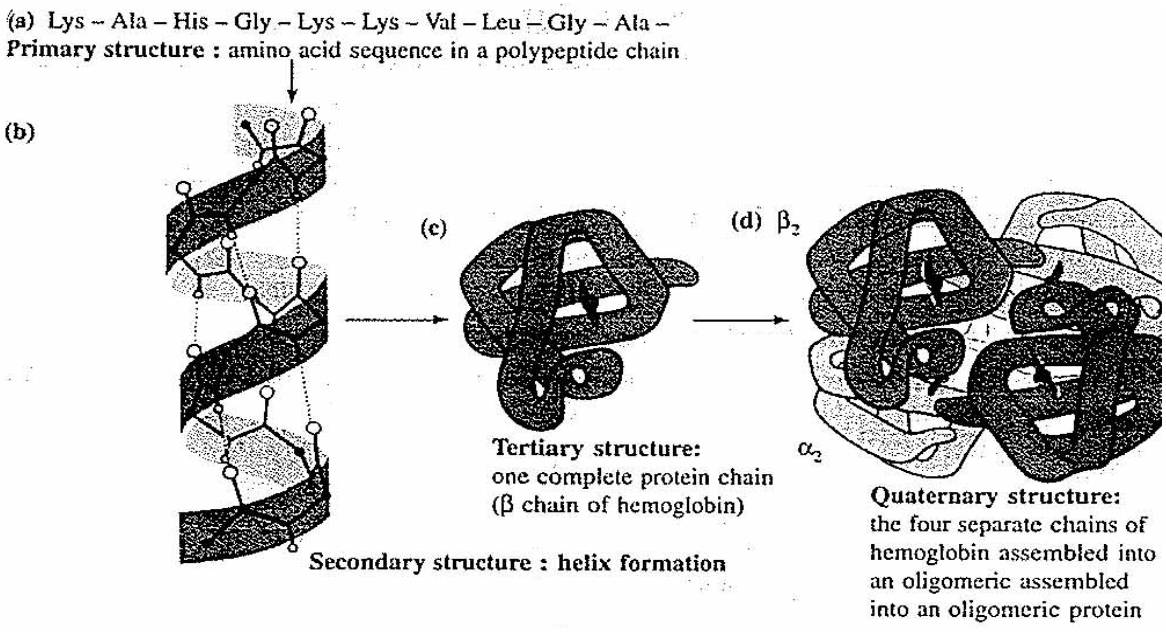


Fig. 13.4: The structure hierarchy in protein

13.6 Primary Structure of protein

The primary structure of a protein refers to the number and sequence of amino acids, the constituent units of the polypeptide chain. The main mode of linkage of the amino acids in proteins is the peptide bond which links the □-carboxyl group of one amino acid residue to the □-amino group of the other. Linus Pauling and Robert Corey (1930), demonstrated the □-carbons of adjacent amino acids are separated by three covalent bonds, arranged $C_{□}$-C-N-$C_{□}$. This indicated a resonance or partial sharing of two pairs of electrons between the carbonyl oxygen and the amide nitrogen. The oxygen has a partial negative charge and the nitrogen a partial positive charge, setting up a small electric dipole. The 4 atoms of the peptide group (C, H, O, and N) lie in a single plane, in such a way that the oxygen atom of the carbonyl group and the hydrogen atom of the amide nitrogen are trans to each other.

All peptide bonds in proteins occur in trans configuration. However, rotation is permitted about the bond between the nitrogen and a-carbon atoms of the main chain (N-$C_{□}$) and between the carbon and carbonyl carbon atoms ($C_{□}$-C).

13.7 Force responsible for holding secondary structure of

protein

Protein synthesis is a multiple dehydration process and peptide bond is, in fact, the backbone of the protein chain. The structure of protein becomes possible linking various amino acids and these amino acids linked to each other by various chemical bonds that are given below:

A.Primary Bond

The principal linkage found in all proteins is the covalent peptide bond, –CO–NH– . It is a specialized amide linkage where C atom of -COOH group of one amino acid is linked with the N atom of -NH_2 group of the adjacent amino acid.

B. Secondary Bonds

These secondary bonds hold the chain in its natural configuration. Some of the secondary bonds commonly found in proteins are listed below:

1. Disulfide Bond (-S-S-)- It formed by the oxidation of the thiol or sulfhydryl (–SH) groups of two cysteine residues to yield a mole of cystine, an amino acid with a disulfide bridge. A disulfide bond has bond strength approximately 50 kcal/mole and with bond length of about 2A° between the two sulfur atoms. Means disulfide bond formation between 2 cystine residues located some distance apart in the polypeptide chain requires that the polypeptide chain be folded back on itself to bring the sulfur groups close together.

As oxytocin has an internal disulfide bond is present between two cysteine units separated from each other in the peptide chain by 4 other amino acid units. In insulin two peptide chains are linked together by 2 disulfide bonds, the presence of an internal disulfide bond in the glycyl (or A) chain between residues 6 and 11 is noteworthy.

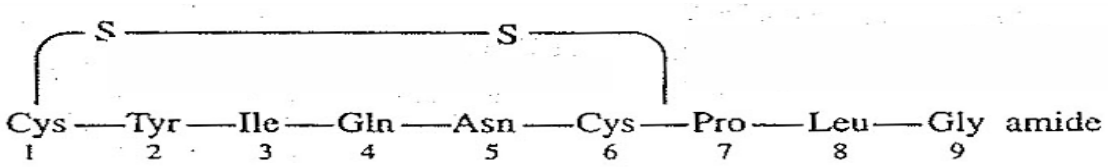


Fig. 13.2: Oxytocin

These two peptide and disulfide bonds are relatively stable and both these bonds collectively or individually maintain the linear form (or the primary structure) of the protein molecule.

2. Hydrogen bond (>CO….HN<) - The hydrogen bond formation has the tendency of hydrogen atom to share electrons with two neighboring atoms; especially O and N (depend on the electronegativity). For example, the carbonyl oxygen of one peptide bond shares its electrons with the hydrogen atom of another peptide bond.

The strength of the hydrogen bond is only 5 to 8 kcal/mole and is maximal when the bond is linear. Hydrogen bonding between amides or peptides plays an important role in stabilizing some conformations of the polypeptide chain **(Fig. 13.3)**.

Since the binding energy of a hydrogen bond amounts to only 1/10th of that of a primary valence, the H bonds are relatively weak linkages but many such bonds collectively exert considerable force and help in maintaining the helical structure (secondary structure). Silk fibroin, composed mainly of glycine, alanine and serine units and it has shows presence of hydrogen bonds involving the imide (>NH) and carbonyl (>C=O) groups of the peptide bonds. In keratin of wool the hydrogen bonds link the side chains so that a single peptide chain is held in a coiled or helical form.

3. Nonpolar or hydrophobic Bond- Amino acids (like alanine, valine, leucine, isoleucine, tethionine, tryptophan, phenylalanine and tyrosine) have the side chains or R groups which are essentially hydrophobic means they have little attraction for water molecules in comparison to the strong hydrogen bonding between water molecules. Such R groups themselves and elimination of water to form linkages between various segments of a chain or between different chains. This is very much like the coalescence of oil droplets suspended in water.

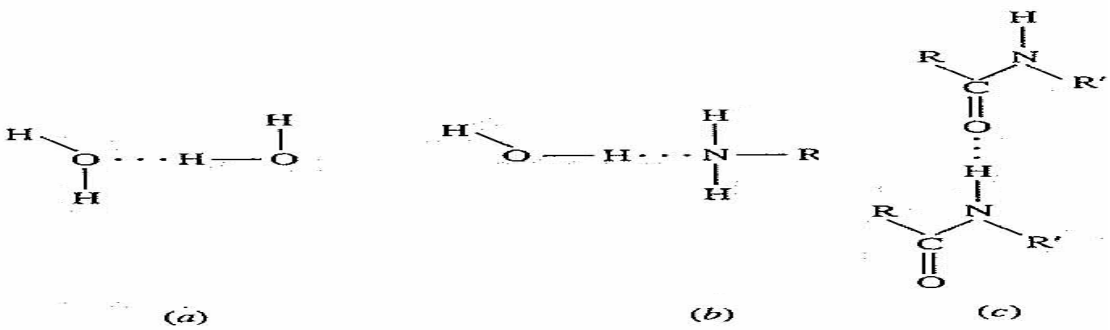


Fig. 13.53: Hydrogen bond (represented by a dotted line) shown in between (a) two water molecules, (b) water and an amine, and (c) two amide groups.

4. Ionic or electrostatic bond- It is also called salt linkage or salt bridge and in this bonding ions possessing similar charge repel each other whereas dissimilar charge attract each other. As divalent cations like magnesium may form electrostatic bonds with two acidic side chains or ionic bonding may be the interaction between the acidic and basic groups of the constituent amino acids. In this bonding two oppositely charged groups are brought close together electrostatic interactions lead to a strong attraction and resulting in the formation of an electrostatic bond.

Ionic bonds although weaker than the hydrogen bonds but these are responsible for maintaining the folded structure (or the tertiary structure) of the globular proteins. The bond strength can be measured by the energy required to break it as one kcal is the quantity of energy needed to raise the temperature of 1,000 g of water by 1°C.

13.8 Secondary Structure of protein

The folding and hydrogen bonding between neighbouring amino acids results in the formation of a rigid and tubular structure called a helix. This constitutes the secondary structure of proteins. On the basis of the nature of hydrogen bond (whether intramolecular or intemolecular), Pauling and Corey (1951) identified two regular types of secondary structure in proteins: alpha helix (α-helix) and beta pleated sheet (β-pleated sheet). The secondary structure shows as to how the polypeptide chains constituting proteins are arranged in space with respect to each other. The actual proteins seldom exist as long thin chains but these chains may be coiled about one another or folded to give helical or compact globular structures.

A very important factor which is responsible for the precise secondary structure of the protein is the stabilizing influence of hydrogen bonding (30-40 kJ/ mole of hydrogen bonding) which exists between the amide hydrogen of one peptide linkage and the amide carbonyl group of another peptide linkage. The most probable component of the secondary structure of proteins may be either □-helix or □-helix.

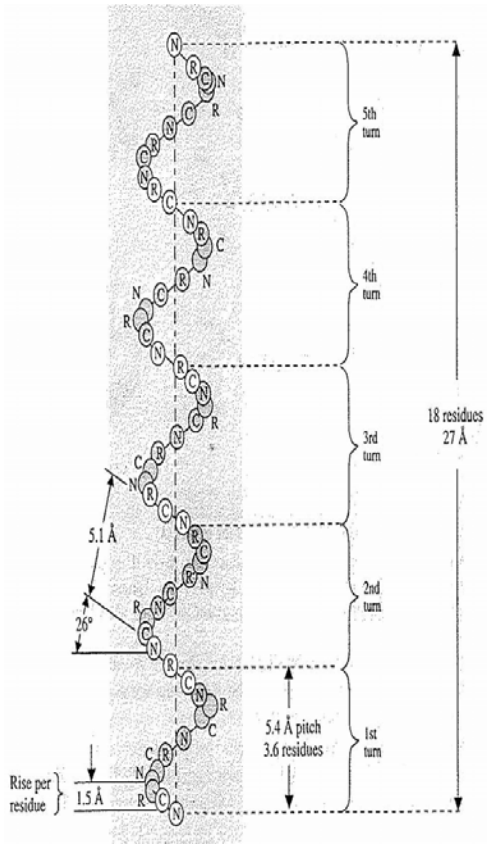
13.8.1 □□□□□□□□-Helix structure of secondary protein

By x-ray diffraction study, William Astbury in 1930s studied fibrous proteins (like

hair and wool) and showed a major periodicity or repeat unit of 5.0 to 5.5 A indicating some regularity in the structure of these proteins. A polypeptide chain with planar peptide bonds would form a right handed helical structure by simple twists about the □-carbon-to-nitrogen and the □-carbon-to-nitrogen and the □-carbon-to-carboxyl carbon bonds. This helical structure called as □-helix, so named because of the mobility of □-carbon atoms.

The □-helix is a rod like structure, tightly coiled polypeptide main chain forms the inner part of the rod, side chains extend outward in a helical array and this □-helix is stabilized by hydrogen bonds between the NH and CO groups of the main chain.

This structure depends on the intramolecular (= intrachain) hydrogen bonding between the NH and CO groups of peptide bonds (Fig. **13.6**). The □-helix has a pitch of 5.4 A° (= 0.54 nm) and contains 3.6 amino acids per turn of the helix, thereby giving a rise per residue of 5.4A° 3.6 = 1.5A° (= 0.15 nm), which is the identity period of □-helix. The amino acid residues in a □-helix, have conformations with □ = - 60° and □ = -45° to - 50°.



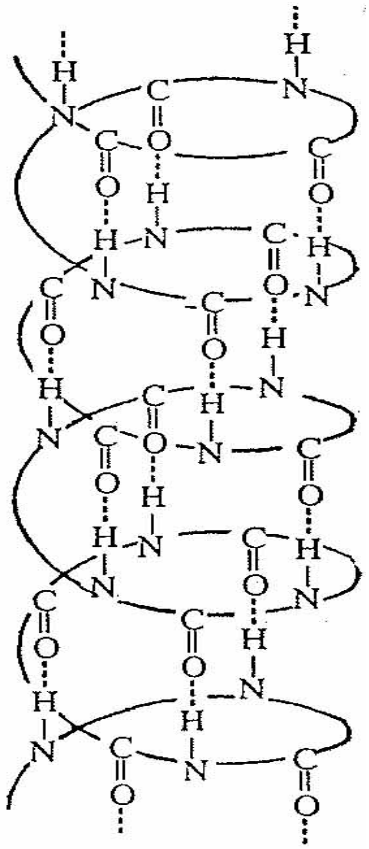


Fig. 13.6: Structure and average dimensions of a □-helix

The helix can be right-handed (clockwise) or left-handed (anticlockwise) □-helices of known polypeptides (L-amino acids) are right-handed. Biologically functional proteins do not usually exhibit cent per cent a-helical structure. Some have a high percentage of their residues in □-helical structures (myoglobin and hemoglobin); others low percentage (chymotrypsin and cytochrome C). The carbonyl group (>CO-O) of every peptide bond is in a position to form a hydrogen bond with the >N-H group of the peptide bond in the next turn of the helix, thereby contributing to the stability of the □-helix. So the right-handed helix is the one that would be expected to occur naturally.

The □-helix occurs in the protein □-keratin, found in skin and its appendages such as hair, nails and feathers and constitutes almost the entire dry weight of hair, wool, feathers, nails, claws, quills, scales, horns, hooves, tortoise shell, and much of the outer layer of skin. The basic structural unit of □-keratin usually consists of 3 right-handed helical polypeptides in a left-handed coil that is stabilized by crosslinking disulfide bonds.

According to Pauling and Corey the □-helix is a spiral arrangement of polypeptide chain, with the chain winding around a central axis, and each amino acid residue rising along the spiral in a uniform manner (Fig. **13.6**). There are either 3.7 or 5.1 amino acid residues in one complete turn of the helix, with a translational distance parallel to the helical axis of 5.4A°. Largely stereochemical considerations revealed that a helix with 3.7 residues per turn was more stable than 5.1 or any other.

The diameter of the helix has been estimated to be about 10A°. In □-helix, each peptide carbonyl oxygen is hydrogen bonded with the amide hydrogen of the fourth amino acid residue further along the helix. This hydrogen bonding prevents free rotation and so the helix is rigid. The overall effect of a helical structure and its stabilization by hydrogen bonds is to create a structure that is cylindrical, in shape, fairly rigid, but capable of undergoing reversible changes in conformation on stretching and bending. Most amino acids are generally accommodated as structural units in the a-helix having the side chains located on the outside and pointing away from the helical axis. The main exception to this is proline which does not fit in a □-helix due to its ring structure. Other exceptions are valine and isoleucine; these are amino acids with bulky side chains which break the helical

structure. Amino acids which do not fit into the helix are termed as helix breakers.

13.8.2 □□□□□□□□-Pleated sheet structure of secondary protein

Pauling and Corey (1951) proposed another type of secondary structure called the □-conformation or pleated sheet. In this side chains are situated above and below the plane of the sheet, with the direction alternating from one residue to the next. The□□-Pleated sheet is repetitive, minimum energy or stable conformation and formation depends on intermolecular and intramolecular hydrogen bonds. The pleated sheet structure is formed by the parallel alignment of a number of polypeptide chains in a plane, with hydrogen bonds between the >C = O and -N-H groups of adjacent chains. The R groups of the constituent amino acids in one polypeptide chain alternately project above and below the plane of the sheet, leading to a two residue repeat unit. The □ sheet structures are quite common in nature and are favoured by the presence of amino acids, glycine and alanine. Silk and certain synthetic fibers such as nylon and orlon are composed of □-structures.

The □-pleated sheet differs markedly from the rod like □-helix:

There are two types of □-pleated sheet structures. If the N-terminal ends of all the participating polypeptide chains lie on the same edge of the sheet, with all C-terminal ends on the opposite edge, the structure is known as a parallel □-pleated sheet. Another type is, if the direction to the chains alternates so that the alternating chains have their N-terminal ends on the same side of the sheet, while their C -terminal ends lie on the opposite edge, the structure is known as the antiparallel □-pleated sheet. Means the hydrogen-bonded polypeptides are aligned in the same N-to-C terminus direction in the parallel pleated sheets and in the opposite N-to-C direction in the antiparallel pleated sheets. □-pleated sheet structure is usually associated with structural proteins or 3-D structures of certain globular proteins like, the enzymes lysozyme and carboxypeptidase.

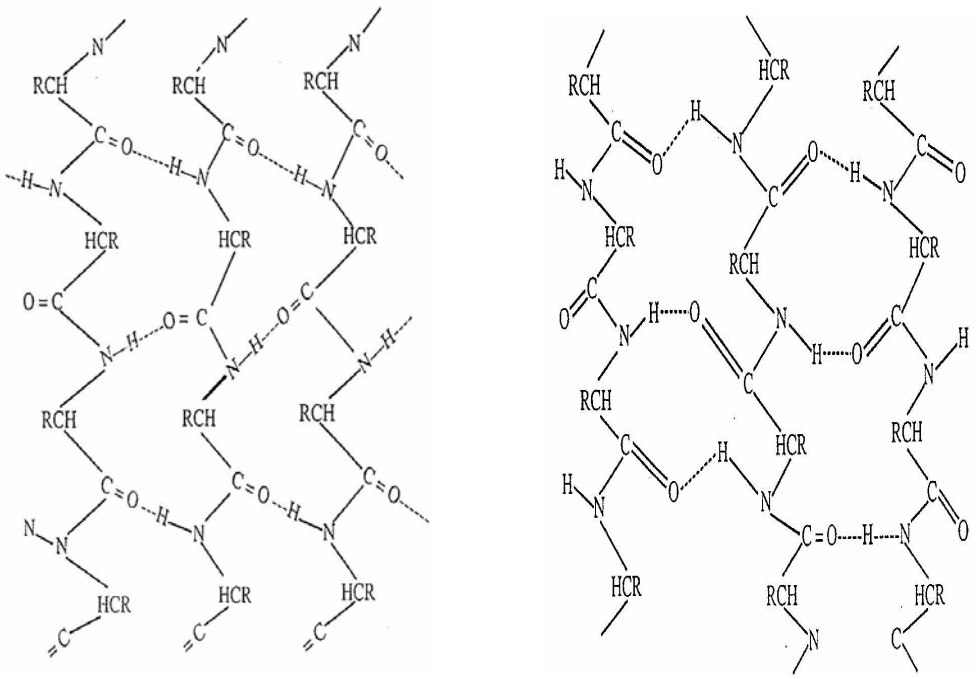


Fig. 13.7: Parallel (left) and antiparallel (right) structure of β -Pleated sheet

In the parallel arrangement, all the chains run in the same direction and in anti parallel arrangement, the chains run alternately in opposite directions (Fig. **13.7**).

The existence of the pleated sheet structure in solid proteins has been confirmed by X-ray analysis as the polypeptide chains are parallel in keratin whereas these are antipaiallel in fibroin. The □-structures have been identified in films and fibres of synthetic polyamino acids. L-alanine can convert the helical form (□-form) to an extended □-form by stretching. Large peptide molecules are not soluble when intramolecularly associated in sheet-like structures but □-structures have been suggested for some dissolved amino acid polymers of relatively low degree of polymerisation.

13.9 Triple helix structure collagen

Collagen is the most abundant protein (found as connective tissues in tendons, cartilage, the organic matrix of bones and the cornea of the eye) of mammals and makes up 25-33% of all the body protein. Collagen is a rod-shaped molecule, about 3,000 A° (= 300 nm) long and only 15A° (=1.5 nm) in diameter. This extracellular protein contains three helical polypeptide chains, each nearly 1,000 residues long. The amino acid sequence of collagen is remarkably regular: nearly every third residue is glycine. Proline is also present to a much greater extent than in most

other proteins. The collagen contains 4-hydroxyprolirie (Hyp) and percentage composition of predominant amino acids found in collagen is: Gly (35%), Ala (11%) and Pro+ Hyp (25%). The amino acid sequence in collagen is generally a repeating tripeptide unit, Gly-X-Pro or Gly-X-Hyp (here X can be any amino acid) and sequence adopts a left-handed helical structure with 3 residues per turn.

The helical motif of its 3 chains is entirely different from □-helix. Hydrogen bonds within a strand (intrachain hydrogen bonds) are absent. Instead of it, each of these 3 helices is stabilized by steric repulsion of the pyrrolidone rings of the proline and hydroxyproline residues. The 3 strands wind around each other in a cable fashion (Fig. 13.7), to form a superhelix sting is right-handed (cf □-keratin). The three strands are stabilized by the interchain formation of hydrogen bonds between the > C = O group of one chain and the >N-H group of another chain. Proline does not have a hydrogen atom attached to its nitrogen when participating in a peptide bond and therefore cannot participate in this interchain hydrogen-bonding. This 3-stranded superhelix is known as the collagen triple helix. The amino acid residue on either side of glycine is located on the outside of the cable, where there is room for the bulky rings of Pro and Hyp residues. The tight wrapping of the collagen triple helix provides great tensile strength with no capacity to stretch.

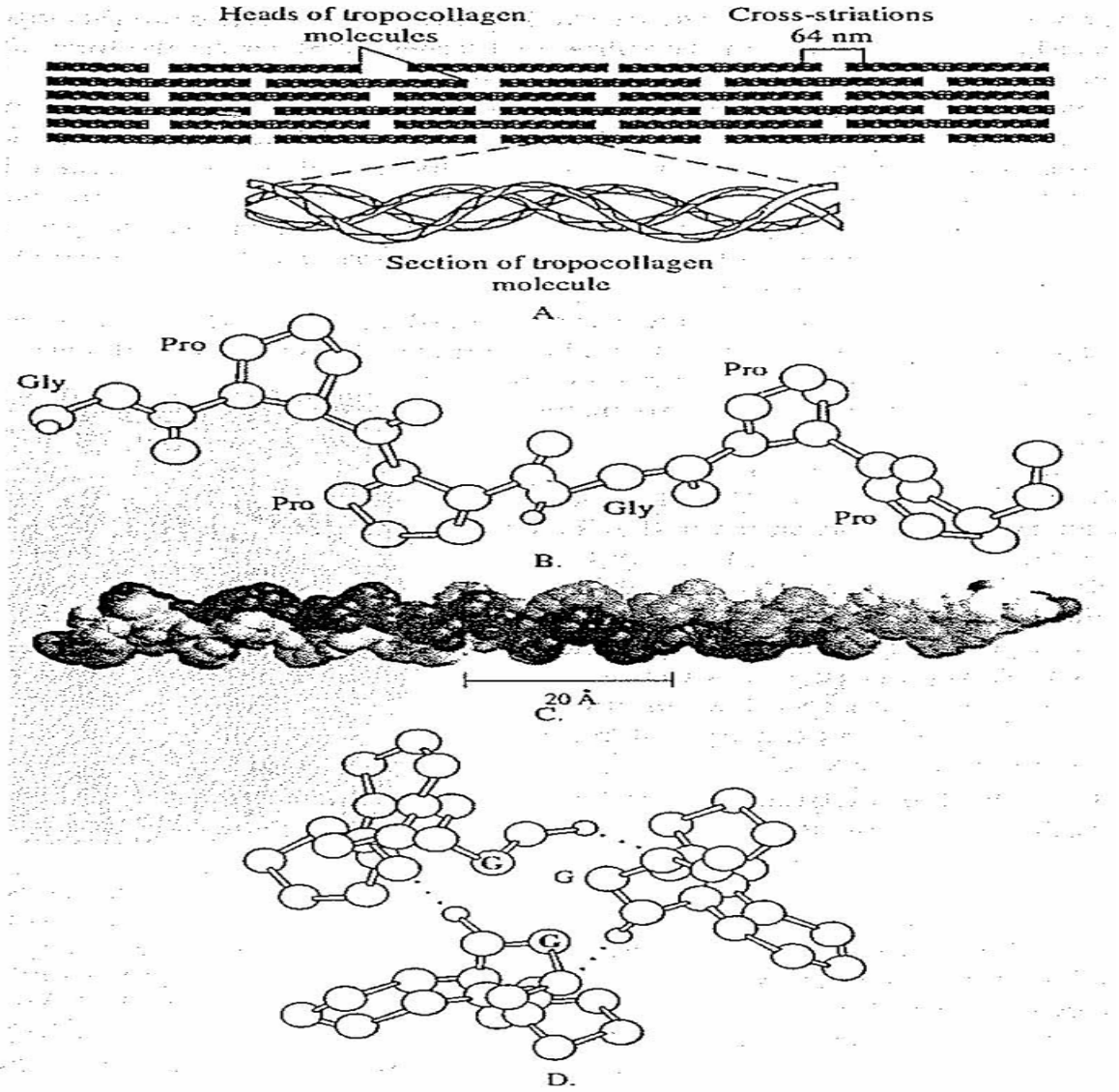


Fig. 13.8: Triple helix structure of collagen (a) collagen fibers and section of tropocollagen molecule (b) conformation of a single strand of triple helix (c) space-filling model of collagen (d) cross section model of collagen

The collagen fibrils consist of recurring 3-stranded polypeptide units called tropocollagen (MW 3, 00,000), arranged head-to-tail in parallel bundles. When all three chains are identical in sequence and known as homotrimers but when two chains are identical and the third differs it is heterotrimers. A series of complex covalent cross-links are formed within and between the tropocollagen molecules in the fibril, leading to the formation of strong mature collagen. The rigid, brittle character of the connective tissue in older people is the result of an accumulation

of covalent cross-links in collagen as they age.

13.10 Summary

More than 200 amino acids have been isolated and identified but twenty amino acids are specified by the genetic code and are utilized by ribosomes. Peptide is composed of two or more amino acids joined through peptide bonds and the term peptide bond is applied to the amide link between amino acid residues and classified as dipeptide, tripeptides, tetrapeptides or olypeptide. Protein has four basic structural levels of organization on the basis of degree of complexity of their molecule and these are known as primary, secondary, tertiary and quaternary. A polypeptide chain in a □-pleated sheet or □-strand has fully extended conformation, rather than being tightly coiled as in the □-helix. The axial distance between adjacent amino acids in □-pleated sheets is 3.5 A°, in contrast with 1.5A° for the □-helix. □-sheet is stabilized by hydrogen bonds between NH and CO groups in different polypeptide strands, whereas in □-helix, the hydrogen bonds are between NH and CO groups in the same strand. The most probable component of the secondary structure of proteins may be either □-helix or □-helix. Collagen is the most abundant proteinof mammals and makes up 25-33% of all the body protein. It is a rod-shaped molecule, about 3,000 A° (= 300 nm) long and only 15A° (=1.5 nm) in diameter. The amino acid sequence of collagen is remarkably regular: nearly every third residue is glycine. Proline is also present to a much greater extent than in most other proteins.

13.11 Self – Learning Exersice

Section A

1 What are esseutial animal acid?
2 How many different amino acids are there?
3 Define proteius
4 How manu basic structured levels of organization are found in proteins? Name them.
5 Name the scientists who ideatified secondary structures.

Section B

1. Discuss the classification and nomenclature of amino acids in detail.
2. Diffeerenite between fibrous & globular proteins.

3. Explain B-platrol sheet for secondary structers of protecins.

Section C

1 Discuss the structure triple structure of collagen.

2 What do you mean by forces responsible for holding secondary structure of protein?

3 What do you mean by secondary structure of protein? Explain it in details.

4 Write short note on following:

Protein structure

Amino acid

Tripetide

Classification of amino acids

Protein classification

5 Give the detailed structure of primary and secondary protein.

Answer from Section A

1 Those that can not be synthoried by body

2 20

3 Bippolymers contoning large no, of amino acids joined to each other by peptic bond

4 4; Primary, Seconhrtiary & Quternary

5 Pauling and corey (1951)

13.12 References and suggested readings

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Unit – 14 : Amino cids, Peptides and Proteins II

Structure of Unit:

14.0 Objective

After studying this unit you should be able to:

- Explain the tertiary and quaternary structure of protein;
- Type of bonds involve in this structure, the amino acids involve in the structure of protein.
- Understand amino acid metabolism, degradation, synthesis and sequence determination of amino acids;
- Chemical / enzymatic/ mass/ spectral/ racemzation/ detection and chemistry of oxytocin and chemistry of tryptophan releasing hormone (TRH).

14.1 Introduction

Tertiary structure and quaternary structure of protein are three-dimensional structure that shows the interactions between amino acid residues relatively far apart in the sequence. Amino acids are the main component of proteins and can easily be determine by using different methods. These amino acids are synthesized and metabolized in different derivatives that help in several biotitic activities of cell and these are also intermediate products. The degradation of amino acids starts with the removal of α-amino group and this amino group is either excreted as ammonia in some of the animals or converted to urea for excretion. All degradative pathways of carbon skeleton are directed to its conversion into such metabolic intermediates which may either be utilized in synthetic pathways (gluconeogenesis) or may be incorporated into TCA cycle and oxidized to produce CO_2 and water and release energy. All amino acids are synthesized by transamination of some keto-acids, which are derived from intermediates of glycolysis, pentose-phosphate pathway and TCA cycle and different pathways of amino acid biosynthesis could be recognized into six groups as oxaloacetate, pyruvate, α-ketoglutrate, 3-phosphoglycerate, phosphoenol pyruvate & erythrose-4- phosphate and ribose -5-phosphate. Oxytocin is a hormone, found in posterior pituitary gland that responsible for uterine contraction. It also excites the musculature of the intestine, gall bladder, ureter and urinary bladder and also causes ejection of milk. The structure of oxytocin was established independently by du Vigneand *et al,* (1953, 1954) and Tuppy *et al,* (1953). Tryptophan, an amino acid found in many foods is (2S)-2-amino-3-(1H-indol-3-yl) propanoic acid and is abbreviated as Trp or W with molecular formula is $C_{11}H_{12}N_2O_2$. Tryptophan is one of the 22 amino acids and the only one with an indole functional group.

14.2 Tertiary structure of protein

Tertiary structure refers to the three-dimensional structure of the polypeptide which results from interactions between amino acid residues relatively far apart in the sequence. In proteins containing more than one polypeptide chain, the term tertiary structure is used in reference to the structure within each chain independently.

The tertiary structure of a protein refers to the orientations of the side chains in the folded molecule spatial arrangement of the polypeptide chain (or chains). The structure assumes under normal conditions of temperature and pH will be its most

stable arrangement and generally called the native conformation of that protein. It reveals an exact description of molecular shape in most small and medium sized proteins.

14.2.1 Types of Bonds in Tertiary Structure of Proteins

The hydrogen bonding is of prime importance in the stabilization of secondary structure, the α-helix and pleated sheets of proteins. Tertiary structure of protein involves hydrogen bonding, ionic, chemical and hydrophobic bonds **(Fig. 14.1).** The disulphide bond also maintains the tertiary structure. Due to covalent nature it is generally included in primary structure. These forces maintain coiling and folding in a definite manner give highly specific internal structure of the protein.

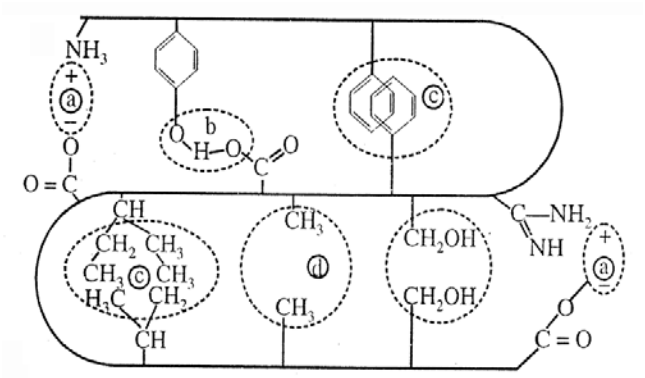


Fig. 14.1: Several types of interactions between side chain substituent's (a) Salt linkages between ionic groups; (b) Hydrogen bonding between polar groups; (c) Hydrophobic interactions between non-polar groups; (d) Van der Waal's interaction between non-polar groups.

Hydrogen bonds in tertiary structures of proteins are expected to form between two amino acids, one of which contains a hydrogen group like -OH as in tyrosine while the other contains a hydrogen acceptor group like a -COOH as in glutamic acid. Ionic bonds in tertiary structures of proteins are expected to form between amino acid side groups which are capable of ionising to form electrically charged species. In these bonds R-groups with unlike charges like NH_3^+ of lysine and COO^- of glutamic acid would be attracted to each other whereas groups having similar charges would repel each other. Hydrophobic (non-polar) bonds in between the hydrocarbon-like side chains (*e.g.* between two methyl or phenyl groups), tend to prefer to be present in the interior of the protein molecule where less water is present.

The distinction between vander Waals type of linkages and hydrophobic linkages is not well defined. This is due to the lack of understanding of the nature and significance of these bonds in determining the structural features of peptides and proteins. In addition to the above mentioned linkages, there also occurs polar group interaction with water on the surface that is of much less importance than the hydrophobic forces.

The various techniques used for studying tertiary structures of proteins are X-ray analysis, viscosity measurements, diffusion, light-scattering, ultra centrifugal method and electron microscopy. J.C. Kendrew, M. Perutz and their co-workers studied myoglobin and haemoglobin by using the X-ray crystallography and mathematical analysis (Fourier synthesis).

(i) A typical globular proteinis compact with extensive folding of polypeptide chain to give a spherical shape. eg myoglobin and haemoglobin.

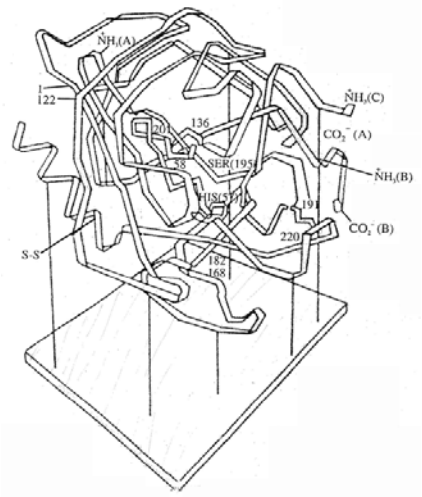


Fig. 14.2: Three-dimensional structure of tosyl-chymotrypsin (tosyl group is at seryl residue 195)

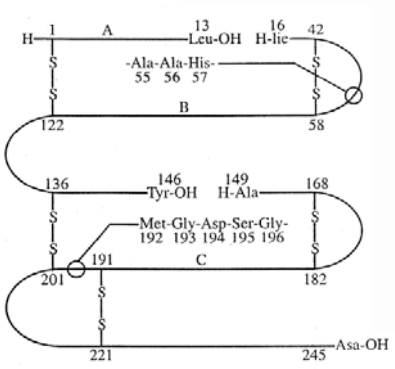


Fig. 14.3: Primary structure of □-chymotrypsin

(ii) A *fibrous protein* has a large helical content and is a rigid molecule of rod shape. □□keratin consists of three (or seven) □-helicals which are wound round each other like strands in a rope, silk, fibroin, the fibrous protein consist of pleated sheets in which polypeptide chains are anti parallel.

14.3 Quaternary structure of protein

The concept of quaternary structure for proteins was initially given by Sorensen and Svedberg in 1930s and the unambiguous determination of quaternary structure is possible only after 30 years by crystallographic methods. Proteins like haemoglobin, consist of more than one polypeptide chain are said to have quaternary structure (oligomeric) and the individual polypeptide chains are known as protomers or subunits. Each of these subunits characterized by its own secondary and tertiary structure and these subunits may or may not be identical. When subunits are held together by hydrogen bonds, they may be separated by reagents like water containing urea which do not break covalent bonds (fig 2.18).

Other examples that show quaternary structures are as follows:

(a) Haemoglobin contains four independent polypeptide chains, two identical □-chains and-two identical □-chains. These chains or subunits are not held together by covalent bonds but by the interactions between the exposed groups of the folded chains (Fig. 14.6)

(b) Lactic dehydrogenase consists of four subunits with molecular weight near 35,000. The subunits are somewhat asymmetric themselves but form a rather cube like aggregate by occupying positions at the corners of a square.

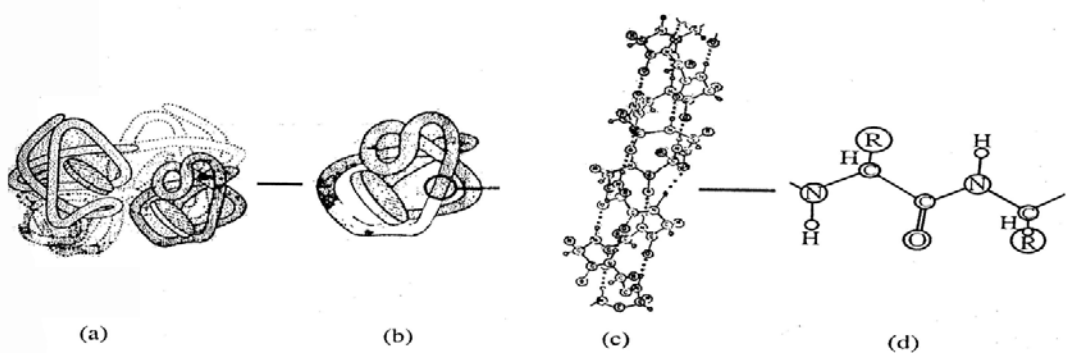


Fig. 14.4: Illustrating the relation among (a) Quaternary structure (b) Tertiary structure (c) Primary structure and (d) Polypeptide structure of proteins.

(c) Formation of multi-enzyme complexes is closely related to the formation of quaternary structure for proteins as pyruvate dehydrogenase of *E. coli* of mw 4,000,000 is composed of three types of enzymes and one of them at least, is in turn composed of subunits.

(d) Quaternary structure is now recognized widely and revealed that majority

of proteins with molecular weights above 50,000 are composed of subunits rather than a single chain.

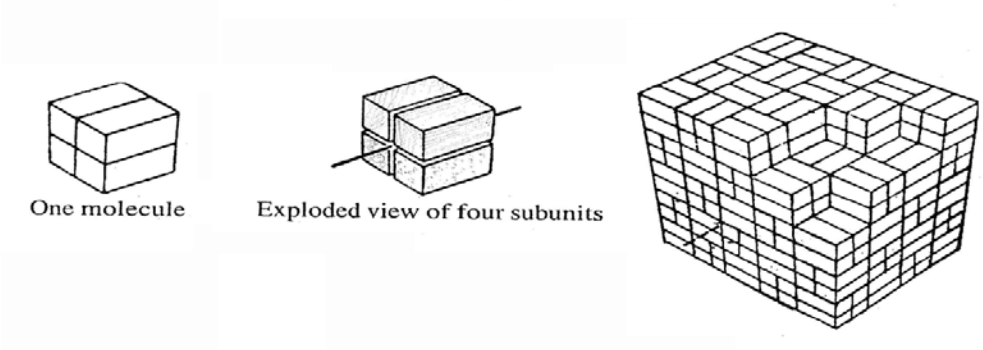


Fig. 14.5: Packing of tetrameric molecules of LDH in a crystal.

Symmetry model represent the quaternary structure for proteins with crystallographic results is most satisfactory. This model is based upon the following postulates as (a) chemically identical polypeptide chains in a protein oligomer are likely to be spatially equivalent and (b) if the free energy of subunit association is sufficiently large to impart a unique oligomeric structure to a protein that structure must define a closed structure of finite extent. There are some apparent exceptions of symmetry model and these can expressed in a More releaxed symmertical model.

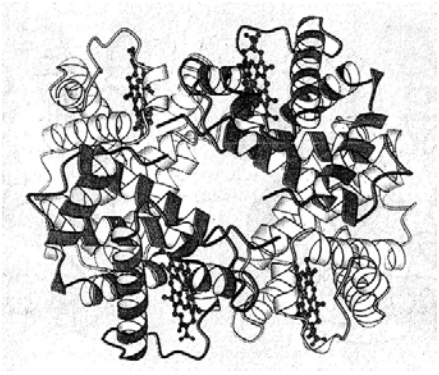


Fig. 14.6: Quaternary structure of hemoglobin molecule, showing interaction of 4 polypeptide chains.

Fibrous (insoluble) Proteins- it is a structural proteins made up of fibers and these fibers are of bundle of fibrils, packed together in a parallel arrangement. The keratins (structural proteins of wool, hair, nails, claws, and hooves) have variable secondary structure. Hair and wool keratins contain □-helical regions and bundles that helices twist together to yield super-helices. On stretching of this

rearrangement change to pleated sheet conformation (□-keratin). Collagen (structural protein of teeth, skin, bone tendon and cartilage) is having an unusual amino acid composition with large amount of glycine, proline and hydroxyproline, the normal type of helical conformation cannot arise and actually the three polypeptide chains get twisted together to a unique helical conformation. The four structures of a protein may be written as follows:

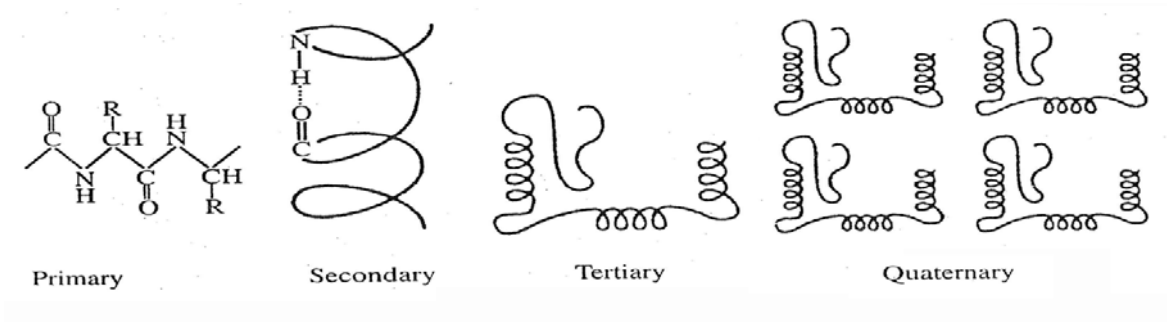


Fig. 14.7 : Structure of Protein

14.4 Amino acid metabolism

The metabolism of amino acid is a big and complicated structure. So the process is classified in two parts (A) degradation of amino acids and (B) Biosynthesis of amino acids for the study-

14.4.1 Degradation of amino acids

The degradation of amino acids starts with the removal of □-amino group and this amino group is either excreted as ammonia in some of the animals or converted to urea for excretion. All degradative pathways of carbon skeleton are directed to its conversion into such metabolic intermediates which may either be utilized in synthetic pathways (gluconeogenesis) or may be incorporated into TCA cycle and oxidized to produce CO_2 and water and release energy.

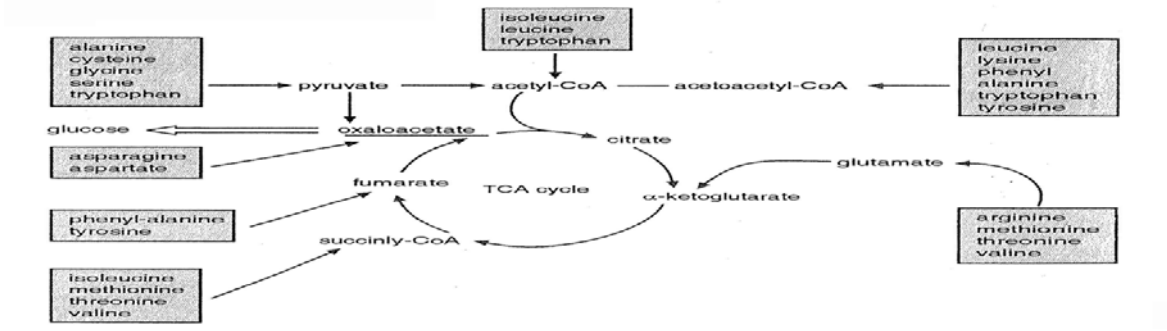


Fig. 14.8: Degradation of amino acids and enterance of degradated products

into TCA cycle

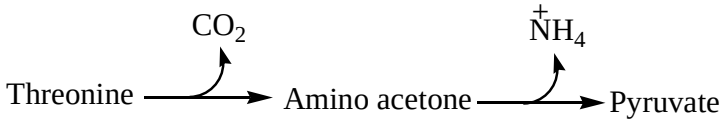
The degradation pathways of all 20 amino acids converge at one of the seven molecules that is pyruvate, acetyl-CoA, aceto-acetyl CoA, α-ketoglutarate, oxaloacetate, fumarate or succinyl-CoA. On the basis of common degradation product the amino acids degradation could be divided into seven groups (Fig. 14.8).

(i) **Amino Acids Degrading into Pyruvate**

The five amino acids degrading to pyruvate are glycine, alanine, serine, cysteine and tryptophan. In some organisms threonine also is degraded to pyruvate but in human beings it is degraded to succinyl-CoA.

Alanine- Alanine yields pyruvate directly on deamination, Serine α-ketoglutarate. Glutamate is later converted to α-ketoglutarate and ammonia in the liver (Alanine + α-ketoglutarate α Pyruvate + Glutamate).

Tryptophan- The side chain of the tryptophan also is cleaved to produce alanine which on deamination gives pyruvate. Glycine- Glycine first changes to serine by serine hydroxymethyl transferase enzyme. This serine is then converted to pyruvate. Serine- it is converted to pyruvate via amino acrylate by the enzyme serine dehydratase. The enzyme is PLP and removes both α-amino and α-hydroxyl groups. Threonine- it is degraded to pyruvate through an intermediate amino acetone.



(ii) **Amino acid degrading to succnyl-CoA**

Methionine- Methionine is converted to α-ketobutyrate then to succinyl-CoA and remaining degradation is like threonine. Isoleucine- it is degraded to acetyl-CoA and propionyl-CoA, propionyl-CoA joins the threonine pathway to produce succinyl-CoA.

(iii) **Amino Acid Degrading to Acetoacetate**

Leucine-it deaminate by transaminase to α-keto acid (α-ketoisocaproate) then isovaleryl-CoA and α-methyl crotonyl-CoA. It is now produce 3-methyl glutaryl-CoA that ultimately change to acetyl-CoA and acetoacetate.

(iv) **Degradation of Phenyl-alanine and Tyrosine**

Both these amino acids are aromatic and, therefore, have a slightly different pathway of their degradation as follows:

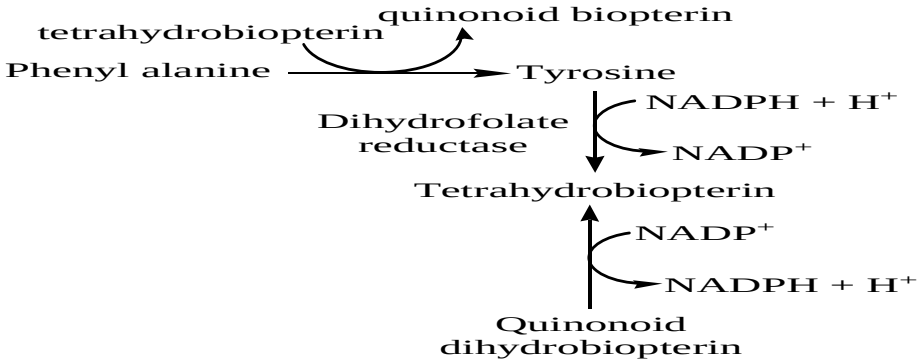
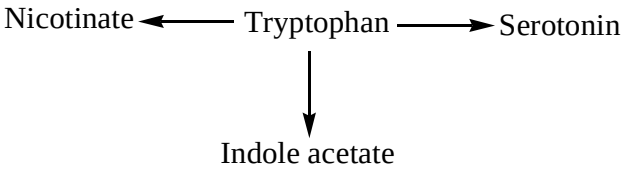


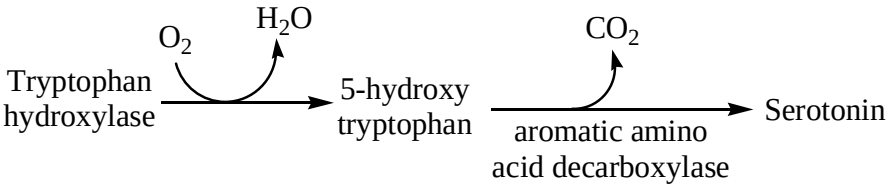
Fig. 14.8: Formation of tetrahydrobiopterin from dihydrobiopterin a reductive process

Degradation of Tryptophan: Tryptophan degradation is very complex. It has two types of degradative pathways. One which leads to anabolic processes, results in the synthesis of nicotinic acid, indole acetic acid or serotonin in three separate pathways.

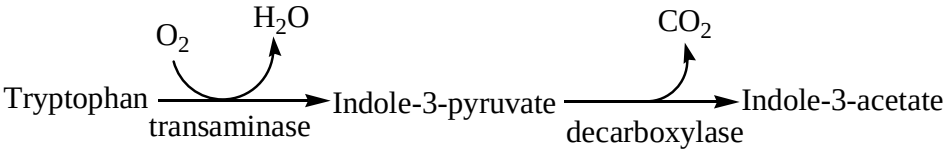
Synthesis of serotonin, indole acetic acid and nicotinate from tryptophan



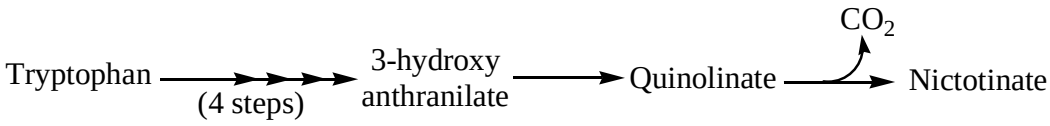
(a) Synthesis of serotonin from tryptophan



(b) Synthesis of indole acetic acid from tryptophan



(c) Synthesis of nicotinate from tryptophan



(v) **Amino Acids degrading to α -Ketoglutarate**

All five carbon amino acids enter the TCA cycle as α -ketoglutarate. These amino acids are Glutamine, Glutamate, Proline, Arginine and Histidine.

Arginine converted to ornithine and release urea. Ornithine is now deaminated and produces glutamate α -semialdehyde finally glutamate is converted to α -ketoglutarate by glutamate dehydrogenase as in case of histidine.

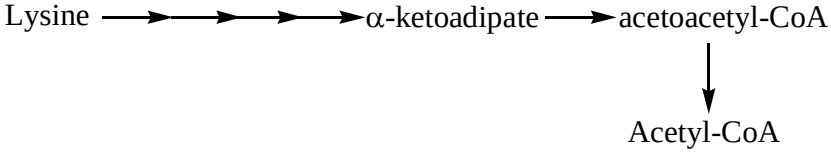
Proline converted to pyrroline 5-carboxylate and produce a linear glutamate α -semialdehyde. Now it converted to glutamate and finally to α -ketoglutarate as like breakdown of arginine.

(vi) **Amino Acids Degrading to Oxaloacetate**

Asparagine and aspartate both amino acids actually aminated to form oxaloacetate. The Aspartate is then converted to oxaloacetate that converted to fumarate by the urea cycle and finally fumarate enters to TCA cycle. Degradation of Lysine produces □-ketoadipic acid and degradation of □-ketoadipic acid follows the pathway like degradation of tryptophan. The end product is acetoacetyl-CoA which is then converted to acetyl-CoA.

(vii) **Degradation Products of Amino Acids are linked to TCA Cycle**

As above stated the degradation pathways of all the twenty protein amino acids and these amino acids are often grouped on the basis of their TCA cycle products. Which do not produce such a product, may enter the cycle as acetyl-CoA. Six out of twenty appear to degrade producing more than one product (Threonine, Tryptophan, Phenyl-alanine, Tyrosine, Isoleucine and Aspartic acid) (Fig. 26).



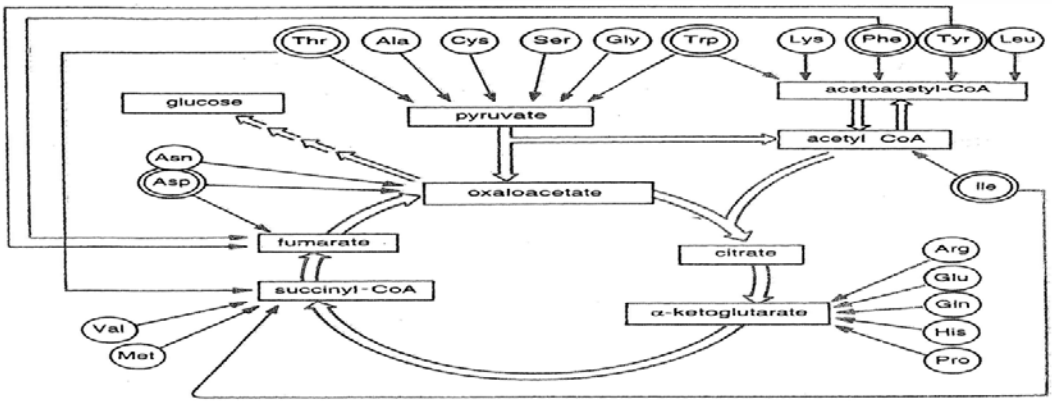


Fig. 14.9: Degradation of amino acids

14.4. Synthesis of amino acids

All amino acids are synthesized by transamination of some keto-acids, which are derived from intermediates of glycolysis, pentose-phosphate pathway and TCA cycle. On the basis of their precursors, the different pathways of amino acid biosynthesis could be recognized into six groups as oxaloacetate, pyruvate, □□ketoglutrate, 3-phosphoglycerate, phosphoenol pyruvate & erythrose-4-phosphate and ribose -5-phosphate, represented as follows:

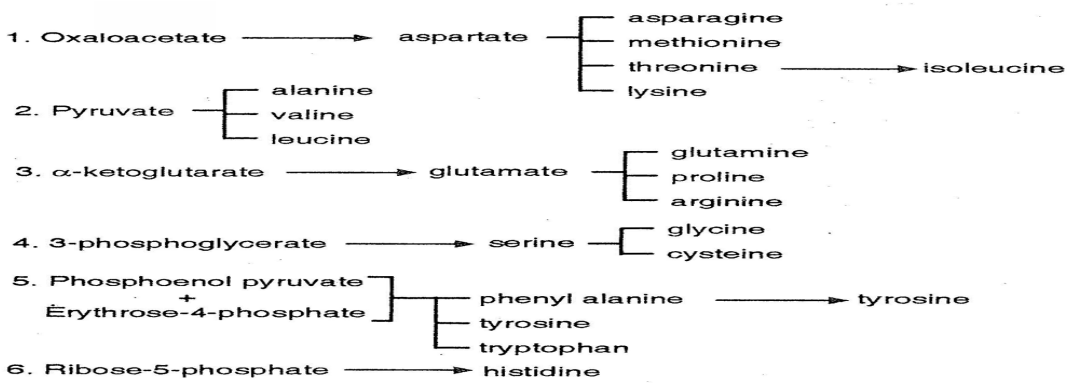


Fig. 14.10: The precursors of amino acids and their derivatives

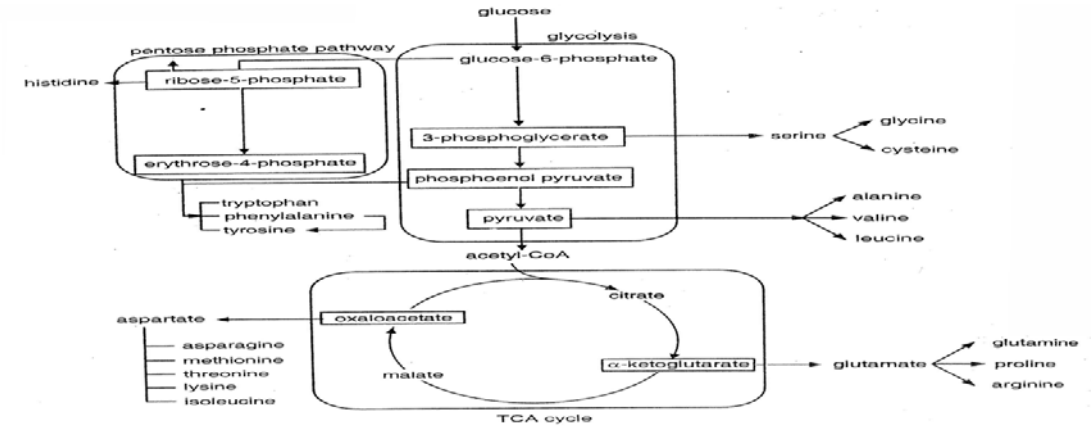
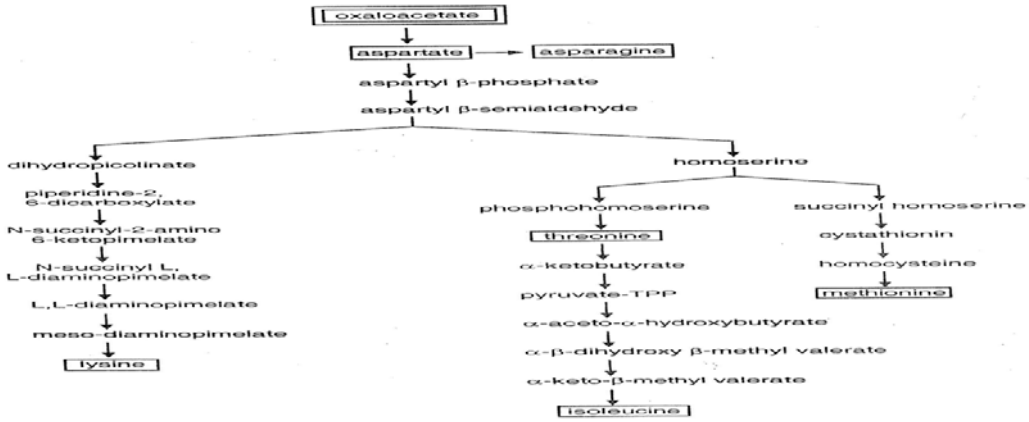


Fig. 14.11: Precursors of amino acid synthesis and metabolic intermediates of glysolysis and TCA cycle.

All the precursor of all the pathways have one step in common that the transfer of amino group from glutamate to respective ketoacids by enzyme amino transferase. All these amino transferases have a prosthetic group, pyridoxal phosphate (PLP), a derivative of pyridoxine (vitamin B6). The important functional group of PLP is the aldehyde group. This group forms covalent Schiff's base intermediates with a linkage with an amino group of a specific lysine residue of the enzyme.

The transamination reaction pathway begins with the pyridoxal phosphate in Schiffs base linkage with specific lysine at the active site of transaminase (internal aldimine). A brief detail of degradation is given below:

(i) Oxaloacetate Precursor- There is five amino acids as Aspartate, Asparagine, Methionine, Threonine (Isoleucine) and Lysine synthesized from oxaloacetate precursor. In this group oxaloacetate is first converted to aspartate by a single step transamination. The amino group is transferred by glutamate.



(ii) Pyruvate Precursor-

Alanine- The pyruvate precursor leads to the synthesis of three amino acids. Synthesis of alanine is the simplest one. It is a simple transamination catalyzed by PLP dependent transaminase. In valine synthesis pyruvate is first decarboxylated by acetolactate synthase and the reaction starts with the TPP carbanion attacking the keto group of pyruvate. Leucine synthesis also starts with a pyruvate precursor.

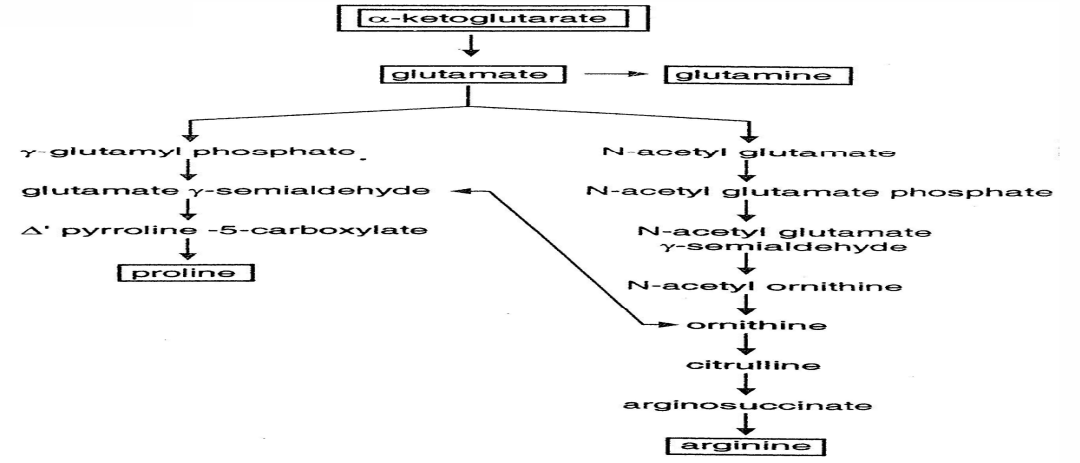


Fig. 14.12: Biosynthetic pathways for the synthesis of pyruvate derived amino acids.

(iii) α-ketoglutarate synthesized glutamate that helps in synthesis of proline, arginine and glutamine.

(iv) 3-phosphoglycerate precursor help in synthesis of serine, glycine and cysteine amino acids.

(v) **Phosphoenol pyruvate & erythrose-4- phosphate (Chorismate Precursor-an aromatic intermediate):** All three amino acids Tryptophan, Tyrosine and Phenyl-alanine) have aromatic ring synthesis of this group of

amino acids starts with aliphatic chain which circularizes to form a six membered ring through a series of steps. Chorismate biosynthesis starts with the condensation of two aliphatic chain precursors, the phosphoenol pyruvate and erythrose 4-phosphate. The methyl carbon of pyruvate joins the aldehyde carbon of erythrose to form a seven carbon intermediate, the 2-keto 3-deoxy D-arabinoheptulosonate 7-phosphate.

(vi) **Ribose-5-phosphate Precursor-** Histidine is an essential amino acid and is not synthesized in animals. Its biosynthesis is known only from bacteria and plants. It requires three precursors the ribose-5-phosphate which contributes five carbons to carbon skeleton, the ATP contributes a carbon and ring nitrogen whereas glutamine provides the second ring nitrogen.

5-phosphoribosyl 1-pyrophosphate □ Histidine

14.5 Sequence determination of amino acids

It can be easily studied by complete hydrolysis of the protein into its constituent amino acids and then their nature and amounts are determined. The protein to be studied is hydrolysed by using 6N HCI at 110°C or enzyme (peptidase) to its constituent amino acids except tryptophan. The tryptophan can be ascertained by the hydrolysis of polypeptide with 2 N alkali. This procedure destroys arginine, cystine, serine, and threonine and racemizes many amino acids. Different method is used to estimate and separate the amino acids but the most common method is ion-exchange chromatography.

(i) Ion-exchange Chromatography-The chromatographic columns are first of all packed with sulphonated polystyrene divinyl resin which has highly polar -SO_3H groups. The solution having amino acid mixture is kept on the column of the resin. By proton transfer, the amino acid gets converted into ammonium ion and the resin into sulphonate anions. The ammonium ions of different amino acids then get adsorbed on the surface of the sulphonic acid resin anion with different strength depending upon the relative acidity of the acid form of the amino acid.

(ii) pH dependent precipitation-The amino acids are practically insoluble in water at their isoelectric points. As amino acids have different isoelectric points, it implies that they have different solubilities and hence can be separated from each other. The pH of the peptide or protein hydrolysate is changed gradually which gives rise to the successive precipitation of amino acids at their respective

isoelectric point.

(iii) Isotopic Dilution Method. The quantity of each amino acid may also be known by isotopic dilution method by C^{14}-labelled variety of the amino acid. The amount of each of the amino acids present in the hydrolysate may also be calculated by means of biological assays. The hydrolysate is allowed to be fed to a micro-organism having a specific requirement for a particular amino acid.

From the relative amount of each of the amino acids present in the protein molecule, the empirical formula in terms of the amino-acids of the protein can be found out. For example, a hydrolysate of one of the insulin chains (B) gave the following on analysis:

Gly_3 Ala_2 Val_3 Leu_4 Pro Phe_3 $(CySH)_3$ Arg His_2 Lys Asp (NH_2) Glu_2 Ser Glu_2 Ser Thr Tyr_2

From the relative amount of each of the amino acid present in a terms of the empirical formula in terms of the amino acids of proteins can be deduced. The minimum molecular weight of the protein is determined from the empirical formula. The molecular weight of protein is also determined by a physical method. When a protein molecule consists of the disulphide bond, the disulphide bond can be broken either by oxidation or reduction. The oxidation is generally carried out with performic acid when there found the cleavage of disulphide bonds present in proteins (or peptides) to produce chains containing cysteic acid residues which are stable and assist the separation of the oxidation mixture by ion-exchange methods.

After establishing the identity of constituting amino acids and their relative amounts ascertain the sequence of amino acids in a peptide can be done. By determining N-and C-terminal groups now it is possible to determine the amino acid sequence of the tripeptide. It is to be remembered that the sequence of amino acids in a tripeptide may be determined by employing one method twice or by use of each method once. The amino acids sequence may be determined by the Edman N-terminal method. As well in the general method of amino acid sequence analysis, both end-group (N- and C- terminal) analyses are not performed on the original protein. The usual practice is to determine one end-group. This is then followed by fragmentation of the protein in at least two different ways into smaller fragments. The latter are then subjected to amino acid sequence determination by end-group analysis. From the structures of small fragments; it is possible to deduce

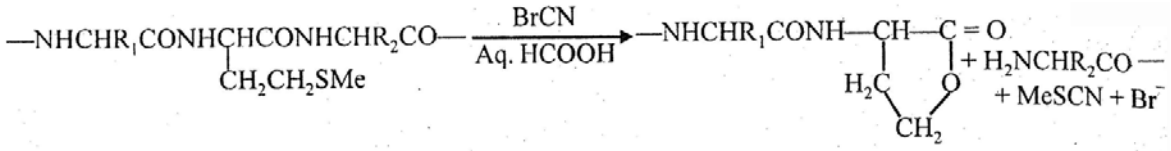
the complete sequence of the amino add in the original protein by over hipping procedure.

As well as in hexapeptide, the partial hydrolysis yield small fragments and these fragments are subjected to amino acid analysis. When amino acids found more than once in a polypeptide chain it increases the difficulty to elucidating the amino acid sequence, in that case overlapping procedure is not of much help. For the determination, hydrolytic reagents are of much use in deciding the amino acid sequence in such cases because these can selectively break peptide bonds.

14.8 Chemical , enzymatic, mass, spectral, racemzation, detection of amino acid,

It is used for specific fragmentation of a protein or polypeptide chain.

(i) **Chemical methods**- the best chemical method is the action of cyanogens bromide on the peptide in aqueous formic acid at room temperature. In this reaction, only peptides in which the CO group forms a part of a methionine residue undergo splitting to form the products likehomoserine lactone and the rest of the peptide.



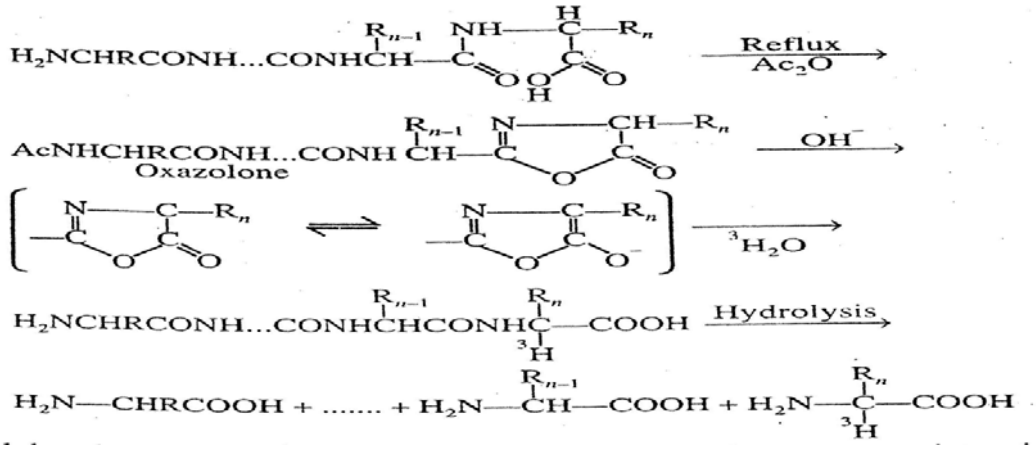
(ii) **Enzymatic method**- Enzymes are biocatalast and quite useful in protein degradation. Enzyme trypsin is able to split such peptide bonds in which the carbonyl group forms a part of a lysine or an arginine residue, chymotrypsin able to split peptide bonds in which the carbonyl group forms a part of a phenylalanine and tyrosine or tryptophan residue. By using these two enzymes separately, the peptide or protein may be splitted in different ways to yield relatively large fragments.

(iii) Mass Spectrometry- it is recent technique used to ascertain the amino acid sequence in the protein or in the various fragments obtained by partial hydrolysis.

The sequence of amino acid in the primary structure, even a change in one amino acid residue may adversely affect the biological activity of a protein. in

haemoglobin, the normal adult haemoglobin molecule (HbA) contains four polypeptide chains, two identical □-chains and two identical □-chains but in sickle cell anaemia (low oxygen-binding capacity), presence of an abnormal haemoglobin molecule (HbS) malfunction traced in both the chains, a particular glutamic acid residue (the sixth amino acid from the N-terminal end) is replaced by a valine 'residue. All other chain residues are identical; and the □-chains are completely identical. Despite this small difference involving a total of two residues out of 574, the HbS molecule does not function properly.

(iv) Racemization method- a new method for the identification of C-terminal residues. The procedure involves the racemization of the C-terminal residue and the concurrent selective labelling of that residue with tritium. The peptide is treated in reaction with acetic anhydride under the influence of alkaline conditions; the hydrogen ion is removed from the a-carbon atom of the C-terminal amino acid, resulting an indicated equilibrium. Now the oxazolone is hydrolysed in the presence of tritium oxide which introduces the tritium level on the □-carbon atom. On completion of acid analysis the amino acid in which radioactivity is detected must derive from the C-terminal residue.



This method has been applied successfully to insulin, angiotensin, and several synthetic peptides.

Proteomics- it is the technical study of all proteins expressed in a cell at a given time. New tools for medical diagnosis and targets for drug design will undoubtedly emerge at an increasing rate as the field of proteomics advances. One of the basic challenges in proteomics is simply separation of all the proteins present in a cell extract. The separated proteins in cell extracts have classically using two-

dimensional polyacrylamide gel electrophoresis (2D PAGE). In 2D PAGE, the mixture of proteins extracted from an organism is separated in one dimension of the gel by the isoelectric point (a technique called isoelectric focusing) and in the second dimension by molecular weight. The protein spots on the gel may then be extracted and analyzed by mass spectrometry or other methods, either as intact proteins or as enzymatic digests. Comparison of the results from mass spectrometry with protein mass spectrometry databases allows identification of many of the proteins separated by the gel. There are limitations to protein separation by 2D PAGE as all proteins cannot estimated by 2D PAGE due to their size, charge, or specific properties. X-ray crystallography, NMR, and mass spectrometry are key tools that will be applied ever more.

14.7 Chemistry of oxytosin

Oxytocin is a hormone, found in posterior pituitary gland that responsible for uterine contraction. It also excites the musculature of the intestine, gall bladder, ureter and urinary bladder and also causes ejection of milk.

This hormone is extracted from the posterior pituitary gland by separation of this gland from the body, dried and extracted with ethanol or acetic acid. The resulting solution is then treated with sodium chloride to coagulate all the proteins. The coagulated proteins, when treated with trichloroacetic acid are dissociated into various proteins *viz.* nor-adrenaline, oxytocin, vasopressin and other impurities. Now paper chromatography was used to separate these various proteins which are finally purified by means of electrophoresis. The structure of oxytocin was established independently by du Vigneand *et al,* (1953, 1954) and Tuppy *et al,* (1953).

Tuppy's Method

In this method the structure of oxytocin was determined from the examination of various fragments which were obtained by the partial hydrolysis of oxytocin, performic acid oxidation product, bromine water oxidation product and of desulphurised oxytocin. Then, ion exchange resins were employed to separate the peptides into acidic and neutral components and these were separated by paper chromatography.

Accoding to this method isoelectric point of oxytocin is 7.7. This value suggests that the presence of a free amino group but the absence of free carboxyl group in

oxytocin. The molecular weight of oxytocin as determined by physical methods was found to be 1000; a value reveals the octapeptide nature of oxytocin.

When oxytocin was completely hydrolysed with acid, a mixture of eight amino acids namely cystine, glycine, leucine, isoleucine, proline, aspartic acid, glutamic acid, tyrosine and ammonia yielded during hydrolysis and the titration experiments. The proportion of ammonia obtained during hydrolysis suggested that oxytocin must contain three carbonamide groups. When oxytocin is oxidised with performic acid it yields a disulphonic acid with a molecular weight which corresponds to an oxytocin disulphonic acid that shows that oxytocin has a ring of compound and the ring involves the S-S linkage of cystine.

When controlled hydrolysis of oxidised oxytocin was done with hydrochloric acid it yielded four dipeptides and two tripeptides along with two molecules of cysteic acid.

(i) Asp □□$CySO_3H$, (ii) $CySO_3H$ □ Tyr, (iii) Leu □ Gly, (iv) IIeu □ Glu, (v) Tyr, (glu, Ileu) (vi) $CySO_3H$ (Leu, Pro)

The DNP method was used to establish the sequence of amino acids in dipeptides (i), (ii), (iii) and (iv) in DNP method, each dipeptide was treated with FDNB followed by hydrolysis with acid to yield dinitrophenyl derivative (the end group) which was identified by chromatography.

When the partial hydrolysis of oxidised oxytocin was done with the *proteinase* it gave glycine amide and tetrapeptides. The amino acids in these peptides were identified by hydrolysis and chromatography and also the end group in these was determined. The sequence of amino acids in (vii) found to be $CySO_3$□Tyr□Gleu□Glu. (vii) $CySO_3H$ (Glu, Tyr, Ileu) and (viii) Asp. ($CySO_3H$, Leu, Pro) the addition of Asp to (vi) yields (viii).

The sequence of amino acids in (viii) is Asp□$CySO_3H$□Pro□Leu. By the enzyme hydrolysis glycine amide was isolated that showed glycine amide formed the end-group. Now the sequence of amino acids that is followed from (iii) and (viii) is as follows: Asp □ $CySO_3H$ □ Pro □ Leu□$GlyNH_2$

The amino terminal group in (vii) is $CySO_3H$. On combining above said two sequences, a new sequence is obtained it would be present in oxidized oxytocin and would explain all the facts.

The Structure of Oxytocin

The oxidised oxytocin is produced without chain fission reveals the presence of S-S oxytocin. If the a-carboxyl groups of Glu and Asp are involved in the peptide linkages then the of oxytocin structure given below:

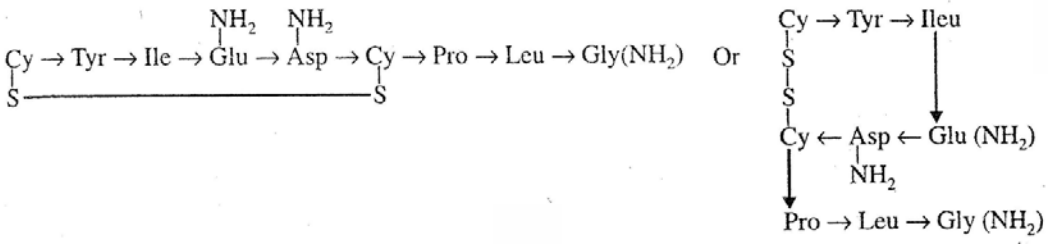


Fig. 14.13: Abbreviated and detailed formula for oxytocin.

Du Vigneaud's Method

It is different from Tuppy's method and by DNP method it was found that oxidised oxytocin had only one N-terminal group and that this was cystine. In this method when oxidised oxytocin was further reacted with bromine water, a dibromopeptide and a heptapeptide were obtained. The dibromopeptide had been found to be $CySO_3H$□$TyrBt_2$ (3, 5-dibromo derivative). This was determined by its hydrolysis and end-group analysis.

When the heptapeptide was hydrolysed, yielded $CySO_3H$, Leu, Ileu, Pro, Glu, Asp, Gly, ammonia and end-group analysis revealed isoleucine at N-terminal residue. Other hand oxytocin has only one terminal amino group so the amino group isoleucine would form the peptide link with tyrosine and the sequence of three residues is as $CySO_3H$ □Tyr□Ileu

When heptapeptide hydrolysed under carefully controlled conditions, it yielded four fragments (xiii)–(xvii) and desulphurised oxytocin was hydrolysed, it yielded four fragments (xviii)-(xxi).

The steps (ix) Asp, $CySO_3H$ (x) $CySO_3H$, Pro (xi) $CySO_3H$, Pro, Leu (xii) $CySO_3H$, Pro, Leu, Gly (xiii) $CySO_3H$, Asp, Glu (xiv) Leu, Gly, Pro (xv) CySSCy, Asp, Glu (xvi) Tyr, CySSCy, Asp, Glu (xvii) Tyr, CySSCy, Asp, Glu, Leu, Ileu (xviii) Ala, Asp (xix) Glu, Ileu (xx) Ala, Asp, Glu (xxi) Ala, Asp, Glu, Leu, Ileu.

No differentiation could be made between Leu and Ileu in peptides (xvii) and (xxi) because both acids appeared together on the chromatograph.

When DNP method was applied to (ix), the sequence found was AsP□$CySO_3H$.

On examining the amino acids in (ix)-(xii), it was shown that the sequence of five residues in oxidised oxytocin might be same as in (xxii) Asp□ $CySO_3H$ □ Pro□Leu□Gly. This explains (xiv) and also exhibits its sequence. As (xiii) contains (ix), Glu might be added to yield the sequence (xxiii) Glu □ Asp □ $CySO_3H$ Pro □ Leu □ Gly. When desulphurisation is done, the $-CH_2S-$ group is converted into the $-CH_3$ group. This means that instead of cystine, two moles of alanine would be produced (Alanine is not present in oxytocin). Thus, (xviii) corresponds to (ixx), (xx), (xxi), (xxii) and (xxiii). From the isolation of (xix), it reveals that Glu is linked to Ileu and as Glu is linked to Asp as shown in (xxiii), Ileu must be in the sequence (xxiv), Ileu □ Glu □ Asp□$CySO_3H$ □Pro □ Leu □ Gly.

As Ileu has now been assigned, it means that (xvii) would be Tyr, CySSCy, Asp, Glu, Ileu and (xxi) would be Ala, Asp, Glu, Ileu. Oxytocin contains the following sequence if Tyr is joined to one half of the cystine residue, Asp is joined to the other half; this also explains (xvi).

Tyr □ CyS

□□□□□

Ileu □ Glu □ Asp □ CyS □ Pro □ Leu □ Gly

The structure accounts for 8 amino acids, cystine contains only free amino group and also oxidation does not bring about fission, oxytocin must be cyclic and this is satisfied by joining Tyr to Ileu. The Gly end is not satisfactory because this residue is present as carbonamide and had been confirmed by Edman's method of end group analysis to oxidised oxytocin in which first four acids in the: order $CySO_3H$, Tyr, IIeu and Glu were removed.The carbonamido groups were placed as described in Tuppy's method and structure of oxytocin same as given by Tuppy.

14.8 Thyrotropin releasing hormone (TRH)

The sequence of TRH was first determined, and the hormone synthesized, by Roger Guillemin and Andrew V. Schally in 1969. Schally first suggested but abandoned it after Guillemin proposed TRH was not actually a peptide. Guillemin's chemist began concurring with these results in 1969, as NIH threatened to cut off funding for the project, leading both parties to return to work

on synthesis. Schally and Guillemin shared the 1977 Nobel Prize in Medicine for their discoveries concerning the peptide hormone production of the brain.

Thyrotropin releasing hormone (**TRH**), also called **thyrotropin releasing factor** (**TRF**), **thyroliberin** or **protirelin**, is tripeptidal hormone that stimulates the release of TSH (thyroid-stimulating hormone) and prolactin from the anterior pituitary. TRH has been used clinically for the treatment of spinocerebellar degeneration and disturbance of consciousness in humans.

TRH is produced by the hypothalamus in medial neurons of the paraventricular nucleus. In the beginning, it is synthesized as a 242-amino acid precursor polypeptide that contains 6 copies of the sequence -Gln-His-Pro-Gly-, flanked by Lys-Arg or Arg-Arg sequences. First, a protease cleaves to the C-terminal side of the flanking Lys-Arg or Arg-Arg and then a carboxypeptidase removes the Lys/Arg residues leaving Gly as the C-terminal residue. This Gly is converted into an amide residue by a series of enzymes collectively known as peptidylglycine-alpha-amidating monooxygenase. Concurrently with these processing steps, the N-terminal Gln (glutamine) is converted into pyroglutamate (a cyclic residue). These multiple steps produce 6 copies of the mature TRH molecule per precursor molecule for human TRH (5 for mouse TRH).

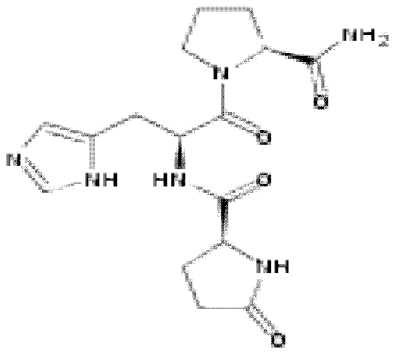


Fig 14.14 structure of thyrotropin releasing hormone

TRH travels across the median eminence to the anterior pituitary gland via the hypophyseal portal system where it stimulates the release of thyroid-stimulating hormone from cells called thyrotropes and excess levels inhibit dopamine which will then stimulate the release of prolactin which in turn decreases GnRH. It can also be detected in other areas of the body including the gastrointestinal system and pancreatic islets, as well as in the brain.

Chemically it is molecular weight is 359.5 Da. Its tripeptide structure is: (pyro) Glu-His-Pro-NH_2. TRH is used clinically by intravenous injection to test the response of the anterior pituitary gland; this procedure is known as a TRH test. This is done as diagnostic test of thyroid disorders such as secondary hypothyroidism and in acromegaly. TRH has anti-depressant and anti-suicidal properties. TRH has been shown in mice to be an anti-aging agent with a broad spectrum of activities that, because of their actions, suggest that TRH has a fundamental role in the regulation of metabolic and hormonal functions.

14.9 Summary

Protein is a complicated structure and consists of amino acids. Tertiary structure and quaternary structure of protein are three-dimensional structure that shows the interactions between amino acid residues relatively far apart in the sequence. The tertiary structure of a protein is a description of the complex and irregular folding of the peptide chain in three dimensions. The protein in these figure have easily discernable helices in particular areas, but that the entire three dimensional structures is more complex and irregular. If it should change at all, the activity of the protein will be lost. These complex structures are held together by a combination of several molecular interactions that involve the R-groups of each amino acid in the chain. The structure of regions of peptide chains that do not form a regular secondary structure is determined by interactions between R-groups. These interactions include : hydrogen bonds between polar R- groups, ionic bonds between charged R-groups, hydrophobic interactions between nonpolar R-groups, covalent bonds the R-group of the amino acid cysteine contains a sulfur atom and this sulfur atom is capable of forming a covalent bond with another sulfur atom on a different cysteine molecule somewhere else on the chain. This bond is known as a disulfide bond and it acts as to stabilize the tertiary structure of those proteins that have such bonds.

The quaternary structure of a protein describes the interactions between different peptide chains that make up the protein. Some proteins (hemoglobin) have more than one peptide chain (multimeric proteins) and the manner in which these chains fit together the quaternary structure. If a protein is made up of only one chain (monomeric), there is no quaternary structure for that protein. The forces that hold different chains together are the same that hold the tertiary structure together,

hydrogen bonding between polar R-groups, ionic bonds between charged R-groups, hydrophobic interactions between nonpolar R-groups, and disulfide bonds. The figure below shows the structure of hemoglobin, a protein that has four subunits. The secondary, tertiary and quaternary structures, and therefore the activity, of a protein are as a direct result of the primary structure. This is most dramatically demonstrated in the genetic disease sickle cell anemia. The protein hemoglobin is made up of four polypeptide chains, two alpha chains and two beta chains. The beta chains of normal hemoglobin have the amino acid glutamate (a negatively charged R-group) in the sixth position. The chain from individuals with sickle cell anemia, however, has the nonpolar amino acid valine in the sixth position. The remainder of the 146 amino acids in the chain is the same in both individuals (as are the alpha chains). This single change in the primary structure of the protein alters the structure of the hemoglobin so that it does not work correctly and causes severe anemia that can kill. Tertiary structure of protein involves hydrogen bonding, ionic, chemical and hydrophobic bonds. Amino acids are the main component of proteins and can easily be determine by using different methods. These amino acids are synthesized and metabolized in different derivatives that help in several biotitic activities of cell and these are also intermediate products. The degradation of amino acids starts with the removal of □-amino group and this amino group is either excreted as ammonia in some of the animals or converted to urea for excretion. All degradative pathways of carbon skeleton are directed to its conversion into such metabolic intermediates which may either be utilized in synthetic pathways (gluconeogenesis) or may be incorporated into TCA cycle and oxidized to produce CO_2 and water and release energy. All amino acids are synthesized by transamination of some keto-acids, which are derived from intermediates of glycolysis, pentose-phosphate pathway and TCA cycle and different pathways of amino acid biosynthesis could be recognized into six groups as oxaloacetate, pyruvate, α-ketoglutrate, 3-phosphoglycerate, phosphoenol pyruvate & erythrose-4-phosphate and ribose-5-phosphate. Oxytocin is a hormone, found in posterior pituitary gland that responsible for uterine contraction. It also excites the musculature of the intestine, gall bladder, ureter and urinary bladder and also causes ejection of milk. Tryptophan, an amino acid found in many foods is (2S)-2-amino-3-(1H-indol-3-yl) propanoic acid and is abbreviated as Trp or W with molecular formula is

$C_{11}H_{12}N_2O_2$. Tryptophan is one of the 22 amino acids and the only one with an indole functional group.

14.10 Self Learning Exercise

Section A

1 Who proposed concept of quaternary tructures for proteins.

2 Write down examples of tertiary & quotarary structure of proten.

3 How many polypoptide chaims are found in Halmoglobin ? Moution details/

4 Give the name of bond types responsible for protein structure determination.

5 Which Amino acid possess an indoli functional groups.

Section B

1. Discuss the tertiary and quaternary structure of proteins in detail.
2. Explain quaterory sturture of amino acids
3. Discuss lquence determination of amino acids/

Section C

1 Discuss the chemical structure of oxytocin and tryptophan.

2 What do you mean by sequence determination of amino acids? Give the methods of determination.

3 What is amino acid metabolism? Explain it in details.

4 Write short note on following:

5 Amino acid degradation

6 Amino acid synthesis

7 Give any of the method of detection of amino acids.

Answer from Section A

1 Soreusen and Svedberg (1930)

2 Myoglobin & Hemoglobin

3 4; 2 & 2 B

4 Peptide bonds, disulfide bonds, hydrogen bonss

5 Tryptho phan

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Unit - 15 : Nucleic acids

Structure of Unit

15.1 Objective

After studying this unit you will be able to:

- Explain the structure of nucleic acid, purine and pyrimidine;
- Type of hydrogen bonding involve in nucleic acid, structure of nucleotide and nucleoside;
- Structure of RNA and its different types of RNA molecules, their role in transcription and translation or protein synthesis. RNA processing and role of RNA in amino acid sequences.
- Double helical structure of deoxyribonucleic acid (DNA), its role in RNA formation, transcription replication translation and base pairing in nucleotide and nucleoside.

15.1 Introduction

Chromatin is the chromosomal material consists of long double stranded DNA molecules, equal mass of histones and nonhistone proteins and a small quantity of RNA. DNA and RNA are the nucleic acids and made up of nucleotide (nitrogenous base, pentose sugar and phosphoric acid) that is a monomeric unit and building block of the polynucleotide chain. A nucleoside is made up of nitrogenous base linked covalently to a pentose sugar by glycosidic bond. The nucleosides of the five nitrogenous bases are named as Adenosine (nucleoside of adenine base), Guanosine (nucleoside of guanine base), Thymidine (nucleoside of thymine base), Cytidine (nucleoside of cytosine base) and Uridine (nucleoside of uracil base). The structure of RNA is similar to that of DNA except for the difference in its pentose (D-ribose) unit and the heterocylic base (uracil in place of thymine). In DNA, purine bases adenine and guanine and the pyrimidine bases cytosine and uracil are present but here they are not present in RNA in equimolar amounts.

There are three classes of ribonucleic acids namely Messenger RNA (mRNA), Transfer RNA (tRNA) or soluble RNA and Ribosomal RNA (rRNA). The synthesis of RNA one of the strands of DNA acts as a template for synthesis of mRNA and complete unit of information for the protein peptide chain is known as the cistron and thus several cistrons. The function of a tRNA is to convey genetic information from the cell nucleus to protein-synthesizing centres in the cell in collaboration with ribosomes and tRNA.

DNA is double stranded, coil around a common axis with adenine residues equal to thymine residues (A=T) and the guanine residues were equal to cytosine residues (G=C) or sum of purine residues was equal to the sum of pyrimidine residues (A+G) = (T+C). The four types of monomeric units of DNA are adenylate, guanylate, cytidylate and thymidylate. All phosphate groups are negatively charged and so they develop repulsive electrostatic forces which may destabillze DNA structure. These negative charges are neutralized by the positively charged side chains of chromosome proteins (histones) and the magnesium (Mg^{+2}). The bases in DNA are stacked one above the other and stacking develops between the stacked molecules dipoledipole interactions or Van der Waal's forces. These forces hold the bases together and thus provide additional strength to the structure. These different forces, though very small, are very effective because they increase in magnitude due to large number of molecules involved.

15.2 Nucleic acids

The sequence of bases that encodes a functional protein molecule is called a gene and most important constituent of chromosomes is DNA. The double–stranded helix of DNA is tightly coiled in each chromosomes thread. Gene is a segment of the DNA molecule containing about 600 base pairs. The genetic message is carried in the sequence of bases along the DNA strand. In transcription, the genetic message is transferred to the mRNA which carries it to the ribosome. Replication ensures that the genes a segment of the DNA molecule are present in identical sets, in all cells of the body of an individual. DNA fulfils the requirement of a genetical material ability to replicate. The genes are arranged in orderly manner along the length of the DNA molecule in the chromosome. Each gene for any particular characteristic has its counterpart in the corresponding locus on the homologous chromosome and these two genes form an allelic pair.

Chromatin is the chromosomal material extracted from nuclei of cells. It consists of long double stranded DNA molecules, equal mass of histones and smaller amount of nonhistone proteins and a small quantity of RNA. It contains a 10 nm repeating unit and repeating units found every 200 base pairs. Nucleic acids are the polynucleotides and there are two types of nucleic acids-DNA and RNA. Avery, Macleod and McCarty (1944) first demonstrated in a series of experiments that DNA contained the genetic information and referred DNA as transforming factor. Two types of bases are generally associated with the nucleotide, purine bases and the pyrimidine bases. A purine is made of a six member heterocyclic and a five member heterocyclic rings both fused together such that they have only nine members in all with four nitrogen atoms (Fig. 15.1).

15.3 Purine and pyrimidine bases of nucleic acid

Normally a purine nucleus substitution at positions C-2, C-6 and N-9 is possible and position 9' is usually reserved for the pentose sugar. A substitution of an amino group at position C-6 gives Adenine (6-amino purine); an amino group at C-2 and oxygen at C-6 gives Guanine and a substitution of only oxygen at C-6 give Hypoxanthine (Fig. 15.1).

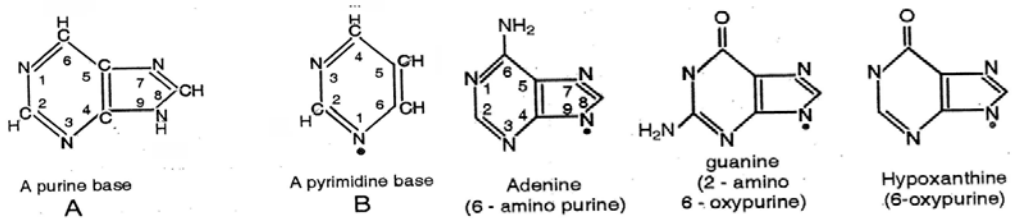


Fig. 15.1: The nucleotide base nuclei- A. Purine base. B. Pyrimidine base, dots indicates the positions for substitution

A pyrimidine is a six member heterocyclic ring with nitrogen at positions 1 and 3 (fig. 15.2). The substitution in this nucleus is possible at positions 1, 2, 4, 5 and 6 or ring can be substitute except the N-3 and N-l is usually for the pentose sugar. If the positions C-2 and C-4 both have a keto group *i.e.,* oxygen, it makes Uracil and oxygen at C-2 and C-4 and a methyl group at C-5 give Thymine. Oxygen at C-2 and an amino group at C-4 give a Cytosine. The unusual bases are the modified forms of the base uracil. If oxygen is replaced by sulfur at position 4 in uracil, derived Thiouracil and when ribose gets linked to carbon at position 5 it makes Pseudouracil. In another uracil derivative, one hydroxyl group each is linked to C-5 and C-6 and form Dihydrouracil.

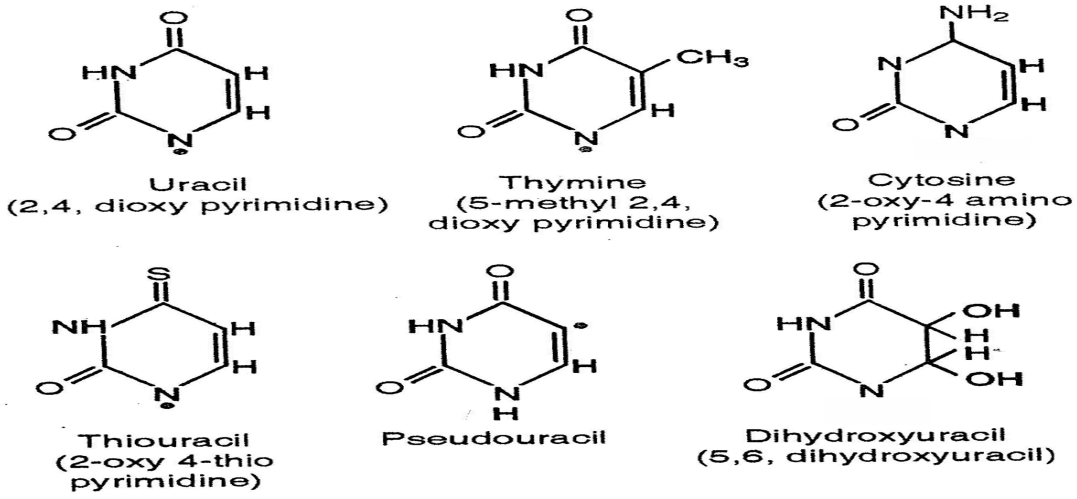


Fig.15.2: The pyrimidine nucleotide bases (dot shows the point of attachment of the pentose sugar

15.4 Base pairing of nucleic acid via H-bonding

The concentration of adenosine (A) equals to thymidine (T) and these are linked by double hydrogen bond (A=T) whereas guanosine (G) linked to cytidine (C) (G=C) by triple hydrogen bond. Means double-stranded molecule is held together by hydrogen bonds between the purine and pyrimidine bases. The pairings between the purine and pyrimidine nucleotides on the opposite strands are dependent upon hydrogen bonding of A with T and G with C. Three (3) hydrogen bonds hold the guanosine nucleotide to the cytosine nucleotide and A-T pair is held together by 2 hydrogen bonds. It represented as G=C and A = T, whereas G-C bond is stronger by 50%. A DNA contains 1,600 to 9,000 nucleotides. The molecules are long and its length is 250 times greater than its breadth. Its structure is highly complex.

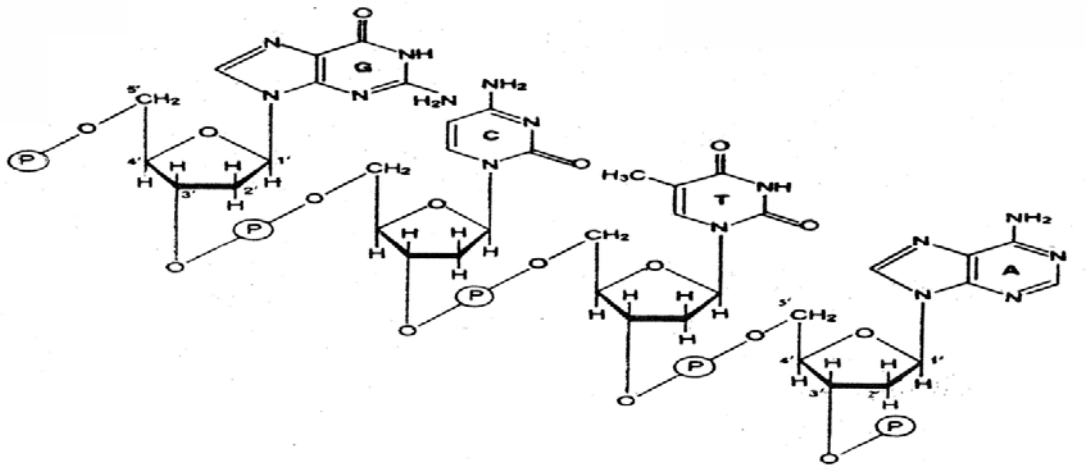


Fig.15.3: A segment of one strand of a DNA molecule : purine (A and G) and pyrimidine bases (T and C) are held together by 3',5'-phosphodiester backbone, one end has a 3'-hydroxyl or phosphate terminus while the other has a 5'-hydroxyl or phosphate terminus. Note the second strand of the double helical will run in opposite direction *i.e.* in the 5' to 3' direction.

The pentose sugar of these nucleotides is the ribose sugar in ring form. Two types of ribose sugars are associated with the nucleotides, the ribose sugar and the deoxyribose sugar. A deoxyribose lacks oxygen at C-2' (Fig. 15.4). In both sugars G-1' is attached to the nucleotide bases. Attachment with ribose makes a ribonucleoside, whereas the attachment with deoxyribose makes a deoxyribonucleoside.

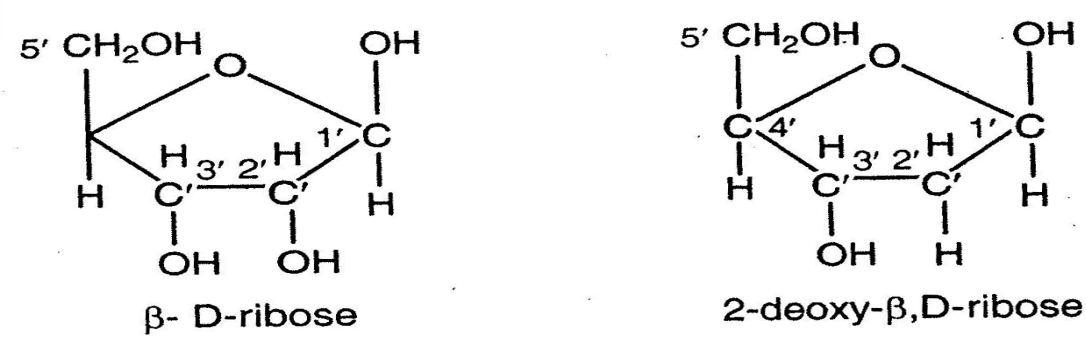
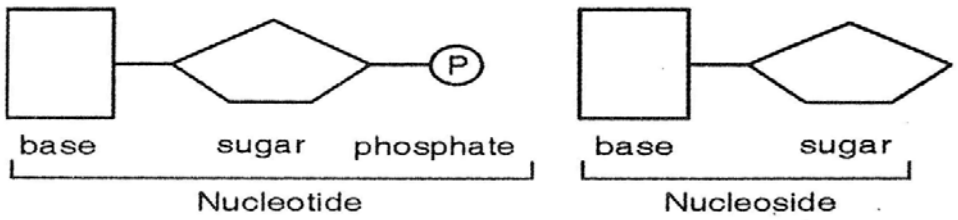


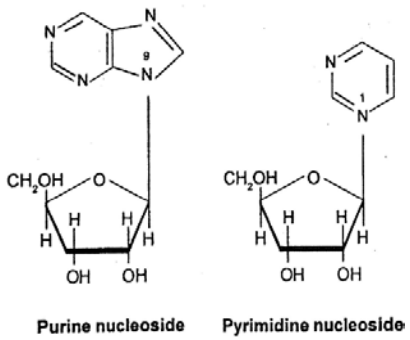
Fig. 15.4: The two pentose sugars, D-ribose and 2'-deoxy D-ribose

Nucleoside and Nucleotide

A nucleoside is made up of nitrogenous base linked covalently to a pentose sugar by glycosidic bond (Fig.15.5). The nucleosides of the five nitrogenous bases are named as Adenosine (nucleoside of adenine base), Guanosine (nucleoside of guanine base), Thymidine (nucleoside of thymine base), Cytidine (nucleoside of cytosine base) and Uridine (nucleoside of uracil base). The glycosidic linkage is present between N1 of the pyrimidine ring and N9 of the purine ring and the C1 of the pentose sugar



Nucleoside and Nucleotide.



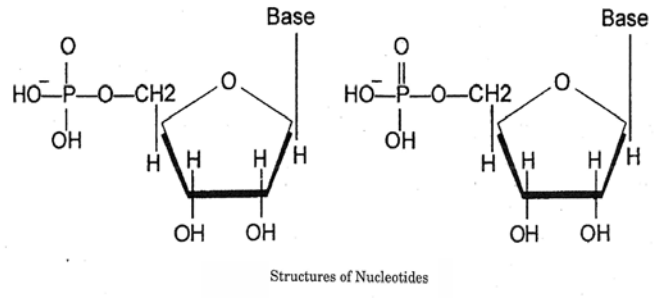


Fig. 15.5: The structure of nucleotide and nucleoside (purine and pyrimidine)

Nucleotide is monomeric unit and building block of the polynucleotide chain that is made up of nitrogenous base, pentose sugar and phosphoric acid (Fig.15.4, Table 15.1). Each nucleotide has a nitrogenous base, a pentose sugar and a phosphate group. The nitrogenous base is linked with the pentose sugar to form a nucleoside. When a phosphate is added to this sugar component of the nucleoside it makes a nucleotide means a nucleotide is a nucleoside phosphate.

Table 15.1: Nomenclature of nucleotides and nucleotide

Base	**Nucleoside**		**Nucleotide**	
Purine				
Adenine	Adenosine/ deoxyadenosine	A	Adenylate/ deoxyadenylate	AMP
Guanine	Guanosine/ deoxyguanosine	G	Guanylate/ deoxyguanylate	GMP
Hypoxanthine	Inosine	I	Inosinate	IMP
Pyrimidines				
Thymine	Thymidine/ deoxythymidine	T	Thymidylate/ deoxythymidylate	TMP

Cytosine	Cytidine/ deoxycytidine	C	Cytidylate/ deoxycytidylate	CMP
Uracil	Uridine	U	Uridylate	UMP

A=Adenine, G=Guanine, I=Inosine, MP=Monophosphate, T=Thymine, C=Cytosine, U=Uracil

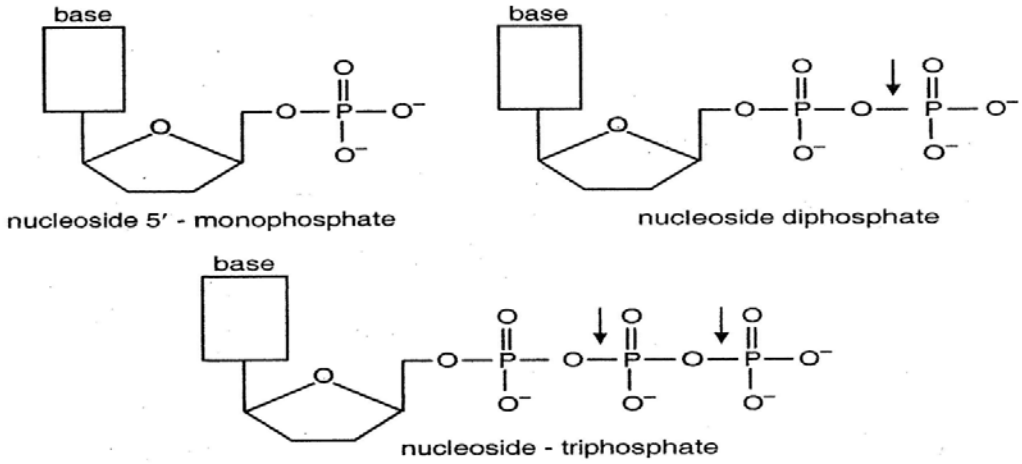


Fig. 15.6: The nucleotide mono, di and triphosphate and arrows mark the position of anhydride bonds

15.5 Structure of ribonucleic acid (RNA)

The structure of RNA is similar to that of DNA except for the difference in its pentose (D-ribose) unit and the heterocylic base (uracil in place of thymine). In DNA, purine bases adenine and guanine and the pyrimidine bases cytosine and uracil are present but here they are not present in RNA in equimolar amounts. The molecule is less organized than the DNA molecule and with a few exceptions occurs as a single, strand. There is internal hydrogen bonding within the chain to keep it in a coiled position. A helical pattern is formed not between two strands, but by the same coiled strand folding back on itself.

RNA exists as a single-strand but the single strand of RNA may fold back on itself like a hairpin (stem loop) and thus acquire the double-stranded pattern and in the region of hairpin loops, A pairs with U and G pairs with C. It can be hydrolysed by

alkali to 2', 3'-cyclic diesters of the mononucleotides via an intermediate compound called 2',3',5'-triester. This intermediate can't be formed in alkali-treated DNA because of the absence of a 2'-hydroxyl group in its molecule. Thus RNA is alkali labile, while DNA is alkali stable. The alkali ability of RNA is useful diagnostically and analytically.

Although RNA exists mainly in the cytoplasm, about 10-20 per cent of cell RNA is found in the nucleolus of the cell nucleus. RNA is polymer of purine and pyrimidine riboncleotides linked together by 3', 5'-phosphodiester bridges and sugar moiety in RNA is ribose. In RNA, one of the pyrimidine base is uracil (in place of thymine of DNA), although other three bases) viz.adenine, guanine and cytosine) are common in RNA as well as DNA, uracil, like thymine of DNA, can form a base pair with adenine by two hydrogen bonds.

RNA exists as a single-stranded molecule rather than as a double-stranded helical molecule. Since single-stranded molecule, its guanine content does not necessarily equal its cytosine content and its adenine, content does not necessarily equal its uracil content. It can be hydrolyzed by alkali to 2', 3' cyclic diesters of the mononucleotides. An intermediate in this hydrolysis is the 2', 3', 5'-triester' which cannot be formed in DNA hydrolysis by alkali because of the absence of a 2'-hydroxyl group. The alkali lability of RNA is useful diagnostically and analytically. RNA molecule does not hybridize with the "antisense" strand, of the DNA of its gene and the sequence of RNA molecule (except U being replaced by T) is the same as that of the antisense strand of the gene. It contains 60 to 6,000 nucleotides and molecule is unbranched.

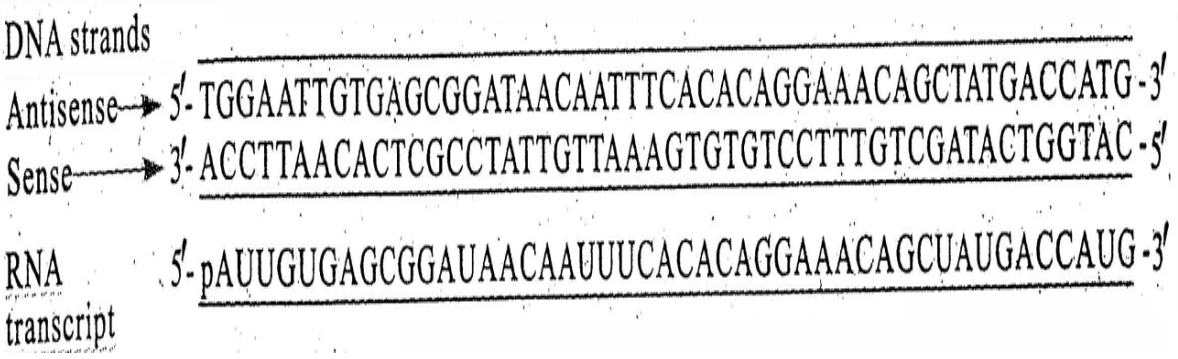


Fig.15.7: Relationship between the sequence of an RNA transcript arid its gene in which the sense and antisense strands are shown

There are three classes of ribonucleic acids in all prokaryotic and eukaryotic

organisms which differ chiefly in molecular weight and base composition namely:

1. Messenger RNA (mRNA)
2. Transfer RNA (tRNA) or soluble RNA
3. Ribosomal RNA (rRNA)

1. The messenger RNA (mRNA)

The m RNA, is single-stranded and complementary to the sense strand of DNA. At the time of processing of mRNA from hnRNA, the 5' terminus is capped by a 7-methylguanosine triphosphate that linked to a 2'-O methyl ribonucleoside at its 5'-hydroxyl through the 3 phosphates and 3'-hydroxyl terminus has attached a polymer of adenylate residues 20-250 nucleotides in length. It has a large molecular weight of 30,000 to 50,000 to have the coded information corresponding to long polypeptide chains. These heterogeneous nuclear RNA (hnRNA) may exceed 107 daltons whereas the mRNA molecules are generally smaller them 2 x 10^6 daltons. These HnRNA molecules are processed to generate the mRNA molecules which then enter the cytoplasm to serve as templates for protein synthesis. The protein-synthesizing machinery begins translating the mRNA into proteins at the 5' or capped terminus means it is the most heterogenous in size and stability.

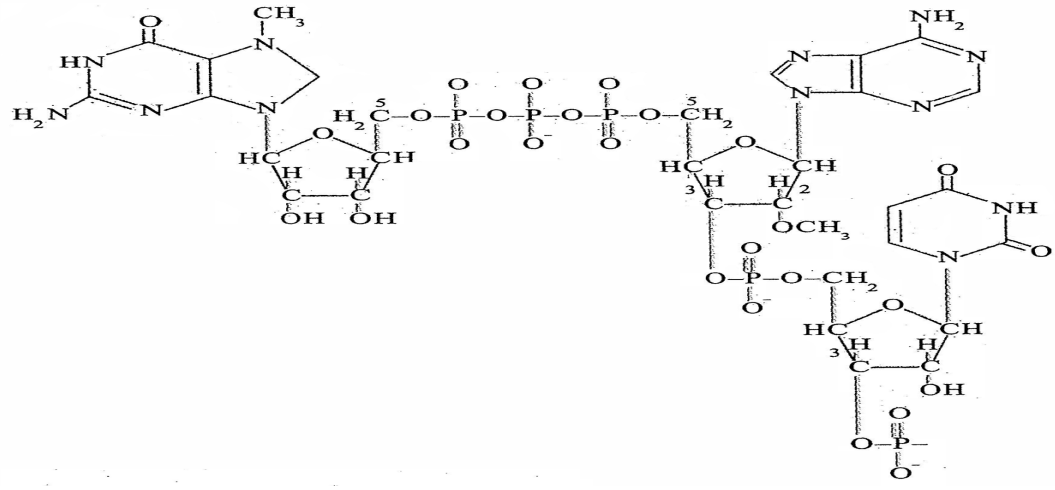


Fig.15.8: The expression of genetic information in DNA and form m RNA transcript that translate by ribosome into specific protein molecule.

It passes from nucleus to cytoplasm conveying information in a gene to the protein synthesizing machinery where serves as a template on which a specific sequence of amino acids is polymerized to form a specific protein molecule ultimate gene

product.

2. The transfer RNA (tRNA) or soluble RNA (sRNA)or Acceptor RNA

The transfer RNA molecules amount to 10 to 20 percent of the total cellular RNA, molecules and consist of about 75 nucleotides with molecular weight of 25,000. There are at least 20 tRNA molecules in every cell; one corresponds to each of the 20 amino acids required for protein synthesis. These serve as adaptors for the translation of the information in the sequence of nucleotides of the mRNA into specific amino acids the protein. The primary structure allows extensive folding and intrastrand complementarily to generate a significant secondary structure which appears like a cloverleaf (Fig.15.9). All tRNA molecules have a common CCA sequence at the 3' termini and carboxyl groups at 3'-hydroxyl group of the adenosyl moiety through an ester bond.

It has anticodon loop at the end of a base paired, stem recognizes the triplet nucleotide or codon of the template mRNA. All tRNA molecules has a loop containing the nucleotides of ribothymine and pseudouridine for binding amino acyl tRNA by ribosome and another loop containing the minor base dihydrouracil recognition of tRNA. They are quite stable in prokaryotes and less stable in eukaryotes.

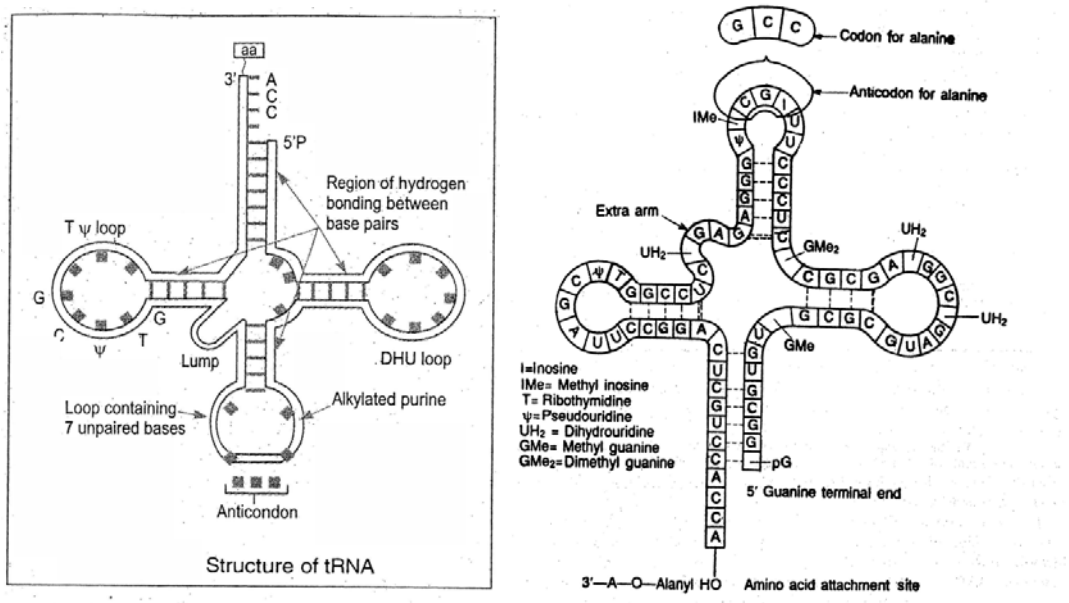


Fig. 15.9: Structure of tRNA (clover leaf model for alanine-tRNA from yeast)

3. The Ribosomal RNA (rRNA) Ribosomes are nucleoprotein particles and

reticular granules of 100-150A°, in diameter which act as the machinery for the synthesis of proteins from mRNA tem plates. They contain 80 per cent of the RNA within the cell. On ribosomes mRNA and tRNA molecules interact to translate into a specific protein molecule the information transcribed from the gene. Ribosomal particles are very complex and mammalian ribosome contains 2 major nucleoprotein subunits - a larger one (60 S) and a smaller one (40 S), the 60 S subunit contains 5 S ribosomal RNA, 5.8 S RNA and 28 S rRNA. There are also more than 50 specific polypeptides. The smaller (40 S) subunit contains a single 18 S rRNA and approximately 30 polypeptide chains. The 5 S rRNA has its own precursor which is independently transcribed.

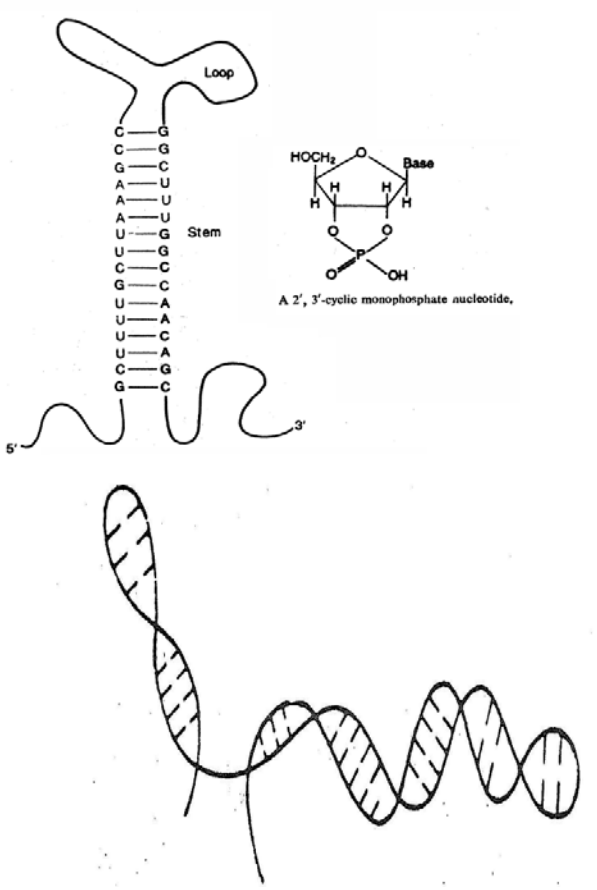


Fig.15.10: Diagrammatic representation of the secondary structure of a single stranded RNA molecule (left) and Single stranded RNA molecule (right)

The biosynthesis of RNA one of the strands of DNA acts as a template for synthesis of mRNA and thus a message may be derived only from certain discrete

sections of the DNA strand and an active strand of DNA carries information for the synthesis of several different protein molecules. The complete unit of information for the protein peptide chain is known as the cistron and thus several cistrons. Thus the function of a tRNA (synthesized from DNA) is to convey genetic information from the cell nucleus *to* protein-synthesizing centres in the cell in collaboration with ribosomes and tRNA.

15.6 Structure of deoxyribonucleic acid (DNA)

DNA is double stranded, each strand being polymer of deoxyribonucleotides. The two strands make a double helix where these strands coil around a common axis (fig. 15.12). Erwin Chargaff and his colleagues (1951) reported that the nucleotide composition of DNA varies from one species to the other but was the same in different parts of the same species.

In DNAs of all the species the adenine residues were equal to thymine residues (A=T) and the guanine residues were equal to cytosine residues (G=C) or sum of purine residues was equal to the sum of pyrimidine residues (A+G) = (T+C).

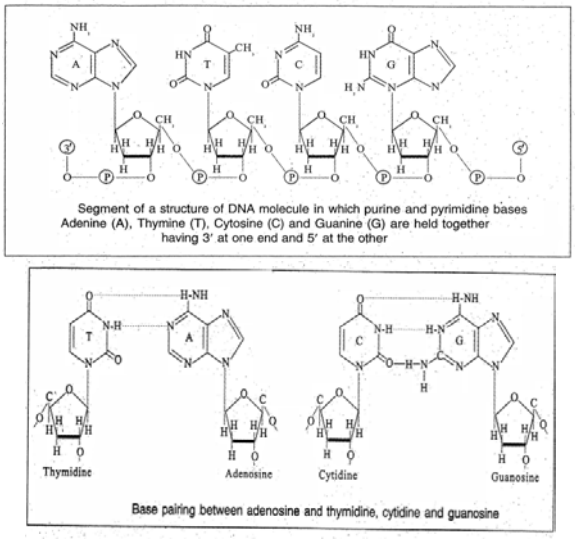


Fig. 15.11: The structure of purine and pyrimidine bases showing the parallel and antiparellel pattern

15.7 Double helix model of DNA

These analytical data and the conclusions known as Chargaff rule played a key role in determining the three dimensional structure of DNA by Watson and Crick. Three dimensional structure given by X-ray crystallographic studies by Franklin

(1953) and Wilkins (1953) proved that DNA has a helical structure with two stages of periodic repeats.

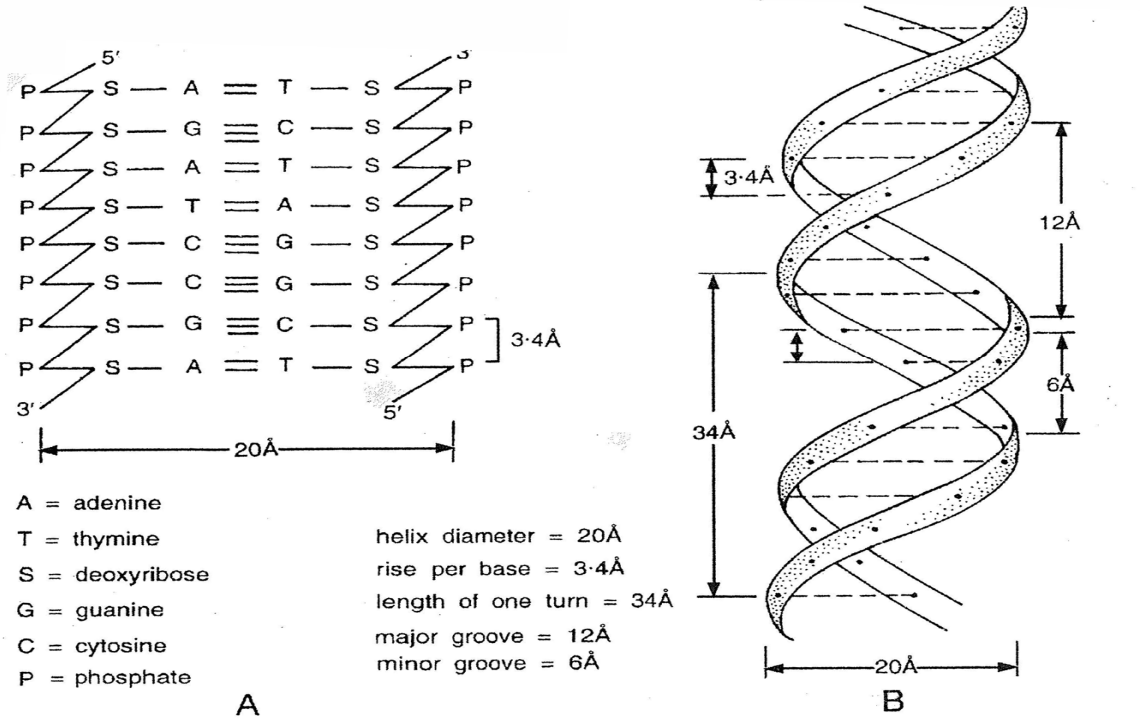


Fig.15.12: Structure of DNA A. shows the sugar phosphate back bone and hydrogen bonding between the bases. B. A helical model of Watson and Crick

The first repeat was after every 3.4A° and the second repeating unit was of 34A° Williams (1952) and Kohler *et al.* (1953) on the basis of electron microscopy reported that DNA was a long fiber with an approximate diameter of 15-20A°. Using these findings Watson and Crick (1953) proposed a three dimensional structure of DNA and important features of their model are:

Two helical and antiparallel polynucleotide chains coiled around a common axis with a right handed helix sense (fig. 15.11). The hydrophilic back-bone of alternating deoxyribose sugar and phosphate are on the outer side of the helix (fig. 15.12). The furanose deoxyribose ring is in C-2' endo conformation. The hydrophobic purine and pyrimidine bases are stacked on the inner side of the helix. These bases are perpendicular to the long axis. The purine base of one strand is opposite and very close to a pyrimidine base of the other strand which are bonded by hydrogen bonds as adenine pairs with thymine by two hydrogen bonds (A=T) and guanine pairs with cytosine forming three hydrogen bonds (G=C). The

adjacent bases along the axis are separated by a distance of 3.4A° (supported by Wilkins) and each helix will have ten bases with rotation by 36° for every base.

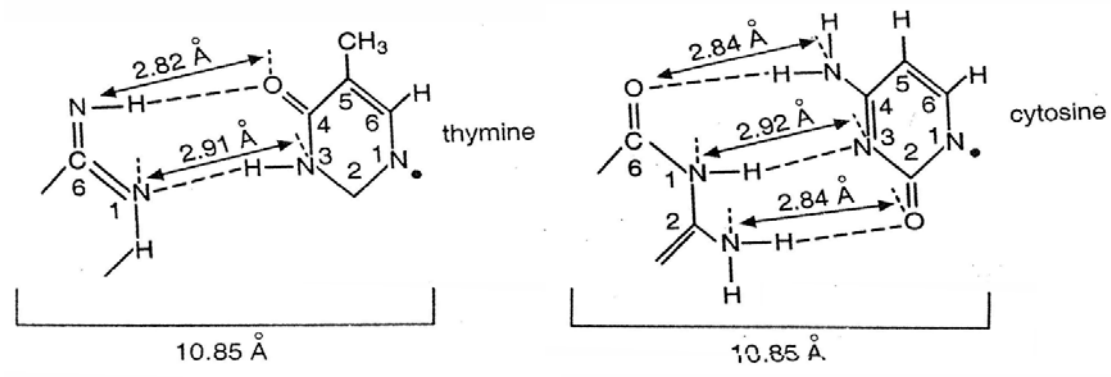


Fig.15.13: Shows hydrogen bonding between bases, the groups involved and the lengths of the bonds

The four types of monomeric units of DNA are adenylate, guanylate, cytidylate and thymidylate. The monomeric units form a single strand of DNA which is held in polymeric form by 3', 5'-phosphodiester bridges. The polymer possesses a polarity; one end has a 5'-hydroxyl or phosphate terminus while the other has a 3'-phosphate or hydroxyl moiety. Since the genetic information is available in the monomeric units within the polymers, there is existence of a mechanism reproducing of replicating this specific information with a high degree of fidelity. The 2 strands of the double helical molecule are anti-parallel i.e. one strand runs in the 5' to 3' direction and the other in the 3' to 5' direction. Since the information resides in the sequence of nucleotides on one strand, the opposite strand is considered as antisense i.e. the complement of the sense strand. The double-stranded DNA molecule shows the properties of a fiber and it is a viscous material in solution and loses its viscosity upon denaturation. Heat, acid and alkali denature the DNA. In the major and minor grooves winding along the molecule parallel to the phosphodiester backbones, specific proteins interact with DNA molecules. In some organisms such as bacteria, bacteriophage and many DNA-containing animal viruses, the two ends of the DNA molecules are jointed to create a closed circle with no terminus. This does not destroy the polarity of the two molecules but it eliminates all 3' and 5' free hydroxyl and phosphoric groups. It contains 1,600 to 9,000 nucleotides and the length is 250 times greater than its breadth with highly complex structure.

The two strands are made of alternating sugar (deoxyribose) and phosphate. The two adjacent deoxyribose sugars are linked by a phosphate which forms a 5'-phosphodiester bond on one side and 3'-phosphodiestet bond on the other side. This makes the phosphate sugar back-bone. Each strand has a polarity, the 5' end starts with phosphate and the other 3' ends with a hydroxyl group at C-3'(fig. 15.12).

The base component of the nucleotide is linked to the first carbon (C-1') of deoxyribose sugar by N-glycosidic bond and N-refers to the N-9 in purines and N-l in pyrimidines. These bases are directed to the inner side of the helix. Since this component is hydrophobic in nature, it is more compatible with the non-aqueous environment and rightly directed to the inner side.

The two bases were only pyrimidines (6-member heterocyclic rings each) they will keep separated by a distance which will not allow hydrogen bonds. The N-l of adenine forms a hydrogen bond with N-H at position 3 in thymine. The second hydrogen bond is formed between NH_2 group at C-6 in the adenine and the oxygen at C-4 in thymine. Guanine pairs with cytosine forming three hydrogen bonds. These hydrogen bonds are formed between NH_2 group at C-2 in guanine and oxygen at C-2 in cytosine, NH at position 1 in guanine and N at position 3 in cytosine and oxygen at C-6 in guanine and NH2 group at C-4 in cytosine (fig. 15.12).

When the two strands coil around each other, they make grooves between two strands. Two G≡C hold them tightly and maintain them as single double stranded structural unit.

All phosphate groups are negatively charged and so they develop repulsive electrostatic forces which may destabilize DNA structure. These negative charges are neutralized by the positively charged side chains of chromosome proteins (histones) and the magnesium (Mg^{+2}).

The bases in DNA are stacked one above the other and stacking develops between the stacked molecules dipoledipole interactions or Van der Waal's forces. These forces hold the bases together and thus provide additional strength to the structure.

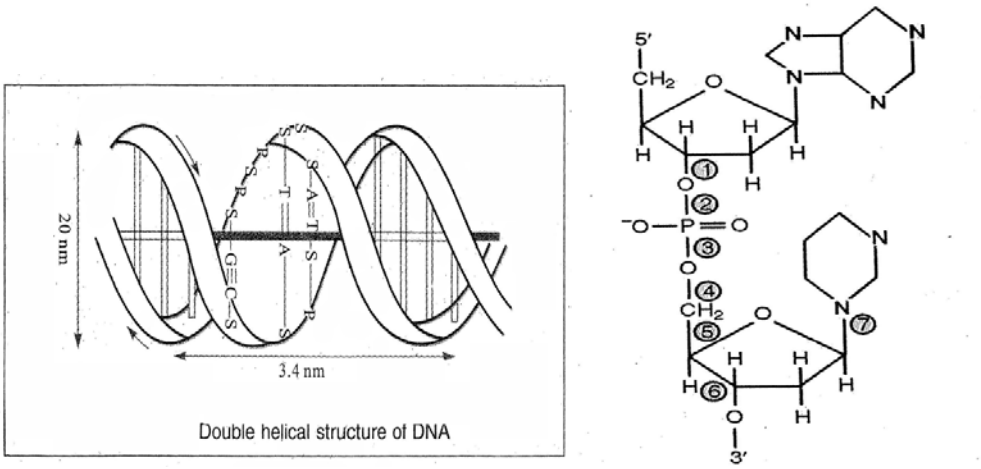


Fig.15.14: Structure of DNA and bonds between two nucleotides in DNA strand

These different forces, though very small, are very effective because they increase in magnitude due to large number of molecules involved.

15.8 Summary

Chromatin is a genetic material consists of long double stranded DNA molecules, equal mass of histones and nonhistone proteins and a small quantity of RNA. DNA is a polynucleotide structure and each nucleotide made up of nitrogenous base, pentose sugar and phosphoric acid but nucleoside has nitrogenous base linked to pentose sugar. Adenine base, guanine, thymine and cytosine are four bases of DNA but in RNA uracil is found in place of thymine. Three types of ribonucleic acids are Messenger RNA (mRNA), Transfer RNA (tRNA) or soluble RNA and Ribosomal RNA (rRNA) found in cytoplasm of cell.

DNA is double stranded, coil around a common axis with adenine residues equal to thymine residues (A=T) and the guanine residues were equal to cytosine residues (G=C) or sum of purine residues was equal to the sum of pyrimidine residues (A+G) = (T+C). The four types of monomeric units of DNA are adenylate, guanylate, cytidylate and thymidylate. All phosphate groups are negatively charged and so they develop repulsive electrostatic forces which may destabillze DNA structure. When the two strands of DNA coil around each other, they make grooves between two strands and G≡C hold them tightly and maintain them as single double stranded structural unit. All phosphate groups are negatively charged and so they develop repulsive electrostatic forces which may destabilize DNA structure.

These negative charges are neutralized by the positively charged side chains of chromosome proteins (histones) and the magnesium (Mg^{+2}). These forces hold the bases together and thus provide additional strength to the structure. These different forces, though very small, are very effective because they increase in magnitude due to large number of molecules involved.

15.9 Self-Learning Exercise

Section A

1 What is nuletide?

2 Who discovered derubli helical structure of DNA?

Section B

1. Discuss the structure of RNA and its type.
2. Differeate between DNA and RNA.

Section C

1. Discuss the role of RNA in protein synthesis saperately.
2. What do you mean by nucleotide and nucleoside? Give their detailed structure.
3. What is RNA processing? Explain it.
4. Write short note on following:
   a. mRNA
   b. tRNA clover leaf model
   c. rRNA structure
   d. Draw a double helix structure of DNA
   e. Base pairing pattern in DNA

5 Write an essay on DNA structure as genetic material.

Answer kye Section A

1 Base+A pentose segar+Phosphoric acid

2 Wate &v Crick

15.10 References and Suggested readings

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Unit- 16 : Chemical and enzymatic hydrolysis of nucleic acid

Structure of Unit

16.0 Objective

After studying this unit you should be able to:

- Explain the structure of gene, nucleic acid and role of DNA in replication;
- Procedure of DNA replication, enzyme involve in it and about okazaki fragments;
- About the genetic code, its role in genetic information transformation, characteristic properties of triplet code.
- Synthesis of purine and pyrimidine or mono or trinucleoside

16.1 Introduction

The most important constituent of chromosomes is DNA, double–stranded helix structure. Gene is a segment of the DNA molecule containing about 600 base pairs. The genes are arranged in orderly manner along the length of the DNA molecule in the chromosome. Each gene for any particular characteristic has its counterpart in

the corresponding locus on the homologous chromosome and these two genes form an allelic pair. Replication ensures that the genes a segment of the DNA molecule are present in identical sets, in all cells of the body of an individual. DNA fulfils the requirement of a genetical material ability to replicate. DNA as the bearer of genetic information in the cell is strongly supported by the Waston-Crick structure for this compound which explains beautifully the phenomenon of replication of DNA. Replication of DNA is the dispersive, conservative and semi-conservative methods. The semi-conservative method of DNA replication is now well accepted, the two strands of DNA molecule separate from each other and each strand gives template to the complementary strand. During replication the adenine nucleotide pairs with thymine,guanine with the cytosine nucleotide of the strand (A=T and G=C pairing) and finally a new stand is formed around each old strand.

Replication may proceed in one or both directions from the point of origin may be unidirectional orbidirecrional replication. In transcription, the genetic message is transferred to the mRNA which carries it to the ribosome. In transcription a messenger RNA strand is copied or transcribed from a DNA strand. The translation process the genetic information present in mRNA (after transcription process completion), directs the order of specific amino acids to form a polypeptide or protein for cell. The translation process consists of activation of amino acids, transfer of the activated amino acid to tRNA, initiation of polypeptide chain synthesis and chain elongation and chain termination. The chain elongation process continues until a termination codon (UAA, UAG or UGA) reaches the ribosome; the chain is terminated and released from the ribosome. It requires release factors (RF-l, RF-2 and RF-3 in prokaryotes and RF in eukaryotes). The relationship between the sequence of bases in DNA/RNA and the sequence of amino acids in a polypeptide chain is called the genetic code. The code indicates that which codon specify which amino acids. Each tRNA molecule has a sequence of three bases the anticodon that reads a codon of mRNA.

16.2 Chemical basis of heredity

The sequence of bases that encodes a functional protein molecule is called a gene. The most important constituent of chromosomes is DNA. The double–stranded helix of DNA is tightly coiled in each chromosomes thread. Gene is a segment of the DNA molecule containing about 600 base pairs. The genetic message is carried

in the sequence of bases along the DNA strand. In transcription, the genetic message is transferred to the mRNA which carries it to the ribosome. Replication ensures that the genes a segment of the DNA molecule are present in identical sets, in all cells of the body of an individual. DNA fulfils the requirement of a genetical material ability to replicate.

The genes are arranged in orderly manner along the length of the DNA molecule in the chromosome. Each gene for any particular characteristic has its counterpart in the corresponding locus on the homologous chromosome and these two genes form an allelic pair.

Seymour Benzer constructed the word cistron, recon and muton on the basis of various functions of gene. The functionl unit is called cistron, unit of recombination called recon, unit of mutation is called muton. Cistron is part of DNA that controls the function of cell. A cistron act code for mRNA and mRNA code for polypeptide synthesis. On the basis of cistron gene may be mono or polycistronic.

Nucleic acids are able to reproduce or store or express and transmit genetic information. In cell division the nucleic acid chain is duplicated preserving in each daughter cell the information contained in the parent cell and serves as a template for the synthesis of another complementary chain. DNA produces mRNA which helps in placing amino acids in the code for protein synthesis. The formation of RNA template is directed by nuclear DNA. rRNA and tRNA are also involved in protein synthesis.

Biological oxidation-reduction involves the transport of hydrogen atoms or electrons through organized systems of substances called hydrogen acceptors or electrons transport agents. The hydrogen acceptors are nucleotides such as NAD, FAD etc. DNA as the bearer of genetic information in the cell is strongly supported by the Waston-Crick structure for this compound which explains beautifully the phenomenon of replication of DNA.

In unphysiological conditions of the environment such as exposure to ultra-violet light, ionizing radiations e.g., X-rays, gamma rays and neutrons and certain chemicals (e.g., nitrogen, mustards, colchicine and certain chemical carcinogens) certain sudden and permanent changes known as mutations occur in the DNA molecules. The mutations are believed to be due to changes in the structure of

conformations of the DNA molecule which thus transfers these changes to the offspring.

16.3 Replication of DNA

The dispersive, conservative and semi-conservative methods of DNA replication have been proposed. In dispersive mode of replication the parental DNA is broken down into smaller fragments. The Conservative method proposes that the two strands of DNA molecule remains joined to each other while, they give programme for the formation to daughter DNA molecule. The Semi-conservative method of DNA replication is now well accepted, the two strands of DNA molecule separate from each other and each strand gives template to the complementary strand.

DNA is a bio-molecule that has property to produce its daughter molecule and the base sequence in daughter molecule is like parent DNA molecule that is called replication. The two strands of DNA double helix are united to each other by hydrogen bonds. The nucleus contains free nucleotides that form nucleotide pool containin gadenine, guanine, cytosine and thymine nirogenous bases. The adenine nucleotide pairs with thymine,guanine with the cytosine nucleotide of the strand (A=T and G=C pairing) and finally a new stand is formed around each old strand.

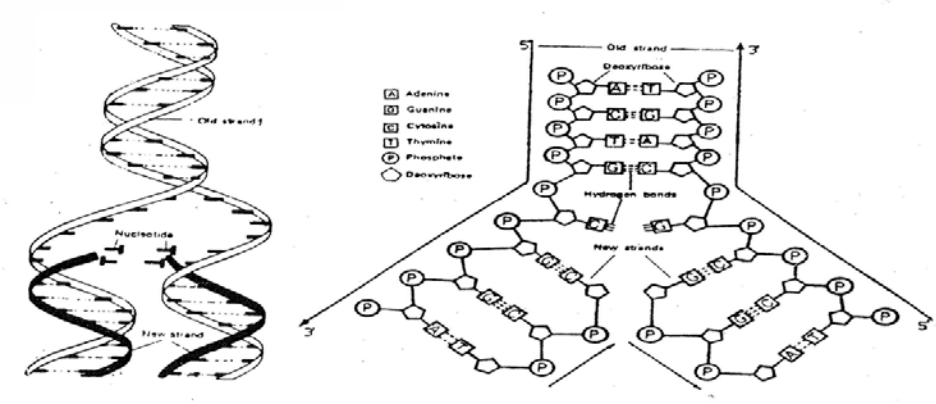


Fig.16.1: Replication of DNA

The chromosome (containing DNA) divides into two during mitosis (actually during interphase) and two daughter chromosomes have identical double helices. The details of different aspects of replication will now be taken up. Replication takes place during the interphase (S-phase) by semi-conservative method (parent double strand have one old and one new strand).

In this process a DNA template, a primer, deoxyribonucleoside triphosphates

(dATP, dGTP, dTTP and dCTP), Mg^{++}, DNA unwinding protein, superhelix relaxing protein, a modified RNA polymerase (synthesize RNA primer), dnaA, dnaB, dnaC-D, dnaE and dnaG genes and polynucleotide ligase are require. In E. coli the products of genes dnaA and dnaC-D are required for initiating new rounds of replication, products of dnaE and dnaG for replication fork movement,dnaG protein for initiation of synthesis of DNA fragments. The locus for the origin of replication is at 74 minutes, and that for termination of replication at 25 minutes. The structural genes for the three DNA polymerases are pol A (for polymerase I), pol B (for polymerase II) and dnaE (for polymerase III and polymerase III). The DNA consists of many replicating units or replicons. The nick presumed to take place at a specific initiation point by an incision enzyme (endonuclease).

The process replication starts with a nick or incision made by an incision enzyme (endonuclease) at a specific point called the origin (Fig. 16.2 and 16.1). In *E. coli* the origin of replication is at about 74 minutes on the chromosome map. In the virus T7 the origin is 17% from one end of the duplex rod chromosome. In E. coli an enzymatic complex found at the point of attachment of DNA on the plasma membrane called replicating point.

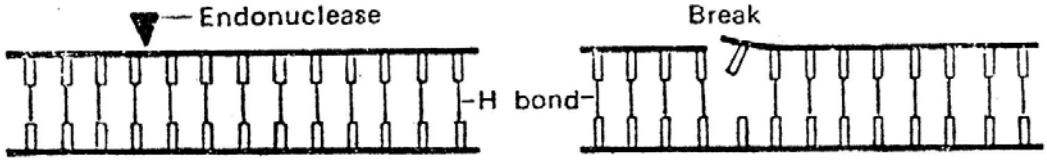


Fig. 16.2: Replication starts with an incision by incision enzyme (endonuclease)

By the help of DNA unwinding protein or DNA binding protein the two strands unwind. This unwinding of the strands imposes strain that relieved by the action of a superhelix relaxing protein. The protein is a tetramer (molecular weight of 18,500 to 22,000) but it may bind to DNA as a monomer or a dimer. This protein released as elongation continues and again participate in unwinding the parental strands.

Unwinding of the strand of DNA double helix has to unwind in order to separate the two strands for replication and simultaneously with unwinding. It cannot wait for the complete unwinding of the DNA molecule. DNA binding proteins bind preferentially to single strands of DNA-and promote unwinding (denaturation) of doubles helical DNA and this region is called Y-shaped replication fork. About

200 molecules of the unwinding protein may be found at each fork. Each molecule of this protein binds to DNA and enhances the binding of the next–molecule that further unwinding of the double helix.

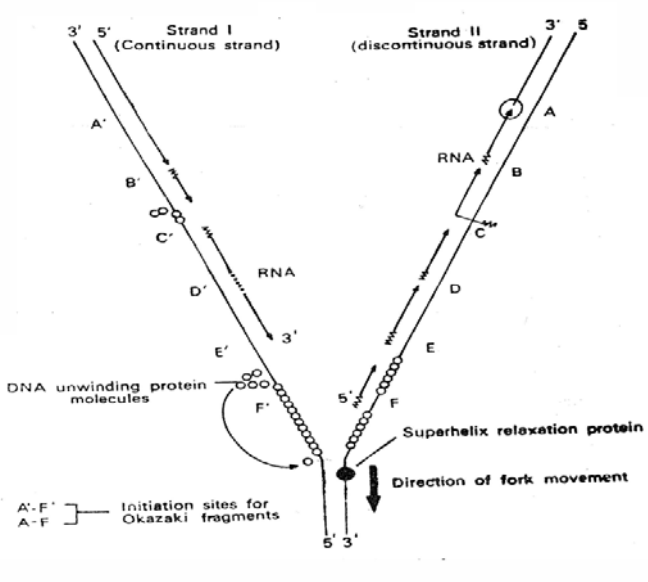


Fig. 16.3: Replication fork showing replication

As the replication fork moves down the DNA double helix the parental strands wind by Superhelix relaxing protein (Swiveling protein, □). This protein has nicking-closing enzymatic activity. Initiation of DNA synthesis requires an RNA primer that is synthesized by DNA template close to the origin and it catalysed by RNA polymerase (Fig. 16.4). Initiation of DNA synthesis-requires an RNA primer. DNA polymerases cannot initiate DNA chains de novo.

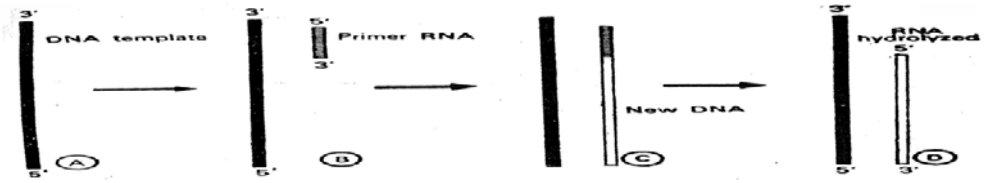


Fig. 16.4: Initiation of DNA synthesis process

(A. DNA template, B. Primer RNAsynthesized on DNA template, C. New DNA synthesized on primer, D. RNA hydrolyzed)

Now Deoxyribose nucleotides are added to the 3' end of RNA primer and the main DNA strand is synthesized on the DNA template. This strand is complementary to the DNA strand and is synthesized by DNA polymerase. Now this enzyme degrades the RNA primer, simultaneously catalyses the synthesis of a short DNA

segment to replace the primer. This segment helps in uniting to the main DNA strand by a DNA ligase. Synthesis of the new DNA strand takes place by addition of DNA nucleotides to the 3'-OH group of the last ribonucleotide of the RNA primer. This synthesis takes place in the 5'□3' direction catalysed by DNA pol III. The RNA primer is hydrolysed by the 5'□3' exonuclease activity of DNA pol I. The resulting gap is filled in by DNA nucleotides by catalytic activity of DNA pol I. The newly made DNA is joined by DNA ligase and RNA primers digested by specific endonucleases (Ribonuclease H).

The Replication has direction and forms replicating forks- Replication may proceed in one or both directions from the point of origin. Replication in one direction is called unidirectional replication (Fig. 16.5), while that in both directions is called bidirecrional replication (Fig. 16.6). In bidirectional replication (eg. *E. coli, Bacillus subtilis, Salmonella typhimurinm, E. coli phages,* the mammalian virus SV40 and mammalian cells, and appears to be more common) and unidirectional replication (eg.*E. coli,*bacteriophages P2 and 186 and also in mitochondrial DNA of mouse LD cells) is found

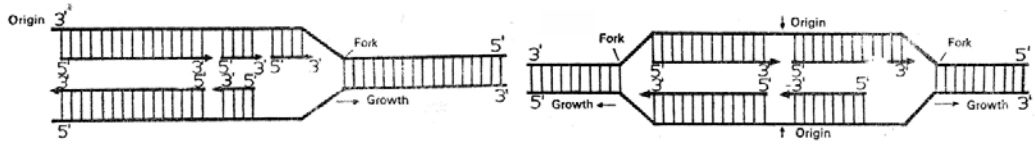


Fig. 16.5 Unidirectional and bidirectional replication of DNA

Replication is also a discontinuous process and short pieces called Okazaki fragments are synthesized. In this process, one strand synthesize continuously and other Okazaki fragments or one strand is synthesized forwards and the other backwards. Both new strands are synthesized in the 5'□3'. The Okazaki pieces are joined by polynucleotide ligase.

Replication of the two parental strands takes place simultaneously as the fork moves along. All DNA polymerases can extend the two DNA strands only in the 5'□3' direction. The two strands-are, polarized in opposite directions. Okazaki et al. (1968) reported that only one strand, the 3'□5' or continuous strand, is continuously replicated but other strand (5'□3') replicates in a discontinuous manner, synthesizing short fragments which have been called Okazaki fragments (Fig. 16.7). This direction of synthesis is opposite to that of the movement of the

replicating fork.

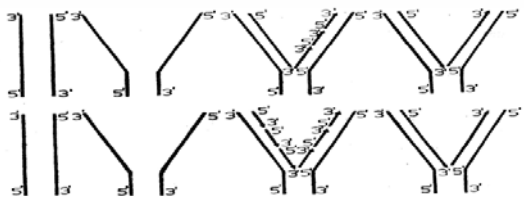


Fig. 16.6: Replication of DNA, two possible schemes.

Polynucleotide ligase enzyme joins these fragements into high molecular weight DNA. In mutants, produce defective ligase, the joining of Okazaki fragments is greatly impaired. Polynucleotide ligase seals single-stranded breaks in DNA molecules during chromosome replication and genetic recombination. E. coli ligase requires nicotinamide adenine dinucleotide (NAD) for activity. This ligase is first adenylated by the AMP moiety of NAD and nicotinamide mononucleotide (NMN) is released.

Ligase + NAD □□Ligase AMP+NMN

The adenylated ligase then reacts with DNA having a single stranded break to yield a repaired phoshodiester bond ligase and AMP.

Ligase AMP + DNA (ss break) □ Repaired DNA + Ligase + AMP

Meselson and Stahl (1958) experiment

M.S. Meselson and F.W. Stahl (1958) proved this method of DNA replication using E. coli and labeled nitrogen (^{15}N). The culture grown in ^{15}N nitrogen source was later transferred to a medium containing ^{14}N. The cells developed in these culture media contained isotopic nitrogen in the nitrogenous base of DNA. Cells grown in ^{15}N will have a greater density (weight per unit volume) than the DNA of cells grown on medium containing ^{14}N. These molecules can be separated by equilibrium density-gradient centrifugation. When a heavy salt solution such as 6 M CsCl is centrifuged at very high speeds (30,000-50,000 revolutions per minute) for 48-72 hours, an equilibrium density gradient is formed. At the equilibrium stage between sedimentation and diffusion, a linear gradient with increasing density, exist from the top to bottom of the tube. DNA molecule will settle where the density of the salt solution is equal to its own density. A DNA molecule with mixed chain i.e., one heavy chain (^{15}N) and one light chain (^{14}N) is present in the solution; two bands will appear in CsCl tube. This confirms the fact that DNA

replicates in a semiconservative method.

16.4 Transcription

In transcription a messenger RNA strand is copied or transcribed from a DNA strand (Figs. 16.7 and 16.8).

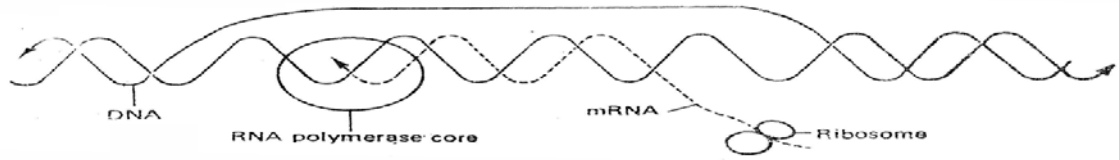


Fig. 16.7: Transcription of mRNA on a DNA strand under the control of the enzyme RNA polymerase

Replication Transcription Translation

DNA → DNA → RNA → Protein

Transcription is the process of copying of a complementary messenger RNA strand on a unwind DNA strand. The nucleotides of this mRNA are complementary to those of the DNA strand except uracil (U) replaces thymine (T) of DNA and complementary pairing is A-U and G-C. in eukaryotes, the mRNA comes out from nuclear pore to cytoplasm and forms a complex with a group of ribosomes (polyribosome) but in prokaryotes the mRNA strand is pulled away from the DNA by a ribosome (Fig. 16.1).

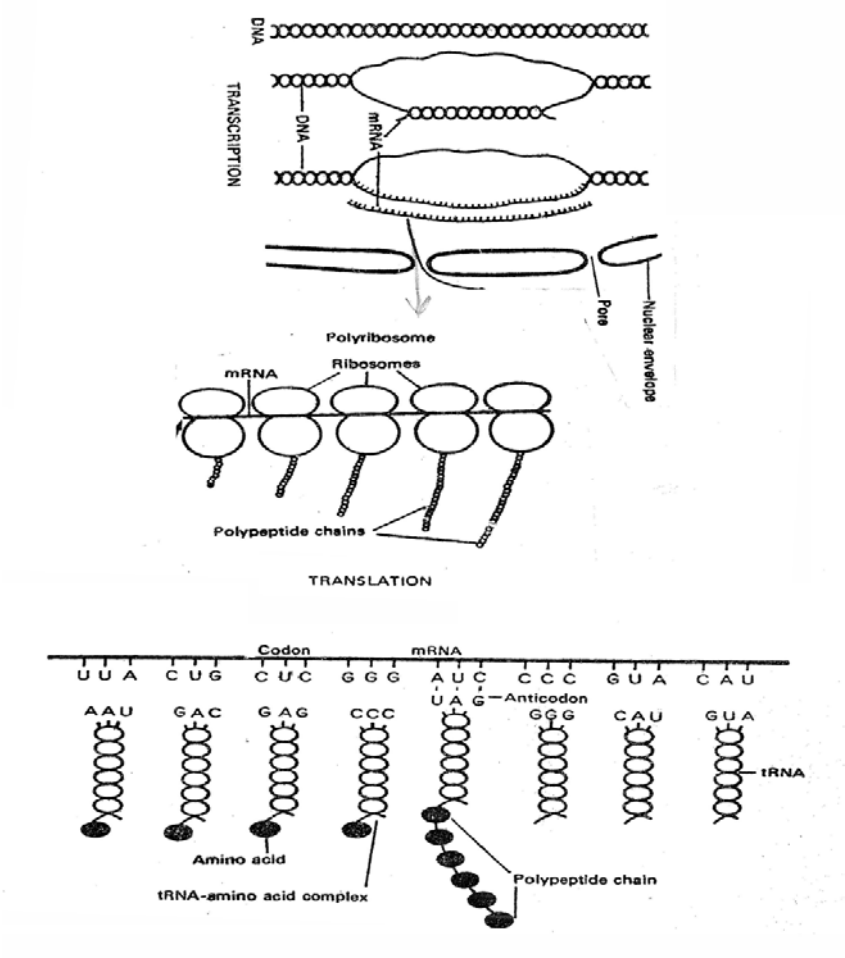


Fig. 16.8: General scheme of protein synthesis

Transcription requires a template (usually double-stranded DNA), ribonucleoside triphosphates (ATP, GTP, UTP and CTP), RNA polymerase and divalent metal ions. RNA polymerase (Fig. 16.9) consists of a core enzyme, (subunits □□□□□□□□□) and a sigma (□) factor. The sigma factor initiates transcription of mRNA on the DNA template and the core enzyme continues transcription.

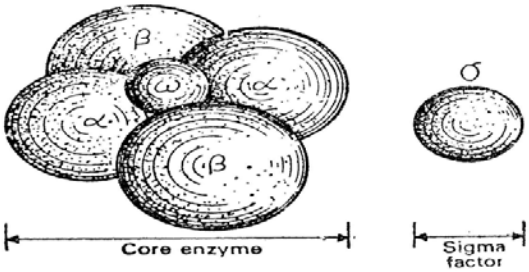
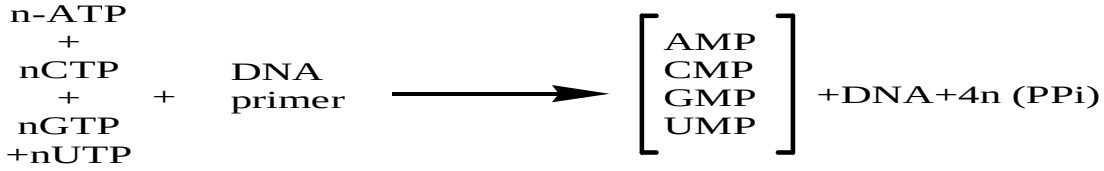


Fig. 16.9: Schematic representation of the enzyme RNA polymerase.

The Biosynthesis of RNA or Transcription process is very much similar to that of DNA. Although DNA consists of a relatively homogeneous family of molecules but there are mainly 3 types of RNA, viz messenger RNA (mRNA), soluble or transfer RNA (s or t RNA) and ribosomal RNA (rRNA). Except mitochondrial RNA all the RNA of the animal cell is synthesized in the nucleus, much of which occurs in the nucleolus and move to cytoplasm. Synthesis of RNA involves the polymerisation of 4 nucleoside triphosphates (viz. ATP, CTP, GTP and UTP) and template DNA. The RNA chain formed DNA, separates from the template DNA chain and it combines to complementary DNA chain via the hydrogen bond finally template DNA recovered unchanged. So the mechanism of RNA synthesis is very much similar to that of DNA synthesis given below:



RNA pool of cell consists of rRNA and tRNA, most of the DNA serves as template for synthesis of mRNA which comprises only about 1 per cent of the total cell RNA. A very small proportion of the DNA serves as template for synthesis of rRNA (0.15% of the total DNA) and tRNA (0.02% of the total DNA). This controversial behaviour is because of very much turnover rate of mRNA than that of rRNA and tRNA means once the rRNA and tRNA have been synthesized, they survive for longer periods, while mRNA exists till it serves its purpose as template for protein synthesis.

In Post-transcriptional processing the biosynthesis of DNA, rRNA and tRNA (or sRNA), the basic skeleton of the nucleic acids is synthesised as usual. But forms of RNA like mRNA, rRNA and tRNA (also DNA) are partially methylated in the nucleus undergo certain rearrangements (leading to pseudouridine) or other modifications of the usual bases (leading to hypoxanthine or dihydrouracil) called post-transcriptional processing. Certain RNA (also DNA) may undergo glucosylation, phosphorylation, acylation, and thiolation after proper nucleic acid synthesis. Methylation is quantitatively the most important among all these reactions and is effected by active-methionine and is catalysed by transmethylases. Only a small proportion of the bases are methylated. NA (Nucleic acid) + S-

Adenosylmethionine → CH_3-Nucleic acid + S-Adenosylhomocysteine

In DNA molecule, the sites of methylation are mainly on adenine and cytosine residues giving 6-methylamino purine and 5-methylcytosine respectively but tRNA contains a number of methylated bases (e.g. A, C, G or U) that possesses methyl groups at the 2'-hydroxyl position of the ribose moiety at certain specific sites.

16.5 Translation

The translation process the genetic information present in mRNA (after transcription process completion), directs the order of specific amino acids to form a polypeptide or protein for cell.

The mRNA has triplet bases called codon that pairs with anticodons of the tRNA molecule in A-U and G-C combination. The codon GUC of mRNA pairs with anticodon CAG of tRNA means series of codons on mRNA determines the series of anticodons of the different tRNA molecules indirectly the amino acids sequence. The translation process consists of (i) activation of amino acids, (ii) transfer of the activated amino acid to tRNA, (iii) initiation of polypeptide chain synthesis and (iv) chain elongation and chain termination (Fig. 16.11).

The 20 amino acids (aa) used in protein synthesis are activated by ATP by specific activating enzymes (E), aminoacyl synthetases to form aminoacyl adenylates (aaa) or aminoacyl AMP. Pyrophosphates (PPi) are released.

$$aa+ATP+E > E.aa\text{-}AMP+PPi$$

This activated amino acid is transferred to a specific tRNA with release of AMP and activating enzyme.

$$E.aa\text{-}AM\ P+ E+tRNA \rightarrow E.aa\text{-}tRNA+AMP+ E$$

The initiation of chain synthesis requires the ribosome subunits, mRNA, an energy source (GTP), activated amino acids attached to tRNA (aa-tRNA) and initiation factors (IF). These factors are called IF-I, IF-2 and IF-3 in prokaryotes, and eIF-2, eIF-2', eIF-$2a_1$, eIF-$2a_2$', e1F-$2a_3$ and e1F-3 in eukaryotes.

The 30S ribosomal subunit attaches to mRNA to form an mRNA-30S complex and process requires IF-3, and Mg^{++}. The initiation amino acid is methionine (Met) of eukaryotes and N-formylmethionine (fMet-tRNA) attaches to the initiation codon, AUG, on mRNA through its anticodon UAC to form the 30S initiation complex. The process requires initiation factors IF-2 and IF-3 as well as GTP. The larger

ribosomal subunit (50S in prokaryotes) joins to the 30S initiation complex to form the complete initiation complex (70S) and larger ribosomal subunit has two binding sites for tRNA, an A or acceptor site and a P or peptidyl site fMet-tRNA binds to the P site. Translocation is the process in which the aa_2-tRNA complex moves from the A site to the P-site and requires EF-G, GTP and Mg^{++}. Translocation involves movement of the ribosome relative to mRNA in the 5'□3' direction. The tRNA molecule of fMet is unloaded from the ribosome. The third amino acid-tRNA complex (aa_3-tRNA) now occupies the vacant P site.

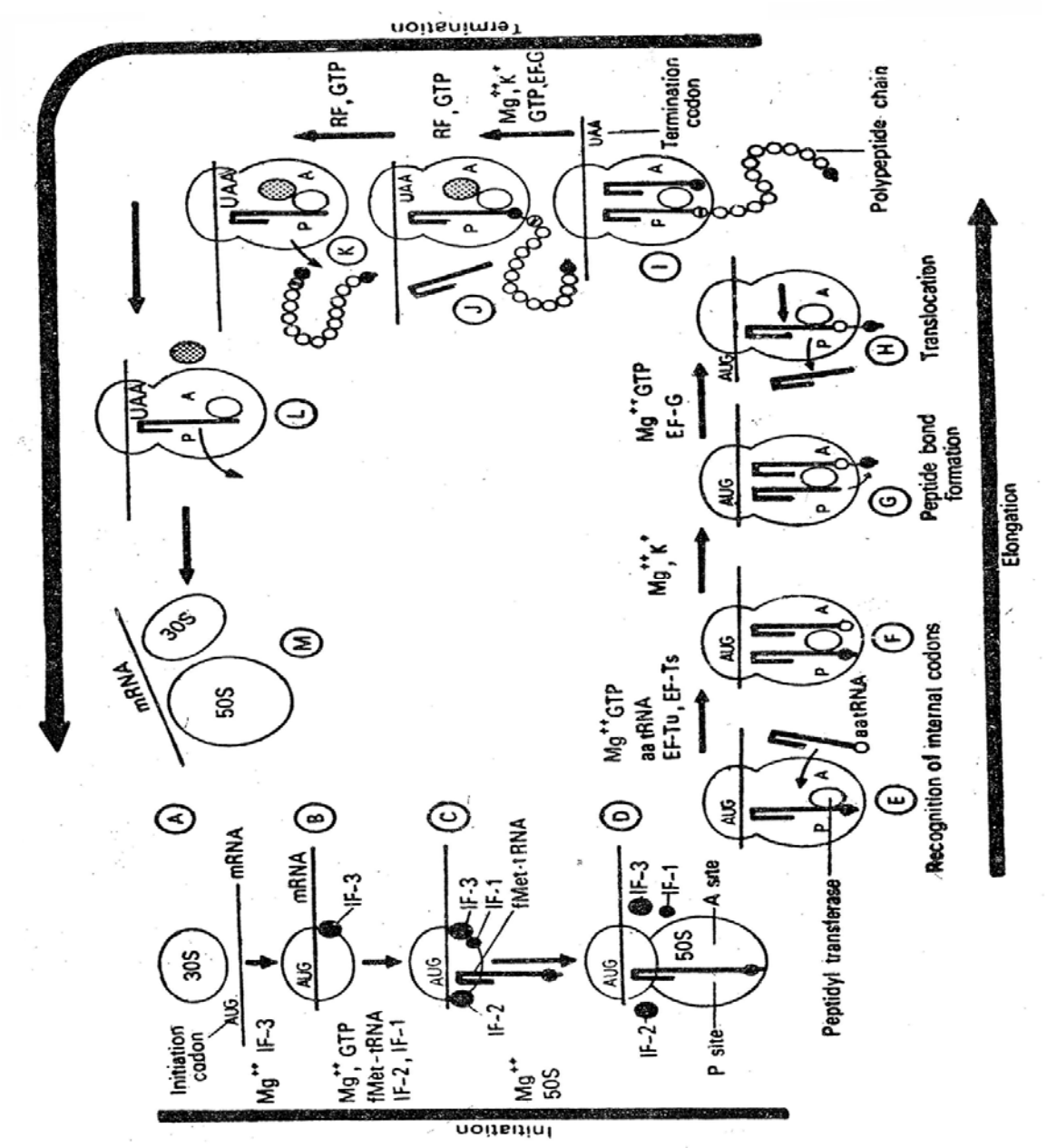


Fig. 16.10 Translation

(A. The 30S ribosomal unit and mRNA, **B.** Attachment of mRNA to 30S subunit. The process requires initiation factor IF-3 and Mg^{++}, C. Attachment of fMet-tRNA to initiation codon AUG of mRNA to form the 30S initiation complex, D. Joining of the 50S subunit to the 30S initiation complex to form the complete initiation complex. Note that fMet-tRNA is at the P site, E. and F. aa-tRNA now occupies the A site. There is enzymatic recognition of internal codons. This process requires factors EF-Tu, EF-Ts, GTP and Mg^{++}, G. Formation of peptide bond by transfer of fMet to second amino acid Mg^{++} and K^{+} required, H. Translocation- involves one-codon movement of mRNA release of tRNA and movement of peptidyl-tRNA from A site to P site, I. Peptidyl tRNA with almost complete polypeptide chain in P site, J. Translocation, transpeptidation and termination codon UAA comes in the recognition site. The Polypeptide chain is attached to tRNA. Release factor interacts with the ribosomes in response to the termination codon, K. Release of complete polypeptide chain by peptidyl-tRNA hydrolysis. This involves interaction of release factor with peptidyl transferase, L. Dissociation of release factor from the ribosome and also perhaps release of tRNA after translocation, M. Dissociation of ribosome and release of mRNA).

Chain elongation of the polypetide requires elongation factors (EF). These are EF-Tu, EF-Ts and EF-G in prokaryotes and EF-1 and EF-2 in eukaryotes. The second amino acid-tRNA complex (aaa-tRNA) now occupies the A site. There is enzymatic recognition of internal codons. The process requires EF-Tu. GTP and Mg^{++}. Formation of a peptide bond takes place by transfer of fMet to the second amino acid (aa_2). Mg^{++} and K^{+} are required. The catalyzing enzyme is peptidyl transferase.

The Chain elongation process continues until a termination codon (UAA, UAG or UGA) reaches the ribosome; the chain is terminated and released from the ribosome. It requires release factors (RF-l, RF-2 and RF-3 in prokaryotes and RF in eukaryotes). In this process the termination codon provides signals to the ribosome for the attachment of release factors. The release factors interact with peptidyl transferase causing hydrolysis of the bond between tRNA, the polypeptide chain, and the chain is released from the ribosome. The tRNA is also unloaded and ribosomal subunits dissociate, mRNA released, for breakdown to nucleotides. Processing of the polypeptide chain takes place after release.

16.6 Genetic code

The relationship between the sequence of bases in DNA/RNA and the sequence of amino acids in a polypeptide chain is called the genetic code. The code indicates that which codon specify which amino acids. Each tRNA molecule has a sequence of three bases the anticodon that reads a codon of mRNA. The tRNA molecules serve as adaptors in proteins synthesis by reading mRNA codons in a sequence known as Crick's Adaptor Hypothesis. About 150 amino acids are found in nature but only 20 are specified by the genetic code and these 20 take part in protein synthesis.

The genes of a cell contain coded information for the maintenance and reproduction of the cell. They direct the arrangement of the 20 types of amino acids into the polypeptide chains of the protein molecules. A polypeptide chain typically contains about 100-300 amino acids, and is formed by specific arrangement of the 20 types of amino acids.

Properties of genetic code: the genetic code has following properties -

1. The genetic code is a triplet code: DNA contains four kinds of nucleotides (of A, T, G and C) and proteins are synthesized from 20 different types of amino acids. In a singlet code each base or letter would specify one amino add. Only 4 of the 20 types of amino acids would be coded unambiguously by a singlet code. In a two-letter or doublet code two bases would specify one amino acid. Here 16 (4 x 4) of the 20 amino acids can be specified. But a triplet or three-letter code first suggested by Gamow (1954), three letters or bases specify one amino acid. Thus 64 (4 x 4 x 4) distinct triplets of purine and/or pyrimidine bases determine the 20 amino acids. These triplets have been called codons. A quadruplet code would have 4x4x4x4 = 256 codons, and would show even more degeneracy than the triplet code.

Type of code	Number of bases in codon	Number of codons	Ambiguous/ degenerate
Singlet code	1	4	Ambiguous
Doublet code	2	4x4=16	Ambiguous

Triplet code	3	4x4x4=64	Degenerate

Table 16.1: The maximum possible number of codons in the singlet, doublet and triplet codes.

2. The code is non-overlapping: DNA molecule is a long chain of nucleotides it could be read either in an overlapping or non-overlapping manner. Non-overlapping of codons means, if a base is a part of one codon in one reading frame, it can't be a part of next codon frame. The reading of the code by these two different ways would yield different results.

Fig. 16.12: Non-overlapping code

3. The code is commaless: The genetic code read in an uninterrupted manner from one end of the nucleic acid chain to the other. A commaless code would not have the comma bases and can be represented thus:

UUU CUC GUA UCC ACC.....Bases

Phe Leu Val Ser Thr.....Amino acids

The code is commaless, i.e. there are no demarcating signals, punctuations signals between two codons. Khorana et al gives clear evidence of a commaless code. Long synthetic polynucleotides with specific repeating sequences were used for translation of protein chains.

4. The code has polarity: Genes specify for the same protein repeatedly it is essential that the code must be read between fixed start and end points the initiation and the termination codons. The code must have obvious that if the code is read in opposite directions it would specify two different proteins, since the codons would have reversed base sequences. It is thus seen that the sequence of amino acids constituting the protein would undergo a drastic change if the code is read in the opposite direction it is due to polarity in codons. The message in mRNA is read in the 5'□3' direction and polypeptide chain is synthesized in the N□C direction from the amino (NH_2) terminal to the carboxyl (COOH) terminal.

5. Codods and anticodons: In translation the codons of mRNA pair with complementary anticodons of tRNA (mRNA is read 5'□3' direction the codons are also written in the 5'□3' direction) means AVG is written as 5' AUG3'. The corresponding anticodon tRNA should therefore be written as 5'CAU3', In such a configuration the first bases of both codon and anticodon would be the ones at the 5' end and third bases at the 3' end.

Base number		1	2	3
Codon (mRNA)	5'	A	U	G 3′
Anticodon (tRNA)	3'	U	A	C 5′
Base number		3	2	1

6. Initiation codons: The starting amino acid in the synthesis of most protein chains is methionine (eukaryotes) or N-formylmethionine (prokaryotes) coded by AUG and called the initiation codon. In some cases GUG also serves as the initiation codon in bacterial protein synthesis. Both AUG and GUG codons show ambiguity in one sense, since each of them codes for two different amino acids. In internal positions AUG codes for methionine and GUG for valine.

7. Termination codons: Three of the 64 codons do not specify any tRNA called nonsense codons. These codons are UAG (amber), UAA (ochre) and UGA (opal or umber) and terminate the polypeptide chain synthesis they are so called termination codons. These codons do not code for any amino acids hence no tRNA species has anticodon complementary to the termination codons. Both in prokaryotes and eukaryote these codons are recognized by release factor (RF).

8. The code is degenerate: Degeneracy means that single amino acid can be coded by more than one codon. Degeneracy is of great selective advantages. There are 64 possible codons in a triplet code of which 61 have been shown to code amino acids. Except for tryptophan and methionine, which have a single codon each, all other amino acids have more than one codon. Phenylalanine, tyrosine, histidine, glutamine, asparagine, lysine, aspartic acid, glutamic acid and cysteine have two codons each. Isoleucine has three codons. Vaiine, proline, threonine, alanine and glycine have fourcodons each. Leucine, arginine and serine have six codons each.

9. The wobble hypothesis: The triplet code is a degenerate one with many more codons than the number of amino acid types coded. An explanation for this degeneracy is provided by the wobble hypothesis proposed by Crick (1966).

According to this hypothesis only the first two positions of a triplet codon on mRNA have a precise pairing with the bases of the tRNA anticodon. The pairing of the third position bases of the codon may be ambiguous, and varies according to the nucleotide present in this position. In UCG, AGU pairing there is a departure from the usual pairing where G pairs with C and A with U and such interaction between the third bases is referred to as wobble pairing.

mRNA codons (serine)	5'	AGC	3'	5' AGU	3'
tRNA anticodon	3'	UCG	5'	3' UCG	5'

Wobble pairing combinations may be: (i) U in the wobble position of the tRNA anticodon can pair with A or G of the mRNA codon, (ii) G can pair with' U or C and (iii) I can pair with A, U or C.

10. Colinearity of gene structure and its polypeptide product: Gene is an unbranched structure consisting of a linear sequence of nucleotide pairs and polypeptide chain also unbranched and consists of a linear series of amino acid residues. This was established by Yanofsky and his co-workers (1964) through a study of E. coli tryptophan synthetase that enzyme has two chains, α and β.

11. The code is universal: The genetic code is valid for all organisms ranging from bacteria to man. The universality of the code was demonstrated by Marshall, Caskey and Nirenberg (1967), who found that E. coli (bacterium), Xenopus laevis (amphibian) and guinea pig (mammal) amino acyl tRNAs use almost the same code. This showed that the code is essentially universal. A change in a single base can account for nearly all amino acid substitutions. This proves the universality of the code. The code has remained constant since the time it was fixed when complex bacteria evolved (about three billion years ago). Any mutation altering the code reading would change the reading of mRNA.

16.7 Chemical synthesis of mono and trinucleoside

The mechanism of biosynthesis of DNA has been largely clarified after discovery of the enzyme DNA polymerase or DNA nucleotidyl transferase that catalyses the polymerisation of the four deoxyribonucleoside triphosphates (i.e. mononuc1eotides) in the presence of Mg^{++} ions and a primer DNA. The four deoxyribonucleotide triphosphates (i.e. mononucleotides) which act as substrate are the 5'-triphosphates of deoxyadenosine (dATP), deoxyguanosine (dGTP),

deoxycytidine (dCTP) and deoxythymidinc (dTTP) as given below:

The energy is provided by the high energy bonds in the linear triphosphate units of the dA TP, dCTP, dGTP and dTTP that is required for the formation of the 3', 5' -phosphodiester bonds of the polydeoxyribonucleotide. As each monomer is incorporated into the new chain it loses its terminal pyrophosphate units (PPi).

In the presence of DNA polymerase, Mg^{++}, the ds DNA act as a template (or primer) separates (a small portion at a time) by break of hydrogen bond between complementary bases. The 4 deoxyribonucleoside triphosphates are attracted from solution in the cellular sap to form hydrogen bonds with their complementary bases on the separated strands of the primer DNA. The DNA template dictates the sequence in which the monomers are assembled. During this each nucleotide loses a pyrophosphate group and forms an ester linkage with the 3' -hydroxyl group of deoxyribose on adjacent new nucleotide via its remaining phosphate group (on the C_5'). Two daughter double helices formed and each consisting of an old strand of the primer DNA and a complementary new strand and final composition and nucleotide sequence of strands are identical with the corresponding strand parent DNA. This process has been named as replication. Some of the acridine drugs (e.g. proflavine) and antibiotics of the mitomycin type inhibit DNA replication. DNA polymerase enzyme has the power to repair broken DNA chains by removing, in a stepwise manner, the broken chain, starting at the 5'-phosphate terminus and re-synthesizing a new chain. Deoxynucleotide are added to the 3'-hydroxyl terminus of the break using the intact chain as template.

Biosynthesis of purine nucleotides takes place by three processes (i) synthesis from amphibolic intermediates, (ii) phosphoribosylation of purines, and (iii) phosphorylation of purines. Adenosine mono phosphate and guanosine monophosphate are synthesized by a common parent nucleotide, inosine monophosphate (IMP). The latter synthesized from the amphibolic intermediate □-D-ribose-5-phosphate (I). Intermediates are 5-phsophoribosyl-l-pyrophosphate (PRPP) (II), 5-phospho-□-D- ribosylamine (III), Glycinamide, ribosyl-5-phosphate (IV), formylglycinamide ribosyl-5-phsophate (V), formylglycinamidine

ribosyl-5-phosphate (VI), aminoimidazole ribosyl-5-phosphate (VII), aminoimidazole carboxylate ribosyl-5-phosphate (VIII), succinyl carboxamide ribosyl-5-phosphate (IX), aminoimidazole carboxamide ribosyl-5-phosphate (X) and formim-idoimidazole carboxamide ribosyl-5- phosphate (XI). Enzyme IMP cyclohydrolase catalyzes the closure of ring (XI) intermediate and forms inosine monophosphate, the first purine nucleotide.

Conversion of IMP to AMP and GMP: After the formation of IMP, the pathway divided or branches in two short reaction sequences lead to the formation of AMP and GMP. Aspartate adds to IMP and forms adenylosuccinate. Release of fumarate forming adenosine 5'-monophosphate (AMP) is catalyzed by adenylosuccinase. IMP is oxidized by NAD^+ and xanthosine monophosphate (XMP) is formed. 6-oxo group of XMP is transamidated by the amide nitrogen of glutamine.

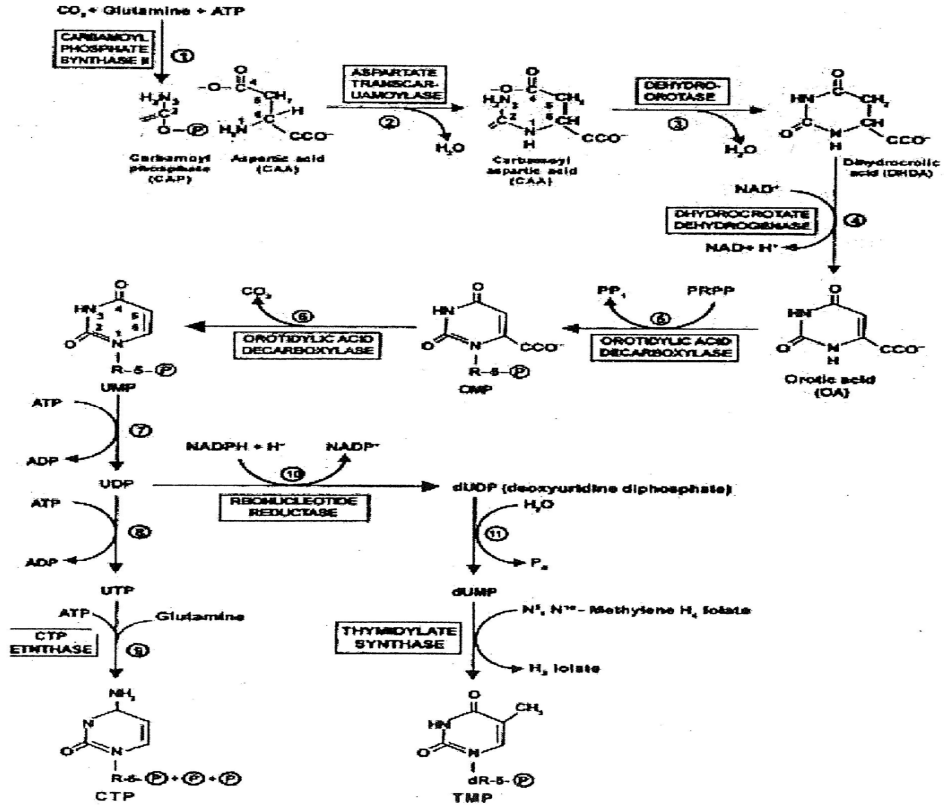


Fig. 16.12: The biosynthetic pathway for pyrimidine nucleotides

Synthesis of di and triphosphate nucleotide: Enzyme nucleoside monophosphate kinase catalyzes formation of diphosphate nucleoside from their monophosphate nucleotides. The phosphate moiety comes from ATP. GDP is again phosphorylated by ATP. ADP is phosphorylated to ATP by oxidativephsophorylation and

secondarily by reactions of glycolysis and the citric acid cycle.

In biosynthesis of pyrimidine nucleotides (Fig. 16.12), first of all the six membere pyrimidine ring is made and then it is attached to ribose-5-phosphate. Carbamoyl phosphate is needed in this process and reaction is catalyzed by aspartate transcarbamoylase. Enzyme dihydroorotase removes water from this intermediate and the pyrimidine ring is closed to form L-dihydroorotate. This compound is oxidized to yield the pyrimidine derivative orotate, a reaction in which NAD^+ is the ultimate electron receptor. 5-phsophoribosyl-l-pyrophosphate provides the ribose-5-phosphate side chain and orotidylate is synthesized that decarobxylated and converted into uridylate. Uridylate after phosphorylation give UTP and cytidylate synthetase catalyzes the formation of CTP from UTP. Nucleotidases (Phospbatases) enzymes hydrolyse the nucleotides to the corresponding nucleosides and inorganic phosphate molecules. These enzymes may or may not display specificity for 5 or 3-monophosphates, and for the deoxyribosyl or ribosyl residues. Nucleosidases (nucleoside phosphorylases) yielded by above reactions may be absorbed and then degraded as discussed in the catabolism of purines and pyrimidines.

16.8 Summary

DNA is the most important constituent of chromosomes. The genes containing about 600 base pairs are arranged in orderly manner along the length of the DNA molecule in the chromosome. Each gene for any particular characteristic has its counterpart in the corresponding locus on the homologous chromosome and these two genes form an allelic pair. Replication of DNA ensures that the genes a segment of the DNA molecule are present in identical sets. In transcription, the genetic message is transferred to the mRNA. DNA replication is a complex process and requires the four deoxynucleoside triphosphates (dGTP, dATP, dCTP, dTTP) as precursors and some enzymes, protein factors to complete this process. DNA polymerase binds two divalent metal ions (typically Mg^{2+} or Zn^{2+}). These metallic ions alter the chemical environment around the correctly base-paired dNTP and the 3OH of the primer. The metal ion reduces the affinity of the 3OH for its hydrogen. DNA as the bearer of genetic information and its replication may be of dispersive, conservative and semi-conservative methods. The semi-conservative method of DNA replication is now well accepted, the two strands of DNA molecule separate

from each other and each strand gives template to the complementary strand. In replication the adenine nucleotide pairs with thymine,guanine with the cytosine nucleotide and a new stand is formed around each old strand. Replication may proceed in one or both directions from the point of origin may be unidirectional orbidirecrional replication. In transcription a messenger RNA strand is copied or transcribed from a DNA strand. The translation process the genetic information present in mRNA (after transcription process completion), directs the order of specific amino acids to form a polypeptide or protein for cell. The chain elongation process continues until a termination codon reaches the ribosome and the chain is terminated finally released from the ribosome. It requires release factors. The relationship between the sequence of bases in DNA/RNA and the sequence of amino acids in a polypeptide chain is called the genetic code. The code indicates that which codon specify which amino acids. These genetic codons have specific characteristics.

16.9 Self-Learning Exercise

Section A

1. Name the process by which mRAN is formed from a DNA temptele.
2. Which componentus are involued in translation
3. Difine Gene
4. Mention tomination codour
5. What do you mean by gentic code.

Section B

1 DNA replicats in a semiconserutiem ethod justify the statements.

2 Briefly discribs proportics of gentic code.

3 What is wobble hypothesis.

Section C

1. Explain the replication of DNA and its role in heredity.
2. Define transcription and translation of DNA and its role in protein synthesis.
3. Write an essay on di and triphosphate nucleotide synthesis.

4. What do you mean by genetic code? Write the characteristic properties of genetic code.
5. Explain the Meselson and Stahl (1958) experiment of DNA semiconservation.
6. Write short note on:

- Okazaki fragments
- Universality of codons
- Biosynthesis of purine nucleotides
- The wobble hypothesis
- Polynucleotide ligase

Answer Key

1 Transcription

2 mRA, DNA, tRAN, ribosomes

3 The sequerce of bases that anrodes a functional protein molicul

4 UAG, UAA, UGA

5 Relationship between the sequre of bases in DNA/RNA and the requence of amino acids in a polypeptdi choine.

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Unit – 17 : Introduction to computers and Computing - Basic structure and functioning of computer with a PC as an illustrative example, Memory, I/O devices. Secondary storage Computer languages

Unit Structure

17.0 Objectives

At the end of the unit learner will be able to :

- Understand parts of computer system.
- Understand working of computer system.
- Understand memory 2/o device.

- Understand computer language.

In this unit we briefly discuss the basic structure and functioning of computers. After studying this unit, students are able to understand the uses and structure of computers.

17.1 Introduction

What are computers?

Computers are machines that perform tasks or calculations, according to given instructions, or based on predefined **programs**. The first fully electronic computer, introduced in 1940s, was huge machines that required a large number of people to operate it. Compared to early machines, today's computers are thousands of times faster and they also can fit on your desk, on your lap, or even in your pocket.

Computers work through an interaction of hardware and software. **Hardware** refers to the parts of computer, which you can see and touch. The most important piece of hardware is a tiny rectangular chip inside your computer called the **central processing unit (CPU)**, or **microprocessor**. It's the "brain" of your computer. This part of computer translates instructions and performs calculations. Hardware items such as monitor, keyboard, mouse, printer, and other components are often called **hardware devices**, or **devices**.

ENIAC (Electronic Numerical Integrator and Computer) was the first general-purpose electronic computer Introduced in 1946. It was built for the United States military to calculate the paths of artillery shells. Physically ENIAC was enormous, weighing more than 27,000 kilograms (60,000 pounds) and filling a large room. To process data, ENIAC used about 18,000 vacuum tubes, each the size of a small light bulb. The tubes burned out easily and had to be constantly replaced.

17.2 Types of computers

Computers range in dimension and capability. At one end of the extent are **supercomputers**, very large computers with thousands of linked microprocessors that perform extremely complex calculations and the other end are tiny computers embedded in cars, TVs, stereo systems, calculators, and appliances. These computers are built to perform a limited number of tasks.

The **personal computer (PC)** is designed to be used by one person at a time. This section describes the various kinds of personal computers: desktops, laptops, handheld computers, and Tablet PCs.

1. **Desktop computers:- Desktop computers** are designed for use at a desk or table. They are typically larger and more controlling than other types of personal computers. Desktop computers are made up of separate apparatus. The main component, called the **system unit**, is usually a rectangular case that sits on or underneath a desk. Other components, such as the monitor, mouse, and keyboard, connect to the system unit.

Desktop computer

2. **Laptops and netbooks:- Laptops** are lightweight mobile PCs with a thin screen. Laptops can operate on batteries, so you can take them anywhere. Unlike desktops, laptops combine the CPU, screen, and keyboard in a single case. The screen folds down onto the keyboard when not in use.

   Netbooks also referred to as **mini notebooks.** Netbooks are small, affordable laptops that are designed to perform a limited number of tasks. They're usually less powerful than laptops, so they're used mainly to browse the web and check e-mail.

Laptop and Netbook

3. **Smartphones:- Smartphones** are mobile phones that have some of the same capabilities as a computer. You can use a smartphone to make telephone calls, access the Internet, organize contact information, send e-mail and text messages, play games, and take pictures. Smartphones usually have a keyboard and a large screen.

Smartphone

4. **Handheld computers:- Handheld computers**, also called **personal digital assistants (PDAs)**, are battery-powered computers small enough to carry almost anywhere. Although not as powerful as desktops or laptops, handheld computers are useful for scheduling appointments, storing addresses and phone numbers, and playing games. Some have more advanced capabilities, such as making telephone calls or accessing the Internet. Instead of keyboards, handheld computers have touch screens that you use with your finger or a **stylus** (a pen-shaped pointing tool).

Handheld computer

5. **Tablet PCs:- Tablet PCs** are mobile PCs that combine features of laptops and handheld computers. Like laptops, they're powerful and have a built-in screen. Like handheld computers, they allow you to write notes or draw pictures on the screen, usually with a tablet pen instead of a stylus. They can also convert your handwriting into typed text. Some Tablet PCs are "convertibles" with a screen that swivels and unfolds to reveal a keyboard underneath.

Tablet PC

17.3 Uses of Computer

In the workplace, many people uses computers to keep their records, analyze data, do research, and manage projects. At home people use computers to find information, store pictures and music, track finances, play games, and communicate with others etc. Computers are also use to connect to the **Internet**. Internet access is available for a monthly fee in most urban areas, and increasingly, in less populated areas. With Internet access, one can communicate with people all over the world and find a vast amount of information. Here are some of the most popular uses of computers:

1. **The web:** The **World Wide Web** (usually called **the web**, or **web**) is a gigantic storehouse of information. The web is the most popular part of the

Internet, partly because it displays most information in a visually appealing format. Headlines, text, and pictures can be combined on a single **webpage**—much like a page in a magazine—along with sounds and animation. A **website** is a collection of interconnected webpages. The web contains millions of websites and billions of webpages.

Example of a webpage (Microsoft Game Studios)

Surfing the web means exploring it. Peoples can find information on the web about almost any topic imaginable. For example, they can read news stories and movie reviews, check airline schedules, see street maps, get the weather forecast for your city, or research a health condition. Most companies, agencies, museums, and libraries have websites with information about their products, services, or collections.

The web is also a shopper's delight. We can browse and purchase products—books, music, toys, clothing, electronics, and much more—at the websites of major retailers. We can also buy and sell used items through websites that use auction-style bidding.

2. **E-mail:- E-mail** (short for **electronic mail**) is a convenient way to communicate with others. When we send an e-mail message, it arrives almost instantly in the recipient's e-mail inbox. We can send e-mail to many people simultaneously, and save, print, and forward e-mail to others. We can send almost any type of file in an e-mail message, including documents, pictures, and music files and with e-mail, we don't need a postage stamp!

3. **Instant messaging:-** Instant messaging is like having a real-time conversation with another person or a group of people. When we type and send an instant message, the message is immediately visible to all participants. Unlike e-mail, all participants have to be online (connected to the Internet) and in front of their computers at the same time. Communicating by means of instant messaging is called **chatting**.
4. **Pictures, music, and movies:-** If we have a digital camera, we can move our pictures from the camera to our computer. Then we can print them, create slide shows, or share them with others by e-mail or by posting them on a website. We can also listen to music on your computer, either by importing music from audio CDs or by purchasing songs from a music website. Or, we can tune in to one of the thousands of radio stations that broadcast over the Internet. If our computer comes with a DVD player, we can watch movies too.
5. **Gaming:-** Thousands of computer games in every conceivable category are available to entertain you. Get behind the wheel of a car, battle frightening creatures in a dungeon, or control civilizations and empires. Many games allow you to compete with other players around the world through the Internet. Windows includes a variety of card games, puzzle games, and strategy games.

17.4 Parts of Computer

The Association for Computing Machinery Computing Curricula 2005 defined "computing" as follows:

"In a general way, we can define computing to mean any goal-oriented activity requiring, benefiting from, or creating computers. Thus, computing includes designing and building hardware and software systems for a wide range of purposes; processing, structuring, and managing various kinds of information; doing scientific studies using computers; making computer systems behave intelligently; creating and using communications and entertainment media; finding and gathering information relevant to any particular purpose, and so on. The list is virtually endless, and the possibilities are vast."

A typical digital computer consists of:

i) A central processor unit (CPU)

ii) A memory

iii) Input Divices

The memory serves as a place to store Instructions, the coded pieces of information that direct the activities of the CPU, and Data, the coded pieces of information that are processed by the CPU. A group of logically related instructions stored in memory is referred to as a Program. The CPU "reads" each instruction from memory in a logically determined sequence, and uses it to initiate processing actions. If the program sequence is coherent and logical, processing the program will produce intelligible and useful results.

The memory is also used to store the data to be manipulated, as well as the instructions that direct that manipulation. The program must be organized such that the CPU does not read a non-instruction word when it expects to see an instruction. The CPU can rapidly access any data stored in memory; but often the memory is not large enough to store the entire data bank required for a particular application. The problem can be resolved by providing the computer with one or more Input Ports. The CPU can address these ports and input the data contained there. The addition of input ports enables the computer to receive information from external equipment (such as a paper tape reader or floppy disk) at high rates of speed and in large volumes.

A computer also requires one or more output Ports that permit the CPU to communicate the result of its processing to the outside world. The output may go to a display, for use by a human operator, to a peripheral device that produces "hardcopy," such as a line-printer, to a peripheral storage device, such as a floppy disk unit, or the output may constitute process control signals that direct the operations of another system, such as an automated assembly line. Like input ports, output ports are addressable. The input and output ports together permit the processor to communicate with the outside the world.
The CPU unifies the system. It controls the functions performed by the other components. The CPU must be able to fetch instructions from memory, decode their binary contents and execute them. It must also be able to reference memory and 1/0 ports as necessary in the execution of instructions. In addition, the CPU should be able to recognize and respond to certain external control signals, such as INTERRUPT and WAIT requests. The functional units within a CPU that enable it to perform these functions are described below.

The architecture of a CPU

A typical central processor unit (CPU) consists of the following interconnected functional units:

1. Registers
2. Arithmetic/Logic Unit (ALU)
3. Control Circuitry

Registers:- Registers are temporary storage units within the CPU. Some registers, such as the program counter and instruction register, have dedicated uses. Other registers, such as the accumulator, are for more general purpose use.

Arithmetic/Logic Unit (ALU):- All processors contain an arithmetic/logic unit, which is often referred to simply as the ALU. The ALU, as its name implies, is that portion of the CPU hardware which performs the arithmetic and logical operations on the binary data.

The ALU must contain an Adder which is capable of combining the contents of two registers in accordance with the logic of binary arithmetic. This provision permits the processor to perform arithmetic manipulations on the data it obtains from memory and from its other inputs.

Using only the basic adder a capable programmer can write routines which will subtract, multiply and divide, giving the machine complete arithmetic capabilities. In practice, however, most ALUs provide other built-in functions, including hardware subtraction, Boolean logic operations, and shift capabilities

The ALU contains Flag Bits which specify certain conditions that arise in the course of arithmetic and logical manipulations. Flags typically include Carry, Zero, Sign, and Parity. It is possible to program jumps which are conditionally dependent on the status of one or more flags. Thus, for example, the program may be designed to jump to a special routine if the carry bit is set following an addition instruction

Control Circuitry:- The control circuitry is the primary functional unit within a CPU. Using clock inputs, the control circuitry maintains the proper sequence of events required for any processing task After an instruction is fetched and decoded, the control circuitry issues the appropriate signals (to units both internal and external to the CPU) for initiating the proper processing action. Often the control

circuitry will be capable of responding to external signals, such as an interrupt or wait request An Interrupt request will cause the control circuitry to temporarily interrupt main program execution, jump to a special routine to service the interrupting device, then automatically return to the main program. A Wait request is often issued by a memory or 1/0 element that operates slower than the CPU. The control circuitry will idle the CPU until the memory or 1/0 port is ready with the data.

17.5 Computer operations

There are certain operations that are basic to almost any computer. A sound understanding of these basic operations is a necessary prerequisite to examining the specific operations of a particular computer.

- **Timing:** The activities of the central processor are cyclical. The processor fetches an instruction, performs the operations required fetches the next instruction, and so on. This orderly sequence of events requires precise timing, and the CPU therefore requires a free running oscillator clock which furnishes the reference for all processor actions. The combined fetch and execution of a single instruction is referred to as an Instruction Cycle. The portion of a cycle identified with a clearly defined activity IS called a State. And the inter vat between pulses of the timing oscillator is referred to as a Clock Period. As a general rule, one or more clock periods are necessary for the completion of a state, and there are several states in a cycle.
- **Instruction Fetch:** The first state(s) of any instruction cycle will be dedicated to fetching the next instruction. The CPU issues a read signal and the contents of the program counter are sent to memory, which responds by returning the next instruction word. The first byte of the instruction is placed in the instruction register. If the instruction consists of more than one byte, additional states are required to fetch each byte of the instruction. When the entire instruction is present in the CPU, the program counter is incremented (in preparation for the next instruction fetch) and the instruction is decoded. The operation specified in the instruction will be executed in the remaining states of the instruction cycle. The instruction may call for a memory read or write, an input or output and/or an internal

CPU operation, such as a register to register transfer or an add registers operation.

- **Memory Read:** An instruction fetch is merely a special memory read operation that brings the instruction to the CPU's instruction register. The instruction fetched may then call for data to be read from memory into the CPU. The CPU again issues a read signal and sends the proper memory address; memory responds by returning the requested word. The data received is placed in the accumulator or one of the other general purposes registers (not the instruction register).
- **Memory Write:** A memory write operation is similar to a read except for the direction of data flow. The CPU issues a write signal, sends the proper memory address, then sends the data word to be written into the addressed memory location.
- **Wait (memory synchronization):** As previously stated, the activities of the processor are timed by a master clock oscillator. The clock period determines the timing of all processing activity.

  The speed of the processing cycle, however, is limited by the memory's Access Time. Once the processor has sent a read address to memory, it cannot proceed until the memory has had time to respond. Most memories are capable of responding much faster than the processing cycle requires. A few, however, cannot supply the addressed byte within the minimum time established by the processor's clock.

  Therefore a processor should contain a synchronization provision, which permits the memory to request a Wait state. When the memory receives a read or write enable signal, it places a request signal on the processor's READY line, causing the CPU to idle temporarily. After the memory has had time to respond, it frees the processor's READY line, and the instruction cycle proceeds
- **Input/Output:** Input and Output operations are similar to memory read and write operations with the exception that a peripheral 1/0 device is addressed instead of a memory location. The CPU issues the appropriate input or output control signal, sends the proper device address and either receives

the data being input or sends the data to be output. Data can be input/output in either parallel or serial form. All data within a digital computer is represented in binary coded form. A binary data word consists of a group 5 of bits; each bit is either a one or a zero. Parallel 1/0 consists of transferring all bits in the word at the same time, one bit per line. Serial 1/0 consists of transferring one bit at a time on a single line. Naturally serial 1/0 is much slower, but it requires considerably less hardware than does parallel 1/0.

- **Interrupts:** Interrupt provisions are included on many central processors, as a means of improving the processor's efficiency. Consider the case of a computer that is processing a large volume of data, portions of which are to be output to a printer. The CPU can output a byte of data within a single machine cycle but it may take the printer the equivalent of many machine cycles to actually print the character specified by the data byte. The CPU could then remain idle waiting until the printer can accept the next data byte. If an interrupt capability is implemented on the computer, the CPU can output a data byte then return to data processing. When the printer is ready to accept the next data byte, it can request an interrupt. When the CPU acknowledges the interrupt, it suspends main program execution and automatically branches to a routine that will output the next data byte. After the byte is output, the CPU continues with main program execution. Note that this is, in principle, quite similar to a subroutine call, except that the jump is initiated externally rather than by the program.

  More complex interrupt structures are possible, in which several interrupting devices share the same processor but have different priority levels. Interruptive processing is an important feature that enables maximum utilization of a processor's capacity for high system throughput.

- **Hold:** Another important feature that improves the throughput of a processor is the Hold. The hold provision enables Direct Memory Access (DMA) operations.

  In ordinary input and output operations, the processor itself supervises the entire data transfer. Information to be placed in memory is transferred from

the input device to the processor, and then from the processor to the designated memory location. In similar fashion, information that goes from memory to output devices goes by way of the processor.

Some peripheral devices, however, are capable of transferring information to and from memory much faster than the processor itself can accomplish the transfer. If any appreciable quantity of data must be transferred to or from such a device, then system throughput will be increased by having the device accomplish the transfer directly. The processor must temporarily suspend its operation during such a transfer, to prevent conflicts that would arise if processor and peripheral device attempted to access memory simultaneously. It is for this reason that a hold provision is included on some processors.

17.6 Computer memory

In computing, memory refers to the physical devices used to store programs (sequences of instructions) or data (e.g. program state information) on a temporary or permanent basis for use in a computer or other digital electronic device. The term primary memory is used for the information in physical systems which function at high-speed (i.e. RAM), as a distinction from secondary memory, which are physical devices for program and data storage which are slow to access but offer higher memory capacity. Primary memory stored on secondary memory is called "virtual memory". An archaic synonym for memory is store. The term "memory", meaning primary memory is often associated with addressable semiconductor memory, i.e. integrated circuits consisting of silicon-based transistors, used for example as primary memory but also other purposes in computers and other digital electronic devices. There are two main types of semiconductor memory: volatile and non-volatile. Examples of non-volatile memory are flash memory (sometimes used as secondary, sometimes primary computer memory) and ROM/PROM/EPROM/EEPROM memory (used for firmware such as boot programs). Examples of volatile memory are primary memory (typically dynamic RAM, DRAM), and fast CPU cache memory (typically static RAM, SRAM, which is fast but energy-consuming and offer lower memory capacity per area unit than DRAM).

Most semiconductor memory is organized into memory cells or bistable flip-flops, each storing one bit (0 or 1). Flash memory organization includes both one bit per memory cell and multiple bits per cell (called MLC, Multiple Level Cell). The memory cells are grouped into words of fixed word length, for example 1, 2, 4, 8, 16, 32, 64 or 128 bit. Each word can be accessed by a binary address of N bit, making it possible to store 2 raised by N words in the memory. This implies that processor registers normally are not considered as memory, since they only store one word and do not include an addressing mechanism.

Memory is primarily of three types:

- Cache Memory
- Primary Memory/Main Memory
- Secondary Memory

Cache Memory:- Cache memory is a very high speed semiconductor memory, which can speed up CPU. It acts as a buffer between the CPU and main memory.

It is used to hold those parts of data and program which are most frequently used by CPU. The parts of data and programs are transferred from disk to cache memory by operating system, from where CPU can access them.

Advantage of the Momery

1. Cache memory is faster than main memory.
2. It consumes less access time as compared to main memory.
3. It stores the program that can be executed within a short period of time.
4. It stores data for temporary use.

Disadvantage of cache momery:

1. Cache memory has limited capacity.
2. It is very expensive.

Mother board

Primary Memory (Main Memory):- Primary memory holds only those data and instructions on which computer is currently working. It has limited capacity and data gets lost when power is switched off.

It is generally made up of semiconductor device. These memories are not as fast as registers. The data and instructions required to be processed earlier reside in main memory. It is divided into two subcategories RAM and ROM.

Characteristic of Main Memory

1. These are semiconductor memories.
2. It is known as main memory.
3. Usually volatile memory.
4. Data is lost in case power is switched off.
5. It is working memory of the computer.
6. Faster than secondary memories.
7. A computer cannot run without primary memory.

RAM andam Acess Memory)

Secondary Memory

This type of memory is also known as external memory or non-volatile. It is slower than main memory. These are used for storing Data/Information permanently.

CPU directly does not access these memories, instead they are accessed via input-output routines. Contents of secondary memories are first transferred to main memory and then CPU can access it. For example, disk, CD-ROM, DVD, etc.

Characteristics of Secondary Memory

1. These are magnetic and optical memories.
2. It is known as backup memory.
3. It is non-volatile memory.
4. Data is permanently stored even if power is switched off.
5. It is used for storage of the data in the computer.
6. Computer may run without secondary memory.
7. Slower than primary memories.

Hard Disk

17.7 Input/ Output devices

In computing, input/output or I/O (or informally, io or IO) is the communication between an information processing system and the outside world, possibly a human or another information processing system. Inputs are the signals or data received by the system, and outputs are the signals or data sent from the system. The term can also be used as part of an action; to "perform I/O" is to perform an input or output operation. I/O devices are used by a person (or other system) to communicate with a computer. For instance, a keyboard or a mouse may be an input device for a computer, while monitors and printers are considered output devices for a computer. Devices for communication between computers, such as modems and network cards, typically serve for both input and output.

Note that the designation of a device as either input or output depends on the perspective. Mouse and keyboards take as input physical movement that the human user outputs and convert it into signals that a computer can understand. The output from these devices is input for the computer. Similarly, printers and monitors take as input signals that a computer outputs. They then convert these signals into representations that human users can see or read. For a human user the process of reading or seeing these representations is receiving input. These interactions between computers and humans is studied in a field called human–computer interaction.

In computer architecture, the combination of the CPU and main memory (i.e. memory that the CPU can read and write to directly, with individual instructions) is considered the brain of a computer, and from that point of view any transfer of information from or to that combination, for example to or from a disk drive, is considered I/O. The CPU and its supporting circuitry may provide memory-mapped I/O that is used in low-level computer programming, such as the implementation of device drivers, or may provide access to I/O channels. An I/O algorithm is one designed to exploit locality and perform efficiently when data reside on secondary storage, such as a disk drive.

Variety of input devices used for computer-

1. **Keyboard:-** The computer keyboard is used to enter text information into the computer, as when you type the contents of a report. The keyboard can also be used to type commands directing the computer to perform certain actions. Commands are typically chosen from an on-screen menu using a mouse, but there are often keyboard shortcuts for giving these same **commands.**

Keyboard

In addition to the keys of the main keyboard (used for typing text), keyboards usually also have a numeric keypad (for entering numerical data efficiently), a bank of editing keys (used in text editing operations), and a row of function keys along the top (to easily invoke certain program functions). Laptop computers, which don't have room for large keyboards, often include a "fn" key so that other keys can perform double duty (such as having a numeric keypad function embedded within the main keyboard keys).

Improper use or positioning of a keyboard can lead to repetitive-stress injuries. Some ergonomic keyboards are designed with angled arrangements of keys and with built-in wrist rests that can minimize your risk of RSIs. Most keyboards attach to the PC via a PS/2 connector or USB port (newer). Older Macintosh computers used an ABD connector, but for several years now all Mac keyboards have connected using USB.

2. **Pointing Devices**:- The graphical user interfaces (GUIs) in use today require some kind of device for positioning the on-screen cursor. Typical pointing devices are: mouse, trackball, touch pad, trackpoint, graphics tablet, joystick, and touch screen. Pointing devices, such as a mouse, connected to the PC via aserial ports (old), PS/2 mouse port (newer), or USB port (newest). Older Macs used ADB to connect their mice, but all recent Macs use USB (usually to a USB port right on the USB keyboard).
3. **Mouse:-** The mouse pointing device sits on your work surface and is moved with your hand. In older mice, a ball in the bottom of the mouse rolls on the surface as you move the mouse, and internal rollers sense the ball movement and transmit the information to the computer via the cord of the mouse.

Mouse

The newer optical mouse does not use a rolling ball, but instead uses a light and a small optical sensor to detect the motion of the mouse by tracking a tiny image of the desk surface. Optical mice avoid the problem of a dirty mouse ball, which causes regular mice to roll unsmoothly if the mouse ball and internal rollers are not cleaned frequently.

A cordless or wireless mouse communicates with the computer via radio waves (often using BlueTooth hardware and protocol) so that a cord is not needed (but such mice need internal batteries).

A mouse also includes one or more buttons (and possibly a scroll wheel) to allow users to interact with the GUI. The traditional PC mouse has two buttons, while the traditional Macintosh mouse has one button. On either type of computer you can also use mice with three or more buttons and a small scroll wheel (which can also usually be clicked like a button)

wirless Mouse

4. **Touch pad:-** Most laptop computers today have a touch pad pointing device. You move the on-screen cursor by sliding your finger along the

surface of the touch pad. The buttons are located below the pad, but most touch pads allow you to perform “mouse clicks” by tapping on the pad itself.

Touch pacl

Touch pads have the advantage over mice that they take up much less room to use. They have the advantage over trackballs (which were used on early laptops) that there are no moving parts to get dirty and result in jumpy cursor control.

5. **Trackpoint:-** Some sub-notebook computers (such as the IBM ThinkPad), which lack room for even a touch pad, incorporate atrackpoint, a small rubber projection embedded between the keys of the keyboard. The trackpoint acts like a little joystick that can be used to control the position of the on-screen cursor.

Track pont

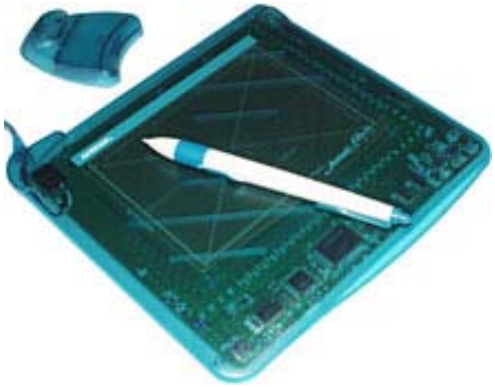
6. **Trackball:-** The trackball is sort of like an upside-down mouse, with the ball located on top. You use your fingers to roll the trackball, and internal rollers (similar to what’s inside a mouse) sense the motion which is transmitted to the computer. Trackballs have the advantage over mice in that the body of the trackball remains stationary on your

desk, so you don't need as much room to use the trackball. Early laptop computers often used trackballs (before superior touch pads came along).

Trackballs have traditionally had the same problem as mice: dirty rollers can make their cursor control jumpy and unsmooth. But there are modern optical trackballs that don't have this problem because their designs eliminate the rollers.

Track ball

7. **Joysticks:-** Joysticks and other game controllers can also be connected to a computer as pointing devices. They are generally used for playing games, and not for controlling the on-screen cursor in productivity software.
8. **Touch screen:-** Some computers, especially small hand-held PDAs, have touch sensitive display screens. The user can make choices and press button images on the screen. You often use a stylus, which you hold like a pen, to "write" on the surface of a small touch screen.
9. **Graphics tablet:-** A graphics tablet consists of an electronic writing area and a special "pen" that works with it. Graphics tablets allows artists to create graphical images with motions and actions similar to using more traditional drawing tools. The pen of the graphics tablet is pressure sensitive, so pressing harder or softer can result in brush strokes of different width (in an appropriate graphics program).



Graphics Tablet

10. **Scanners:-** A scanner is a device that images a printed page or graphic by digitizing it, producing an image made of tiny pixels of different brightness and color values which are represented numerically and sent to the computer. Scanners scan graphics, but they can also scan pages of text which are then run through OCR (Optical Character Recognition) software that identifies the individual letter shapes and creates a text file of the page's contents.
11. **Microphone**:- A microphone can be attached to a computer to record sound (usually through a sound card input or circuitry built into the motherboard). The sound is digitized—turned into numbers that represent the original analog sound waves—and stored in the computer to later processing and playback.
12. **MIDI Devices**:- MIDI (Musical Instrument Digital Interface) is a system designed to transmit information between electronic musical instruments. A MIDI musical keyboard can be attached to a computer and allow a performer to play music that is captured by the computer system as a sequence of notes with the associated timing (instead of recording digitized sound waves).

Variety of output devices used for computer-

CRT Monitor:- The traditional output device of a personal computer has been the CRT (Cathode Ray Tube) monitor. Just like a television set (an older one, anyway) the CRT monitor contains a large cathode ray tube that uses an electron beam of varying strength to "paint" a picture onto the color phosphorescent dots on the inside of the screen. CRT monitors are heavy and use more electrical power than flat panel displays, but they are preferred by some graphic artists for their accurate color rendition, and preferred by some gamers for faster response to rapidly changing graphics.

Monitor

Monitor screen size is measured diagonally across the screen, in inches. Not all of the screen area may be usable for image display, so the viewable area is also specified. The resolutionof the monitor is the maximum number of pixels it can display horizontally and vertically (such as 800 x 600, or 1024 x 768, or 1600 x 1200). Most monitors can display several resolutions below its maximum setting. Pixels (short for picture elements) are the small dots that make of the image displayed on the screen. The spacing of the screen's tiny phosphor dots is called the dot pitch (dp), typically 0.28 or 0.26 (measured in millimeters). A screen with a smaller dot pitch produces sharper images.

Your computer must produce a video signal that a monitor can display. This may be handled by circuitry on the motherboard, but is usually handled by

a video card in one of the computer's expansion slots; often the slot is a special one dedicated to video use, such as an AGP slot (Accelerated Graphics Port). Video cards are also called video display adapters, and graphics cards. Many video cards contain separate processors and dedicated video memory for generating complex graphics quickly without burdening the CPU. These accelerated graphics cards are loved by gamers.

1. **Flat Panel Monitor:-** A flat panel display usually uses an LCD (Liquid Crystal Display) screen to display output from the computer. The LCD consists of several thin layers that polarize the light passing through them. The polarization of one layer, containing long thin molecules called liquid crystals, can be controlled electronically at each pixel, blocking varying amounts of the light to make a pixel lighter or darker. Other types of flat panel technology exist (such as plasma displays) but LCDs are most commonly used in computers, especially laptops.

Flat Panel Monitor

Older LCDs had slow response times and low contrast, but active matrix LCD screens have a transparent thin film transistor (TFT) controlling each pixel, so response, contrast, and viewing angle are much improved.

Flat panel displays are much lighter and less bulky than CRT monitors, and they consume much less power. They have been more expensive than CRTs in the past, but the price gap is narrowing. You will see many more flat panels in the future.

As with CRTs, the display size of a flat panel is expressed in inches, and the resolution is the number of pixels horizontally and vertically on the display.

2. **Ink Jet Printer:-** For hardcopy (printed) output, you need some kind of printer attached to your computer (or available over a network). The most common type of printer for home systems is the color ink jet printer. These printers form the image on the page by spraying tiny droplets of ink from the print head. The printer needs several colors of ink (cyan, yellow, magenta, and black) to make color images. Some photo-quality ink jet printers have more colors of ink.

Ink Jet Printer

Ink jet printers are inexpensive, but the cost of consumables (ink cartridges and special paper) make them costly to operate in the long run for many purposes.

3. **Laser Printer:-** A laser printer produces good quality images by the same technology that photocopiers use. A drum coated with photosensitive material is charged, then an image is written onto it by a laser (or LEDs) which makes those areas lose the charge. The drum then rolls through toner (tiny plastic particles of pigment) that are attracted to the charged areas of the drum. The toner is then deposited onto the paper, and then fused into the paper with heat.

   Most laser printers are monochrome (one color only, usually black), but more expensive laser printers with multiple color toner cartridges can produce color output.

   Laser printers are faster than ink jet printers. Their speed is rated in pages per minute (ppm). Laser printers are more expensive than ink jets, but they are cheaper to run in the long term if you just need good quality black & white pages.

Laser Printer

4. **Other Printers:-** Multi-function printers are available that not only operate as a computer printer, but also include the hardware needed to be a scanner, photocopier, and FAX machine as well.

   Dot matrix printers use small electromagnetically activated pins in the print head, and an inked ribbon, to produce images by impact. These printers are slow and noisy, and are not commonly used for personal computers anymore (but they can print multi-layer forms, which neither ink jet or laser printers can).

5. **Sound Output:-** Computers also produce sound output, ranging from simple beeps alerting the user, to impressive game sound effects, to concert quality music. The circuitry to produce sound may be included on the motherboard, but high quality audio output from a PC usually requires a sound card in one of the expansion slots, connected to a set of good quality external speakers or headphones.

   Multimedia is a term describing computer output that includes sound, text, graphics, movies, and animation. A sound card is an example of a multimedia output device (as is a monitor that can display graphics).

17.8 Computer languages

A programming language is an artificial language designed to communicate instructions to a machine, particularly a computer. Programming languages can be used to create programs that control the behavior of a machine and/or to express algorithms.

The earliest programming languages preceded the invention of the computer, and were used to direct the behavior of machines such as Jacquard looms and player pianos. Thousands of different programming languages have been created, mainly

in the computer field, and still many are being created every year. Many programming languages require computation to be specified in an imperative form (i.e., as a sequence of operations to perform), while other languages utilize other forms of program specification such as the declarative form (i.e., the desired result is specified, not how to achieve it).

```
1   // class declaration
2   public class ProgrammingExample {
3
4       // method declaration
5       public void sayHello() {
6
7           // method output
8           System.out.println("Hello World!");
9       }
10  }
```

(Programming Language)

The description of a programming language is usually split into the two components of syntax (form) and semantics (meaning). Some languages are defined by a specification document (for example, the C programming language is specified by an ISO Standard), while other languages (such as Perl) have a dominant implementation that is treated as a reference.

17.9 Review Questions

1. Define CPU and uses of it.
2. What are the uses of computer?
3. Describe the type of computer system withits architecture.

17.10 References

1. Computer Architecture & Organization (SIE) (Schaum\'s Outline Series) 2nd Edition by Raj Kamal, Nicholas Carter
2. Schaum's Outline of Principles of Computer Science by Carl Reynolds, Paul Tymann
3. http://www.unm.edu/~tbeach/terms/inputoutput.html

UNIT–18 : Operating System and Data Processing

Structure of Unit

18.1 Objective

At the end of the unit learner will be able to

- Understand the concept of Operating System.
- Understand the role of Operating System.
- Come across with the programming principles.
- Learn the concept of Data Processing.
- Will be able to design the program in form of flow charts.
- Can develop the algorithm of computer program.

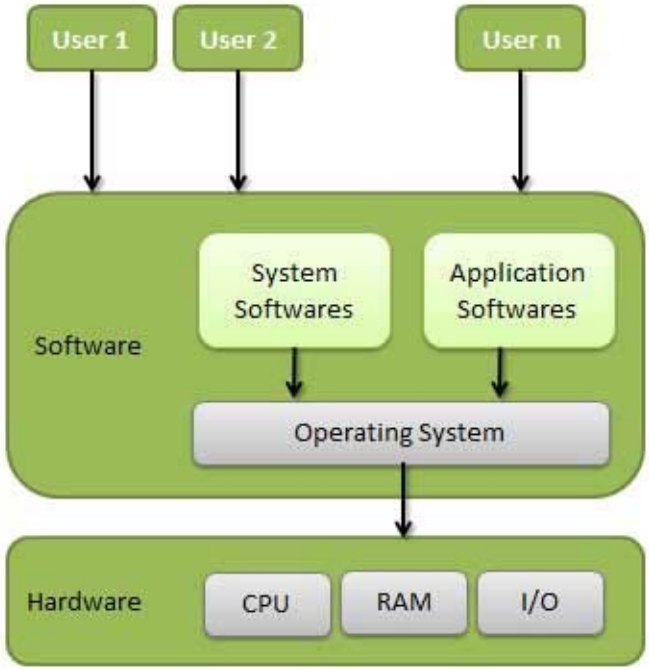
18.2 Introduction

This unit deals with the introduction and concept of operating systems. Unit details the applications and role of operating systems. Unit mentions the examples and types of operating system like UNIX and Windows. The afterward part of the unit

explain the data processing and the basic principles behind a good program. Unit also highlights the importance of algorithms and its design. In the last there is a brief introduction of flow chart of a computer program.

18.3 Operating System

An OS is a program which acts as an interface between computer system users and the computer hardware. It provides a user-friendly environment in which a user may easily develop and execute programs. Otherwise, hardware knowledge would be mandatory for computer programming. So, it can be said that an OS hides the complexity of hardware from uninterested users.



Computer System

18.4 Functions of Operating System and its Types

Following are some of important functions of an operating System.

- Memory Management
- Processor Management
- Device Management
- File Management

- Security
- Control over system performance
- Job accounting
- Coordination between other software and users

➢ **Memory Management**

Memory management refers to management of Primary Memory or Main Memory. Main memory is a large array of words or bytes where each word or byte has its own address.

Main memory provides a fast storage that can be access directly by the CPU. So for a program to be executed, it must in the main memory. Operating System does the following activities for memory management.

- Keeps tracks of primary memory i.e. what part of it are in use by whom, what part are not in use.
- In multiprogramming, OS decides which process will get memory when and how much.
- Allocates the memory when the process requests it to do so.
- De-allocates the memory when the process no longer needs it or has been terminated.

➢ **Processor Management**

In multiprogramming environment, OS decides which process gets the processor when and how much time. This function is called process scheduling. Operating System does the following activities for processor management.

- Keeps tracks of processor and status of process. Program responsible for this task is known as traffic controller.
- Allocates the processor (CPU) to a process.
- De-allocates processor when processor is no longer required.

➢ **Device Management**

OS manages device communication via their respective drivers. Operating System does the following activities for device management.

- Keeps tracks of all devices. Program responsible for this task is known as the I/O controller.
- Decides which process gets the device when and for how much time.
- Allocates the device in the efficient way.
- De-allocates devices.

➢ **File Management**

A file system is normally organized into directories for easy navigation and usage. These directories may contain files and other directions. Operating System does the following activities for file management.

- Keeps track of information, location, uses, status etc. The collective facilities are often known as file system.
- Decides who gets the resources.
- Allocates the resources.
- De-allocates the resources.
- Other Important Activities

Following are some of the important activities that Operating System does.

- **Security** -- By means of password and similar other techniques, preventing unauthorized access to programs and data.
- **Control over system performance** -- Recording delays between request for a service and response from the system.
- **Job accounting** -- Keeping track of time and resources used by various jobs and users.
- **Error detecting aids** -- Production of dumps, traces, error messages and other debugging and error detecting aids.

- **Coordination between other softwares and users** -- Coordination and assignment of compilers, interpreters, assemblers and other software to the various users of the computer systems.

Types of Operating System

Operating systems are there from the very first computer generation. Operating systems keep evolving over the period of time. Following are few of the important types of operating system which are most commonly used.

- **Real-time**

  A real-time operating system is a multitasking operating system that aims at executing real-time applications. Real-time operating systems often use specialized scheduling algorithms so that they can achieve a deterministic nature of behavior. The main objective of real-time operating systems is their quick and predictable response to events.

- **Multi-user**

  A multi-user operating system allows multiple users to access a computer system at the same time. Time-sharing systems and Internet servers can be classified as multi-user systems as they enable multiple-user access to a computer through the sharing of time. Single-user operating systems have only one user but may allow multiple programs to run at the same time.

- **Multi-tasking vs. single-tasking**

  A multi-tasking operating system allows more than one program to be running at the same time, from the point of view of human time scales. A single-tasking system has only one running program. Multi-tasking can be of two types: pre-emptive and co-operative. In pre-emptive multitasking, the operating system slices the CPU time and dedicates one slot to each of the programs. Unix-like operating systems such as Solaris and Linux support pre-emptive multitasking. 16-bit versions of Microsoft Windows used cooperative multi-tasking. 32-bit versions of both Windows NT and Win9x, used pre-emptive multi-tasking.

- **Distributed**

  A distributed operating system manages a group of independent computers and makes them appear to be a single computer. The development of networked

computers that could be linked and communicate with each other gave rise to distributed computing. Distributed computations are carried out on more than one machine. When computers in a group work in cooperation, they make a distributed system.

- **Embedded**

Embedded operating systems are designed to be used in embedded computer systems. They are designed to operate on small machines like PDAs with less autonomy. They are able to operate with a limited number of resources. They are very compact and extremely efficient by design. Windows CE and Minix 3 are some examples of embedded operating systems.

18.5 Examples of Operating System

There are many different operating systems. Each does the same thing: they control all input, processing and output. Some important operating systems are as following:

- DOS: Disk Operating System
- Windows
- UNIX and Linux
- MacOS

18.6 Introduction to DOS

Disk Operating System - one of the first operating systems for the personal computer. When you turned the computer on all you saw was the command prompt which looked like **c:\ >**. You had to type all commands at the command prompt which might look like **c:\>wp\wp.exe**.

It was not very "user friendly"

DOS

DOS (Disk Operating System) was the first widely-installed operating system for personal computers. It is a master control program that is automatically run when you start your PC. DOS stays in the computer all the time letting you run a program and manage files. It is a single-user operating system from Microsoft for the PC. It was the first OS for the PC and is the underlying control program for Windows 3.1, 95, 98 and ME. Windows NT, 2000 and XP emulate DOS in order to support existing DOS applications. To use DOS, you must know where your programs and data are stored and how to talk to DOS.

Getting Started with DOS:

Each time you switch on the computer, the computer checks its memory and all the attached devices, to be sure that everything is working properly. The system beeps after it has made sure that all is well. The process of checking is called as POST or On Self Test and then the computer begins loading DOS into the memory. Loading DOS into memory is also called as “Booting The System”.

The sequence of events that takes place from switching on the power till the MS-DOS prompt is seen is as follows:

POST
BOOT RECORD

DOS KERNEL
DEVICE DRIVERS
COMMAND.COM
AUTOEXEC.BAT
DOS PROMPT

Important Terms:

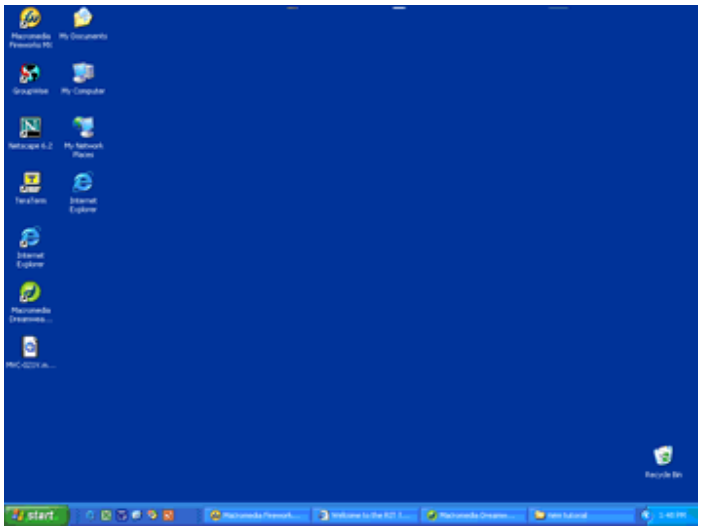
- **Program:** Programs, often called as application programs or system programs, are series of instructions written in a form understandable to computers. These instructions are stored in files and instructs the computer to perform a task accordingly.
- **File :** A file is collection of related information. Like the contents of file folder in a desk.
- **Filename:** Each file on a disk has to have a name. This name has two parts a file name and an extension.
- **Directory:** A directory on a disk is like a table of contents in a book. It contains the name of the file, size of file, date and time are stamped for files created or modified.
- **Drive Name:** A complete drive name consists of a drive letter and a colon. When issuing a command you may need to use the drive name to locate the file.
- **MS-DOS Prompt:** The DOS prompt is the means by which you enter DOS commands from the keyboard. The most common prompt is **C:>** when a prompt like this is displayed it means that DOS is ready to accept your commands and process it.
- **Command:** When you type in a MS-DOS command, you are asking the computer to perform a certain task specific to the command. For example, CHKDSK command to check the integrity of your disk.

18.7 Introduction to Windows and UNIX

In this section, a brief introduction of windows and UNIXsystems are preserted.

Windows Operating System:

Windows is a personal computer operating system from **Microsoft** that, together with some commonly used business applications such as **Microsoft Word** and **Excel**, has become a de facto "standard" for individual users in most corporations as well as in most homes. Windows contains built-in networking, which allows users to share files and applications with each other if their PCs are connected to a network. In large enterprises, Windows clients are often connected to a network of UNIX and NetWare servers. The server versions of **Windows NT** and **2000**> are gaining market share, providing a Windows-only solution for both the client and server.



Window Screen

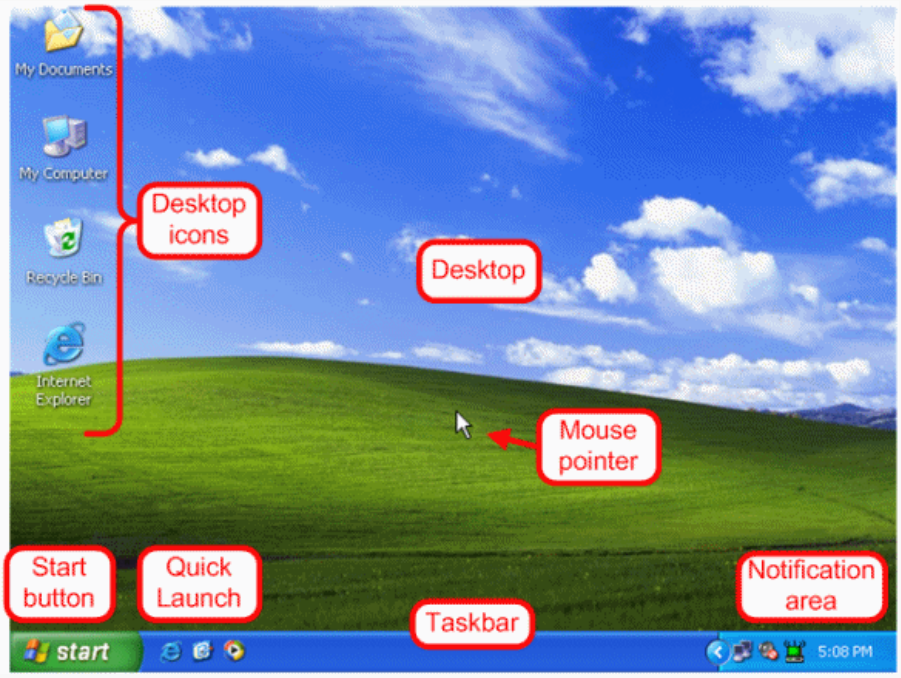
The Windows operating system, a product of Microsoft, is a **GUI** (graphical user interface) operating system. This type of "user friendly" operating system is said to have **WIMP** features:

- **W**indows
- **I**cons
- **M**enus
- **P**ointing device (mouse)

The first version of Microsoft Windows (**Microsoft Windows 1.0**) came out in November 1985. It had a graphical user interface, inspired by the user interface of the Apple computers of the time. On August 24, 1995, Microsoft launched the operating system **Microsoft Windows 95**. Windows 95 signified Microsoft's willingness to transfer some of MS-DOS's capabilities into Windows.

Basic Elements of Windows

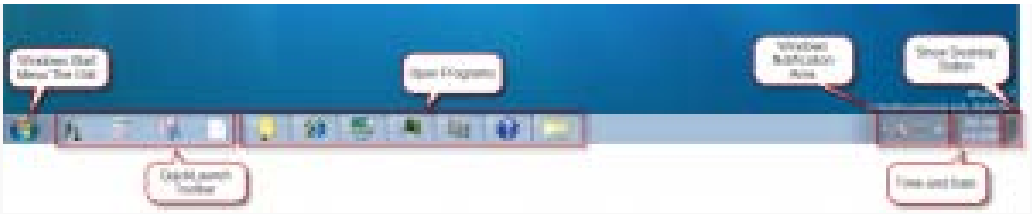
- **Desktop**



Windows Desktop

Desktop is the working area on Windows operating system where we place and arrange application and document windows to work efficiently. When you turn on a computer, the desktop is displayed first. Desktop contains icons of useful applications and shortcuts of frequently required documents. We use wallpapers on desktop background to make desktops attractive. Wallpapers are the images displayed on the desktop background.

- **Taskbar**



Windows Taskbar

A horizontal bar at the bottom of desktop is taskbar that displays the icons of opened windows, start button and system tray. Quick launch toolbar, language toolbar and some other toolbars can be enabled to display on taskbar if preferred. Usually quick launch toolbar is displayed to the left of taskbar just after the start button and language bar on the right side just before the system tray. System tray displays the icons of applications that are running in background and provides method to access them and control them.

System clock, volume control icon and so on are available on system tray.

- **My Computer**

A section of Microsoft Windows that was introduced with the release of Microsoft Windows 95 and included with all versions of Windows after that. My Computer allows the user to explore the contents of their computer drives as well as manage their computer files. Although the name has changed to Computer, the program still acts identical to the earlier My Computer.

- **My Documents**

My Documents is a folder created automatically by Windows as a convenient repository for any files you create. You can then create as many sub-folders as you like within the My Documents folder to organize your files further. My Documents is the default folder for many Windows applications to save your files.

My Documents as a central file store, Windows has gone a step further by placing other special folders including My Pictures and My Music within My Documents.

- **Start Menu**

Start Menu

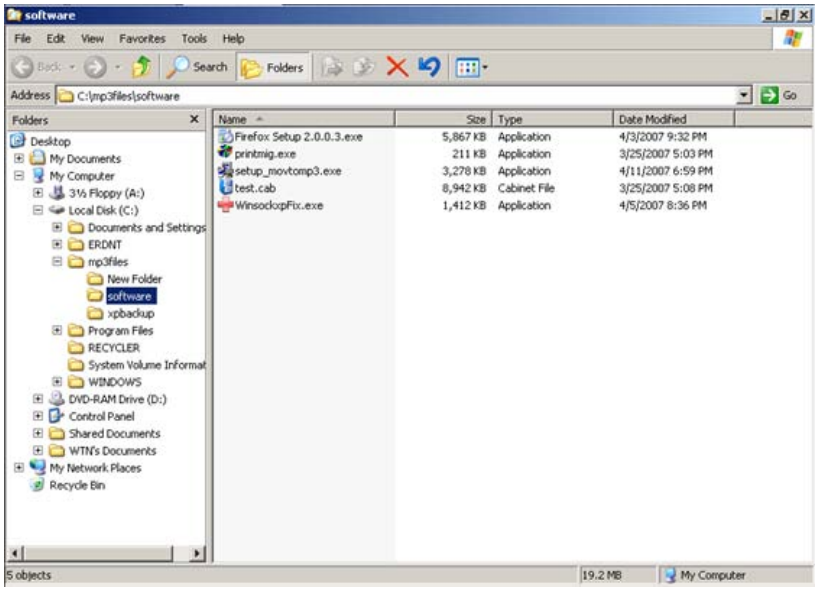
A button on the bottom left corner of your desktop on the TaskBar used to begin almost any task on your computer is Start Button. Windows 95, 98, NT and later up to Windows 7 use the Start button.

A single left-click on the Start button opens the Start menu. In the Programs section of the Start menu, you have access to many of the applications on your computer. In the Settings section of the Start Menu you can access your computer's settings, printer, TaskBar and Start Menu options. From the Start menu you can also Shut Down your computer and install programs.

If you right-click your mouse on the Start button, a local menu appears. Two items on this menu are particularly useful:

Open: clicking this item opens the Start Menu folder as a window on your desktop. The Start Menu folder contains a Programs shortcut you can double-left-click to open your Programs folder as a window on your desktop. This is an alternate method for accessing your programs and documents.

- **Windows Explorer**



Windows Explore

Windows Explorer is the operating systems File and Folder Manager. You've probably used Windows Explorer without even realizing it. Every time you open, say, your Documents folder or the photos folder on a memory card, that's an instance of Windows Explorer. The tool's fundamental purpose is to let you view, open, copy, move, and otherwise manage your files and folders. So learning how to use it is key for tasks like importing photos from the memory card, copying files to a flash drive, setting up folders to keep your data organized, and so on.

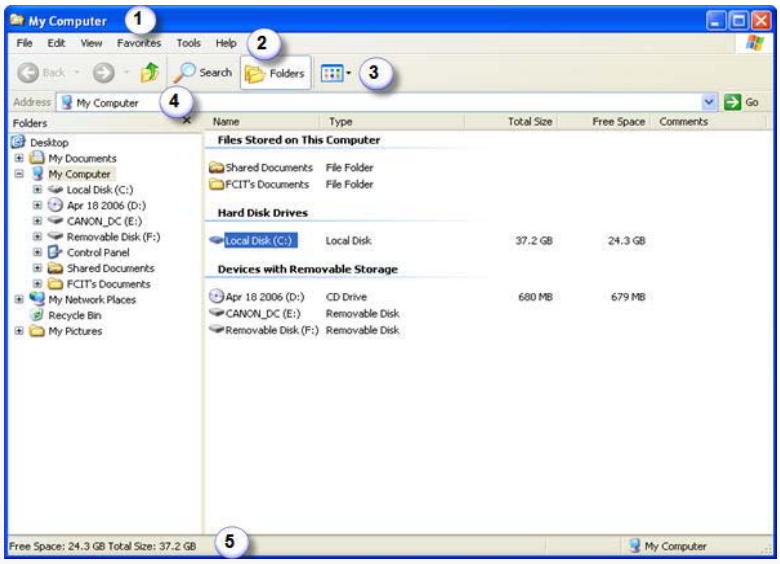
File management with Windows Explorer

In computer, we create new files everyday and most of them are stored safely for future use. Every computer naturally has thousands of files. Some are system files required for the computer system itself to operate. Some other are executable files that starts and runs an application. Some are configuration files and some user files. In this pile of files, the task of organize them efficiently and making them readily available whenever required is known as file management.

Following are some of the basic tasks in file management:

- Searching for Files

- Creating Folder Directories
- Saving Files
- Copying Files
- Moving Files
- Deleting Files



Windows Explore

1. Title bar 2. Menu Bar 3. Tool bar 4. Address bar 5. Status bar

The tool in Windows for this task is Windows Explorer. **Windows Explorer** is the file management application in Windows. Windows Explorer can be used to navigate your hard drive and display the contents of the folders and subfolders you use to organize your files on your hard drive. Windows Explorer is automatically launched any time you open a folder in Windows XP. You can also right-click on a folder and select Explore to open that folder using Windows Explorer.

The following is the standard method to launch Windows Explorer.

- Click on Start, Programs, Accessories, Windows Explorer; or right-click on the Start button and click Explore.
- Size the window for your desired viewing. You can also size each of the vertical windows within the larger one to see all the information.

Common File Management Tasks with Windows Explorer

- Selecting Files and Folders
- Dragging files and folders
- Creating a new folder
- Renaming files or folders
- Deleting Files and Folders
- File names in Windows
- Searching Files and Folders
- Copying Files and Folders
- Moving Files

UNIX OPERATING SYSTEM

The **Unix** system is a multi-user, multi tasking operating system which means that it allows a single or multiprocessor computer to simultaneously execute several programs by one or several users. It has one or several command interpreters (shell) as well as a great number of commands and many utilities (assembler, compilers for many languages, text processing, email, etc.). Furthermore, it is highly portable, which means that it is possible to implement a Unix system on almost all hardware platforms.

Currently, Unix systems have a strong foothold in professional and university environments thanks to their stability, their increased level of security and observance of standards, notably in terms of networks.

- **Types of UNIX**

There are many different versions of UNIX, although they share common similarities. The most popular varieties of UNIX are as follows:

- Sun Solaris,
- GNU/Linux, and
- MacOS X.

The UNIX Operating System

The UNIX operating system is made up of three parts; the kernel, the shell and the programs.

- **The kernel**

The kernel of UNIX is the hub of the operating system: it allocates time and memory to programs and handles the filestore and communications in response to system calls.

As an illustration of the way that the shell and the kernel work together, suppose a user types **rm myfile** (which has the effect of removing the file **myfile**). The shell searches the filestore for the file containing the program **rm**, and then requests the kernel, through system calls, to execute the program **rm** on **myfile**. When the process **rm myfile** has finished running, the shell then returns the UNIX prompt % to the user, indicating that it is waiting for further commands.

➢ The shell

The shell acts as an interface between the user and the kernel. When a user logs in, the login program checks the username and password, and then starts another program called the shell. The shell is a command line interpreter (CLI). It interprets the commands the user types in and arranges for them to be carried out. The commands are themselves programs: when they terminate, the shell gives the user another prompt (% on our systems).

The adept user can customise his/her own shell, and users can use different shells on the same machine. Staff and students in the school have the **tcsh shell** by default.

The tcsh shell has certain features to help the user inputting commands which one described as follow.

Filename Completion - By typing part of the name of a command, filename or directory and pressing the [**Tab**] key, the tcsh shell will complete the rest of the name automatically. If the shell finds more than one name beginning with those letters you have typed, it will beep, prompting you to type a few more letters before pressing the tab key again.

History - The shell keeps a list of the commands you have typed in. If you need to repeat a command, use the cursor keys to scroll up and down the list or type history for a list of previous commands.

Files and Processes

Everything in UNIX is either a file or a process.

A process is an executing program identified by a unique PID (process identifier).

A file is a collection of data. They are created by users using text editors, running compilers etc.

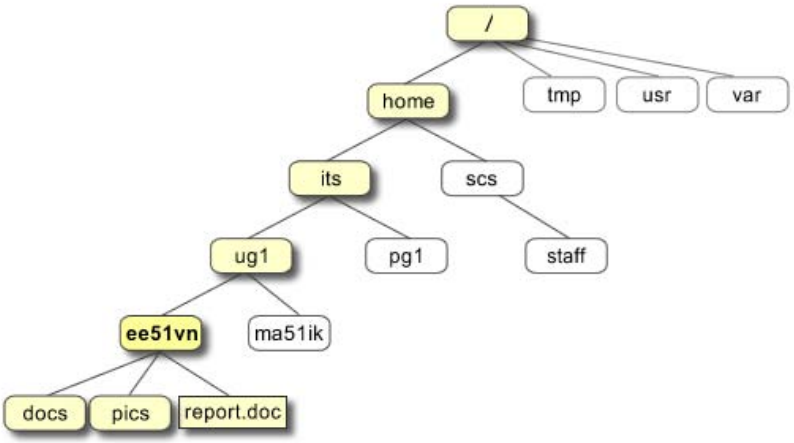
Examples of files:

- a document (report, essay etc.)
- the text of a program written in some high-level programming language

- instructions comprehensible directly to the machine and incomprehensible to a casual user, for example, a collection of binary digits (an executable or binary file);
- a directory, containing information about its contents, which may be a mixture of other directories (subdirectories) and ordinary files.

The Directory Structure

All the files are grouped together in the directory structure. The file-system is arranged in a hierarchical structure, like an inverted tree. The top of the hierarchy is traditionally called **root** (written as a slash /)

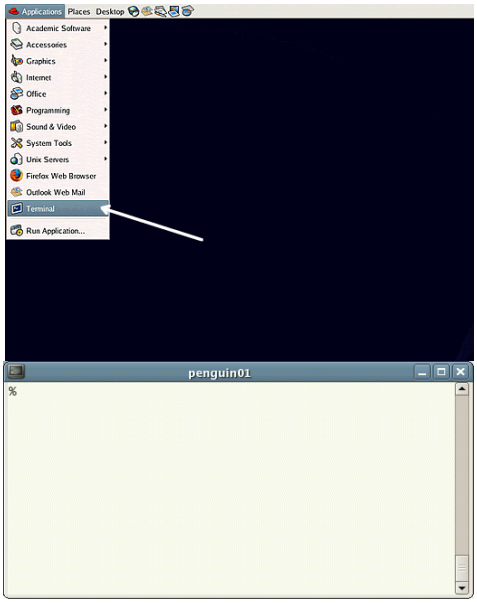


Directory Structure

In the diagram above, we see that the home directory of the undergraduate student **"ee51vn"** contains two sub-directories (**docs** and**pics**) and a file called **report.doc**. The full path to the ile **report.doc** is **"/home/its/ug1/ee51vn/report.doc"**

Starting a UNIX Terminal

To open an UNIX terminal window, click on the "Terminal" icon from Applications/Accessories menus.

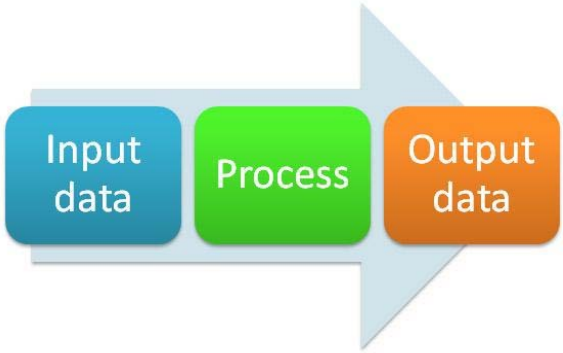


Starting a VNIX Terominal

An UNIX Terminal window will then appear with a % prompt, waiting for you to start entering commands.

18.8 Data Processing

Data processing is broadly, "the collection and manipulation of items of data to produce meaningful information." In this sense it can be considered a subset of *information processing*, "the change (processing) of information in any manner detectable by an observer."



Data Processing Functions:

Data processing may involve various processes, including:

- Validation – Ensuring that supplied data is "clean, correct and useful."
- Sorting – "arranging items in some sequence and/or in different sets."
- Summarization – reducing detail data to its main points.
- Aggregation – combining multiple pieces of data.
- Analysis – the "collection, organization, analysis, interpretation and presentation of data."
- Reporting – list detail or summary data or computed information.

Types of Data Processing:

Data processing may be categorize in the following types:

- Manual Data Processing
- Automatic Data Processing
- Electronic Data Processing

18.9 Principles of Programming

Reasons for Studying Concepts of Programming Languages:

- Increased ability to express ideas
- Improved background for choosing appropriate languages
- Increased ability to learn new languages
- Better understanding of significance of implementation
- Overall advancement of computing

Programming Domains

Scientific applications – Large number of floating point computations – Fortran

- Business applications – Produce reports, use decimal numbers and characters – COBOL
- Artificial intelligence – Symbols rather than numbers manipulated – LISP
- Systems programming – Need efficiency because of continuous use – C
- Web Software – Eclectic collection of languages: markup (e.g., XHTML), scripting (e.g.,

  PHP), general-purpose (e.g., Java)

Language Evaluation Criteria

- Readability: the ease with which programs can be read and understood
- Writability: the ease with which a language can be used to create programs
- Reliability: conformance to specifications (i.e., performs to its specifications)
- Cost: the ultimate total cost

Influences on Language Design

- Computer Architecture – Languages are developed around the prevalent computer architecture, known as the von Neumann architecture
- Programming Methodologies – New software development methodologies (e.g., object-oriented software development) led to new programming paradigms and by extension, new programming languages.

Language Categories

• Imperative – Central features are variables, assignment statements, and iteration

– Examples: C, Pascal

• Functional – Main means of making computations is by applying functions to given parameters

– Examples: LISP, Scheme

• Logic – Rule-based (rules are specified in no particular order)

– Example: Prolog

• Object-oriented – Data abstraction, inheritance, late binding

– Examples: Java, C++

• Markup – New; not a programming per se, but used to specify the layout of information in Web documents

– Examples: XHTML, XML

18.10 Algorithms

To make a computer do anything, you have to write a computer program. To write a computer program, you have to tell the computer, step by step, exactly what you want it to do. The computer then "executes" the program, following each step mechanically, to accomplish the end goal.

When you are telling the computer *what* to do, you also get to choose *how* it's going to do it. That's where **computer algorithms** come in. The algorithm is the basic technique used to get the job done.

"An **algorithm** is a sequence of unambiguous instructions for solving a problem, i.e., for obtaining a required output for any legitimate input in a finite amount of time"

Let's follow an example to help get an understanding of the algorithm concept. Let's say that you have a friend arriving at the airport, and your friend needs to get from the airport to your house. Here are four different algorithms that you might give your friend for getting to your home:

The taxi algorithm:

1. Go to the taxi stand.
2. Get in a taxi.
3. Give the driver my address.

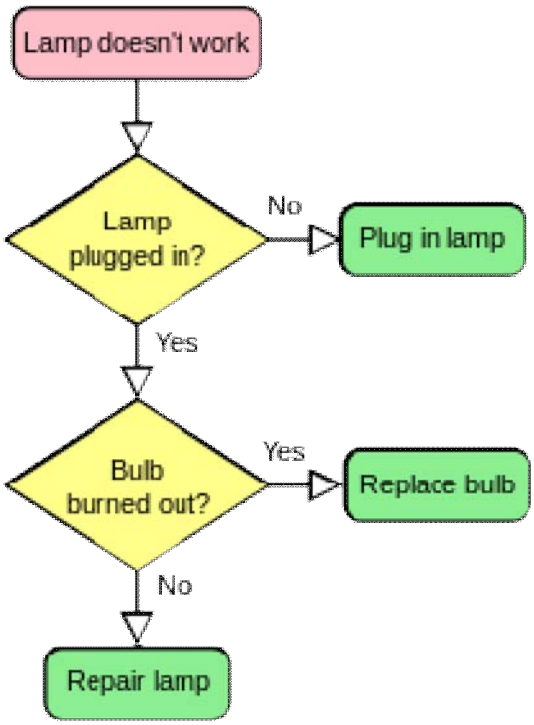
In computer programming, there are often many different ways -- algorithms -- to accomplish any given task. Each algorithm has advantages and disadvantages in

different situations. **Sorting** is one place where a lot of research has been done, because computers spend a lot of time sorting lists. Here are five different algorithms that are used in sorting:

- Binary sort
- Merge sort
- Bubble sort
- Shell sort
- Quicksort

18.11 Flowchart

A **flowchart** is a type of diagram that represents an algorithm or process, showing the steps as boxes of various kinds, and their order by connecting them with arrows. This diagrammatic representation illustrates a solution to a given problem. Process operations are represented in these boxes, and arrows; rather, they are implied by the sequencing of operations. Flowcharts are used in analyzing, designing, documenting or managing a process or program in various fields.



Flow Chart

Common Flowchart Symbols

Different flow chart symbols have different meanings. The most common flow chart symbols are:

Terminator: An oval flow chart shape indicating the start or end of the process.

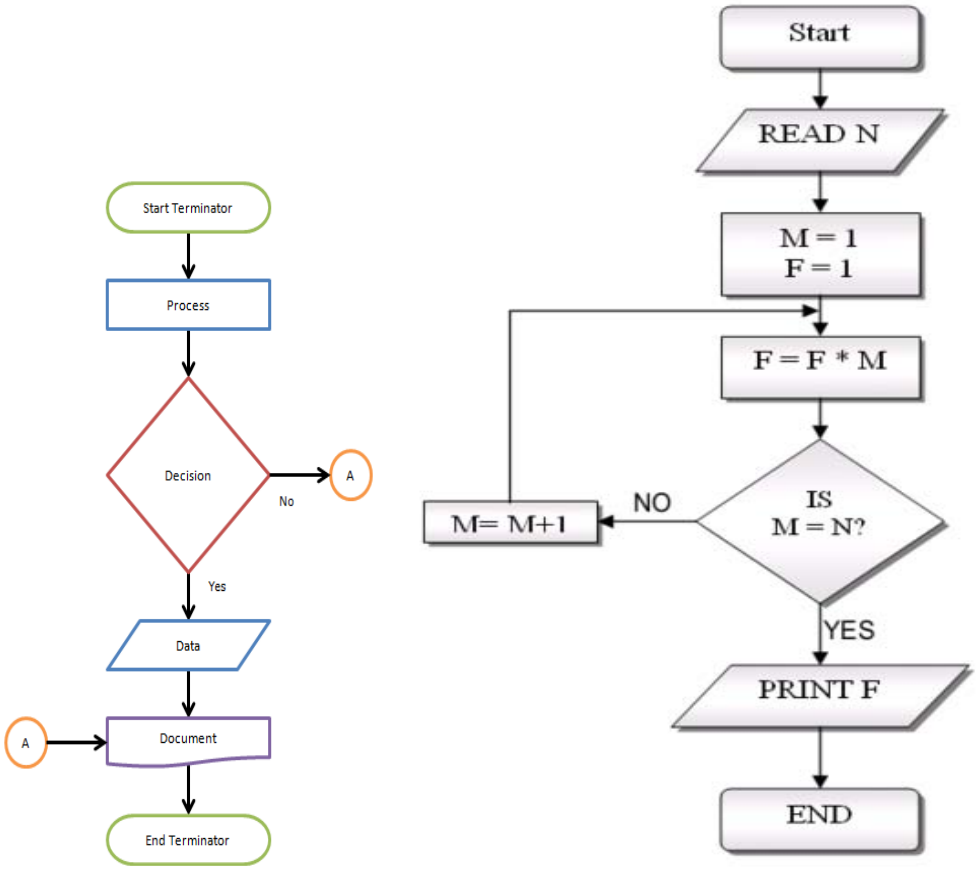
Process: A rectangular flow chart shape indicating a normal process flow step.

Decision: A diamond flow chart shape indication a branch in the process flow.

Connector: A small, labeled, circular flow chart shape used to indicate a jump in the process flow.

Data: A parallelogram that indicates data input or output (I/O) for a process.

Document: Used to indicate a document or report (see image in sample flow chart below).



A simple flowchart for computing factorial N (N!)

18.12 Summary

An Operating system is concerned with the allocation of resources and services, such as memory, processors, devices and information. The Operating System correspondingly includes programs to manage these resources, such as a traffic controller, a scheduler, memory management module, I/O programs, and a file system. DOS, UNIX and Windows are most used operating systems. Apart of OS we have learned about Data Processing concept and basic principles of programming in computers. We can use algorithm for a better solution of a problem and design principles of flow charts.

All above mentioned concepts are very useful for the chemist to use computers in their problem solutions.

18.13 Review Questions

1. What do you understand by Operating System? Explain with an example.
2. Explain the services provided by operating system.
3. What is UNIX? Define its features.
4. What are the basic elements of Windows Operating System?
5. Define Data Processing and explain its functions.
6. List the attributes of a good program.
7. Explain the use of an algorithm to solve a problem.
8. Discuss the elements of Flow Chart with an example.

18.14 References

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5. A. Silberschatz and Peter B Galvin: Operating System Principals, Wiley India Pvt. Ltd
6. Tanenbaum: Modern Operating System, Prentice Hall.
7. Horowitz and Sahani: Fundamental of Computer algorithms.

Unit -19: Computer Programming in FORTRAN/C/BASIC, Elements of the computer language. Constants and variables, Operations and Symbols Expressions, Arithmetic assignment statement, Input and output Format statement, Termination statements. Branching statements such as IF or GO TO statement

Unit Structure

19.0 Objectives

In this unit we learn about the Computer Programming in FORTRAN/C/BASIC. After studying this unit, students are able to write computer programs and run them in their computers.

19.1 Introduction

What is Programming?

A *program* is a set of step-by-step instructions that directs the computer to do the tasks you want it to do and produce the results you want.

There are at least three good reasons for learning programming:

1. Programming helps you understand computers. The computer is only a tool. If you learn how to write simple programs, you will gain more knowledge about how a computer works.

2. Writing a few simple programs increases your confidence level. Many people find great personal satisfaction in creating a set of instructions that solve a problem.

3. Learning programming lets you find out quickly whether you like programming and whether you have the analytical turn of mind programmers need. Even if you decide that programming is not for you, understanding the process certainly will increase your appreciation of what programmers and computers can do.

A set of rules that provides a way of telling a computer what operations to perform is called a programming language. There is not, however, just one programming language; there are many. In this chapter we will learn about controlling a computer through the process of programming.

What Programmers Do?

In general, the programmer's job is to convert problem solutions into instructions for the computer. That is, the programmer prepares the instructions of a computer program and runs those instructions on the computer, tests the program to see if it is working properly, and makes corrections to the program. The programmer also writes a report on the program. These activities are all done for the purpose of helping a user fill a need, such as paying employees, billing customers, or admitting students to college.

The programming activities just described could be done, perhaps, as solo activities, but a programmer typically interacts with a variety of people. For example, if a program is part of a system of several programs, the programmer coordinates with other programmers to make sure that the programs fit together well. If you were a programmer, you might also have coordination meetings with users, managers, systems analysts, and with peers who evaluate your work-just as you evaluate theirs.

19.2 Programming process

Developing a program involves steps similar to any problem-solving task. There are five main ingredients in the programming process:

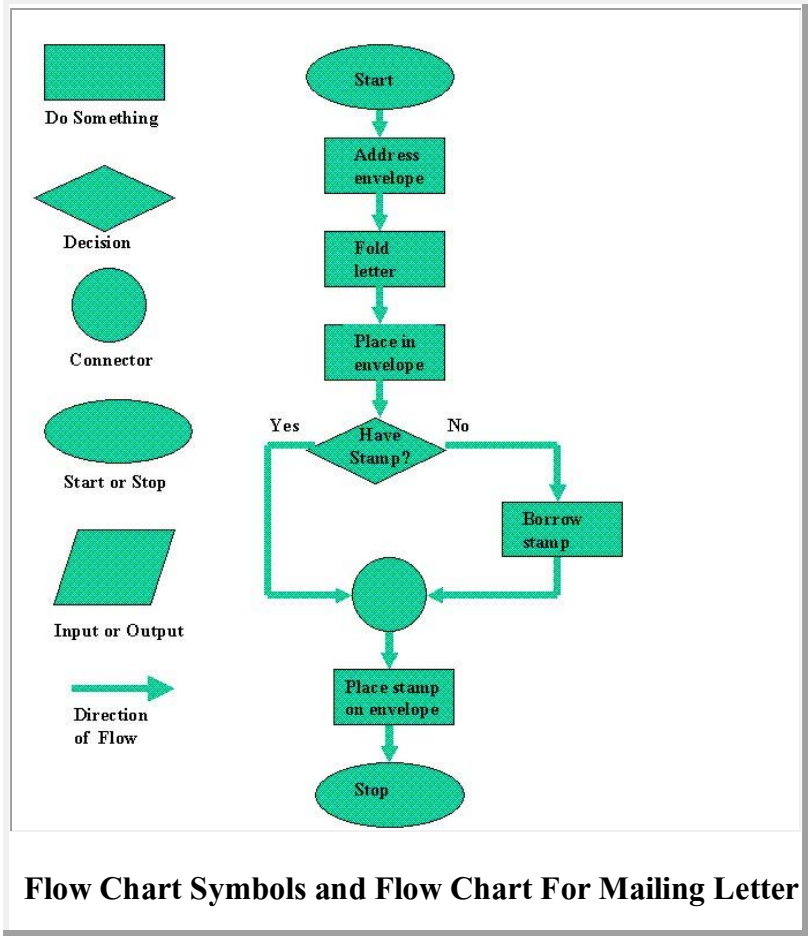
1. Defining the problem
2. Planning the solution
3. Coding the program
4. Testing the program
5. Documenting the program

Let us discuss each of these in turn.

1. **Defining the Problem**:- Suppose that, as a programmer, you are contacted because your services are needed. You meet with users from the client organization to analyze the problem, or you meet with a systems analyst who outlines the project. Specifically, the task of defining the problem consists of identifying what it is you know (input-given data), and what it is you want to obtain (output-the result). Eventually, you produce a written agreement that, among other things, specifies the kind of input, processing, and output required. This is not a simple process.

2. **Planning the Solution** :- Two common ways of planning the solution to a problem are to draw a flowchart and to write pseudocode, or possibly both. Essentially, a flowchart is a pictorial representation of a step-by-step solution to a problem. It consists of arrows representing the direction the program takes and boxes and other symbols representing actions. It is a map of what your program is going to do and how it is going to do it. The American National Standards Institute (ANSI) has developed a standard set of flowchart symbols. Figure 1 shows the symbols and how they might be used in a simple flowchart of a common everyday act-preparing a letter for mailing.

Pseudocode is an English-like nonstandard language that lets you state your solution with more precision than you can in plain English but with less precision than is required when using a formal programming language.



Flow Chart Symbols and Flow Chart For Mailing Letter

3. **Coding the Program** :-As the programmer, your next step is to code the program-that is, to express your solution in a programming language. You will translate the logic from the flowchart or pseudocode-or some other tool-to a programming language. As we have already noted, a programming language is a set of rules that provides a way of instructing the computer what operations to perform. There are many programming languages: BASIC, COBOL, Pascal, FORTRAN, and C are some examples. You may find yourself working with one or more of these. We will discuss the different types of languages in detail later in this chapter.

Although programming languages operate grammatically, somewhat like the English language, they are much more precise. To get your program to work, you have to follow exactly the rules-the syntax-of the language you are using. Of course, using the language correctly is no guarantee that your program will work, any more than speaking grammatically correct English means you know what you

are talking about. The point is that correct use of the language is the required first step. Then your coded program must be keyed, probably using a terminal or personal computer, in a form the computer can understand

4. **Testing the Program** :-Some experts insist that a well-designed program can be written correctly the first time. In fact, they assert that there are mathematical ways to prove that a program is correct. However, the imperfections of the world are still with us, so most programmers get used to the idea that their newly written programs probably have a few errors. This is a bit discouraging at first, since programmers tend to be precise, careful, detail-oriented people who take pride in their work. Still, there are many opportunities to introduce mistakes into programs, and you, just as those who have gone before you, will probably find several of them. Eventually, after coding the program, you must prepare to test it on the computer. This step involves these phases:

- **Desk-checking.** This phase, similar to proofreading, is sometimes avoided by the programmer who is looking for a shortcut and is eager to run the program on the computer once it is written. However, with careful desk-checking you may discover several errors and possibly save yourself time in the long run

- **Translating.** A translator is a program that (1) checks the syntax of your program to make sure the programming language was used correctly, giving you all the syntax-error messages, called diagnostics, and (2) then translates your program into a form the computer can understand.

- **Debugging.** A term used extensively in programming, debugging means detecting, locating, and correcting bugs (mistakes), usually by running the program. These bugs are logic errors, such as telling a computer to repeat an operation but not telling it how to stop repeating. In this phase you run the program using test data that you devise. You must plan the test data carefully to make sure you test every part of the program

5. **Documenting the Program** :-Documenting is an ongoing, necessary process, although, as many programmers are, you may be eager to pursue more exciting computer-centered activities. Documentation is a written detailed description of the programming cycle and specific facts about the program.

The wise programmer continues to document the program throughout its design, development, and testing. Documentation is needed to supplement human memory and to help organize program planning.

19.2 Levels of Language

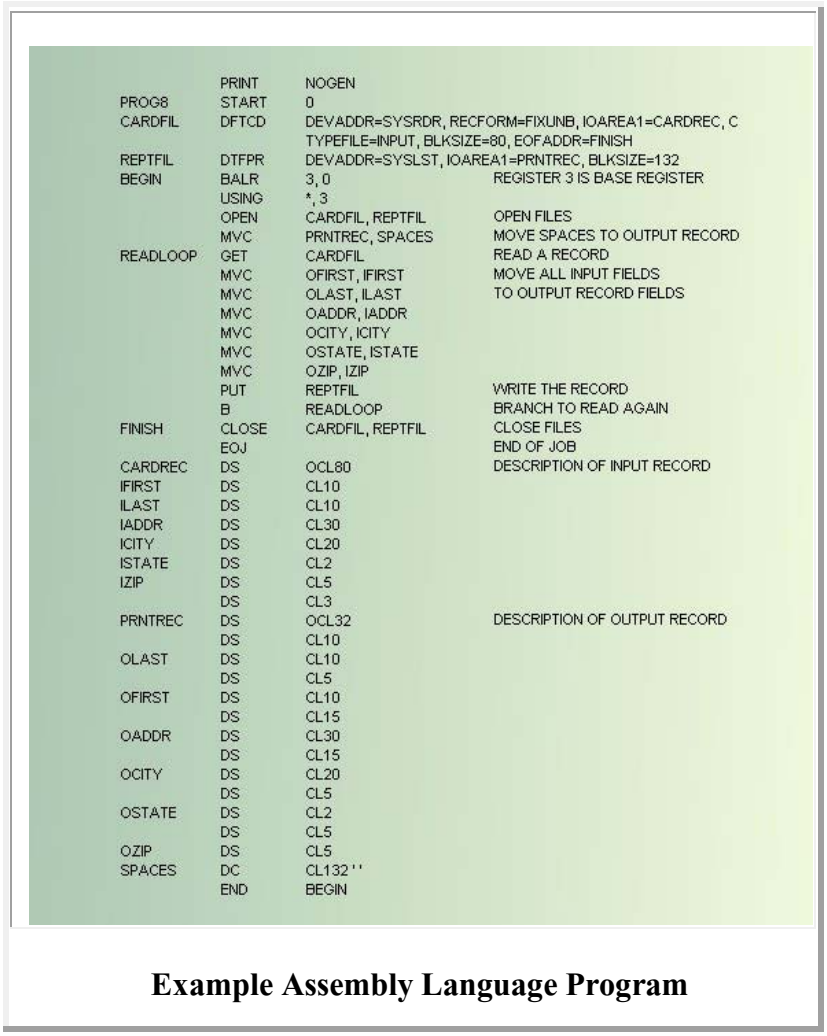
Programming languages are said to be "lower" or "higher," depending on how close they are to the language the computer itself uses (Os and 1s = low) or to the language people use (more English-like-high). We will consider five levels of language. They are numbered 1 through 5 to correspond to levels, or generations. In terms of ease of use and capabilities, each generation is an improvement over its predecessors. The five generations of languages are

- Machine language
- Assembly languages
- High-level languages
- Very high-level languages
- Natural languages

1. Machine Language:- Humans do not like to deal in numbers alone-they prefer letters and words. But, strictly speaking, numbers are what machine language is. This lowest level of language, machine language, represents data and program instructions as 1s and Os-binary digits corresponding to the on and off electrical states in the computer. Each type of computer has its own machine language.

2. Assembly Languages :- Today, assembly languages are considered very low level-that is, they are not as convenient for people to use as more recent languages. At the time they were developed, however, they were considered a great leap forward. To replace the Is and Os used in machine language, assembly languages use mnemonic codes, abbreviations that are easy to remember: A for Add, C for Compare, MP for Multiply, STO for storing information in memory, and so on. Although these codes are not English words, they are still- from the standpoint of human convenience-preferable to numbers (Os and 1s) alone.

Furthermore, assembly languages permit the use of names- perhaps RATE or TOTAL-for memory locations instead of actual address numbers. just like machine language, each type of computer has its own assembly language.



```
            PRINT   NOGEN
PROG8       START   0
CARDFIL     DTFCD   DEVADDR=SYSRDR, RECFORM=FIXUNB, IOAREA1=CARDREC, C
                    TYPEFILE=INPUT, BLKSIZE=80, EOFADDR=FINISH
REPTFIL     DTFPR   DEVADDR=SYSLST, IOAREA1=PRNTREC, BLKSIZE=132
BEGIN       BALR    3, 0            REGISTER 3 IS BASE REGISTER
            USING   *, 3
            OPEN    CARDFIL, REPTFIL    OPEN FILES
            MVC     PRNTREC, SPACES     MOVE SPACES TO OUTPUT RECORD
READLOOP    GET     CARDFIL             READ A RECORD
            MVC     OFIRST, IFIRST      MOVE ALL INPUT FIELDS
            MVC     OLAST, ILAST        TO OUTPUT RECORD FIELDS
            MVC     OADDR, IADDR
            MVC     OCITY, ICITY
            MVC     OSTATE, ISTATE
            MVC     OZIP, IZIP
            PUT     REPTFIL             WRITE THE RECORD
            B       READLOOP            BRANCH TO READ AGAIN
FINISH      CLOSE   CARDFIL, REPTFIL    CLOSE FILES
            EOJ                         END OF JOB
CARDREC     DS      0CL80               DESCRIPTION OF INPUT RECORD
IFIRST      DS      CL10
ILAST       DS      CL10
IADDR       DS      CL30
ICITY       DS      CL20
ISTATE      DS      CL2
IZIP        DS      CL5
            DS      CL3
PRNTREC     DS      0CL32               DESCRIPTION OF OUTPUT RECORD
            DS      CL10
OLAST       DS      CL10
            DS      CL5
OFIRST      DS      CL10
            DS      CL15
OADDR       DS      CL30
            DS      CL15
OCITY       DS      CL20
            DS      CL5
OSTATE      DS      CL2
            DS      CL5
OZIP        DS      CL5
SPACES      DC      CL132''
            END     BEGIN
```

Example Assembly Language Program

The programmer who uses an assembly language requires a translator to convert the assembly language program into machine language. A translator is needed because machine language is the only language the computer can actually execute. The translator is an assembler program, also referred to as an assembler. It takes the programs written in assembly language and turns them into machine language. Programmers need not worry about the translating aspect; they need only write programs in assembly language. The translation is taken care of by the assembler.

Although assembly languages represent a step forward, they still have many disadvantages. A key disadvantage is that assembly language is detailed in the extreme, making assembly programming repetitive, tedious, and error prone. This drawback is apparent in the program in Figure 2. Assembly language may be easier to read than machine language, but it is still tedious.

3. High-Level Languages :-The first widespread use of high-level languages in the early 1960s transformed programming into something quite different from what it had been. Programs were written in an English-like manner, thus making them more convenient to use. As a result, a programmer could accomplish more with less effort, and programs could now direct much more complex tasks. These so-called third-generation languages spurred the great increase in data processing that characterized the 1960s and 1970s. During that time the number of mainframes in use increased from hundreds to tens of thousands. The impact of third-generation languages on our society has been enormous.

Of course, a translator is needed to translate the symbolic statements of a high-level language into computer-executable machine language; this translator is usually a compiler. There are many compilers for each language and one for each type of computer. Since the machine language generated by one computer's COBOL compiler, for instance, is not the machine language of some other computer, it is necessary to have a COBOL compiler for each type of computer on which COBOL programs are to be run. Keep in mind, however, that even though a given program would be compiled to different machine language versions on different machines, the source program itself-the COBOL version-can be essentially identical on each machine.

Some languages are created to serve a specific purpose, such as controlling industrial robots or creating graphics. Many languages, however, are extraordinarily flexible and are considered to be general-purpose. In the past the majority of programming applications were written in BASIC, FORTRAN, or

COBOL-all general-purpose languages. In addition to these three, another popular high-level language is C, which we will discuss later.

4. Very High-Level Languages :-Languages called very high-level languages are often known by their generation number, that is, they are called fourth-generation languages or, more simply, 4GLs.

Definition

Will the real fourth-generation languages please stand up? There is no consensus about what constitutes a fourth-generation language. The 4GLs are essentially shorthand programming languages. An operation that requires hundreds of lines in a third-generation language such as COBOL typically requires only five to ten lines in a 4GL. However, beyond the basic criterion of conciseness, 4GLs are difficult to describe.

Characteristics

Fourth-generation languages share some characteristics. The first is that they make a true break with the prior generation-they are basically non-procedural.

Productivity

Folklore has it that fourth-generation languages can improve productivity by a factor of 5 to 50. Consider this request: Produce a report showing the total units sold for each product, by customer, in each month and year, and with a subtotal for each customer. In addition, each new customer must start on a new page. A 4GL request looks something like this:

```
TABLE FILE SALES
SUM UNITS BY MONTH BY CUSTOMER BY PRODUCT
ON CUSTOMER SUBTOTAL PAGE BREAK
END
```

Even though some training is required to do even this much, you can see that it is pretty simple. The third-generation language COBOL, however, typically requires

over 500 statements to fulfill the same request. If we define productivity as producing equivalent results in less time, then fourth-generation languages clearly increase productivity.

Benefits

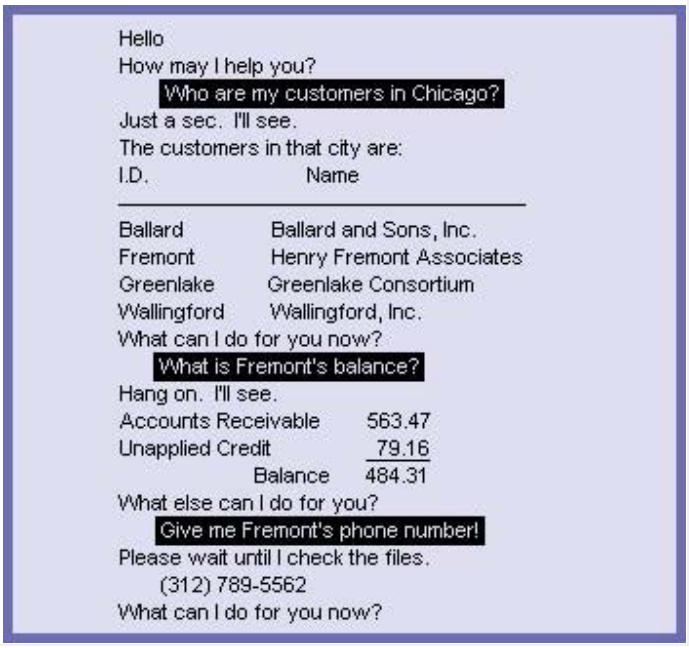
Fourth-generation languages are beneficial because

- They are results-oriented; they emphasize what instead of how.
- They improve productivity because programs are easy to write and change.
- They can be used with a minimum of training by both programmers and nonprogrammers.
- They shield users from needing an awareness of hardware and program structure.

It was not long ago that few people believed that 4GLs would ever be able to replace third-generation languages. These 4GL languages are being used, but in a very limited way.

***Query Languages* :-** A variation on fourth-generation languages are query languages, which can be used to retrieve information from databases. Data is usually added to databases according to a plan, and planned reports may also be produced. But what about a user who needs an unscheduled report or a report that differs somehow from the standard reports? A user can learn a query language fairly easily and then be able to input a request and receive the resulting report right on his or her own terminal or personal computer. A standardized query language, which can be used with several different commercial database programs, is Structured Query Language, popularly known as SQL. Other popular query languages are Query-by-Example, known as QBE, and Intellect.

5. Natural Languages :-The word "natural" has become almost as popular in computing circles as it has in the supermarket. Fifth-generation languages are, as you may guess, even more ill-defined than fourth-generation languages. They are most often called natural languages because of their resemblance to the "natural" spoken English language.



Example of Natural Language Interaction

A manager can say the same thing any number of ways. For example, "Get me tennis racket sales for January" works just as well as "I want January tennis racket revenues." Such a request may contain misspelled words, lack articles and verbs, and even use slang. The natural language translates human instructions-bad grammar, slang, and all-into code the computer understands. If it is not sure what the user has in mind, it politely asks for further explanation.

Consider this request that could be given in the 4GL Focus: "SUM ORDERS BY DATE BY REGION." If we alter the request and, still in Focus, say something like "Give me the dates and the regions after you've added up the orders," the computer will spit back the user-friendly version of "You've got to be kidding" and give up. But some natural languages can handle such a request. Users can relax the structure of their requests and increase the freedom of their interaction with the data.

An example of a natural language is shown in Figure 3. Natural languages excel at easy data access. Indeed, the most common application for natural languages is interacting with databases.

19.4 Basics of C language

Before we embark on a brief tour of C's basic syntax and structure we offer a brief history of C and consider the characteristics of the C language.

In the remainder of the Chapter we will look at the basic aspects of C programs such as C program structure, the declaration of variables, data types and operators. We will assume knowledge of a high level language, such as PASCAL.

It is our intention to provide a quick guide through similar C principles to most high level languages. Here the syntax may be slightly different but the concepts exactly the same.

C does have a few surprises:

- Many High level languages, like PASCAL, are highly disciplined and structured.
- **However beware** -- C is much more flexible and free-wheeling. This freedom gives C much more power that experienced users can employ. The above example below (mystery.c) illustrates how bad things could really get.

History of C

The milestones in C's development as a language are listed below:

- UNIX developed c. 1969 -- DEC PDP-7 Assembly Language
- BCPL -- a user friendly OS providing powerful development tools developed from BCPL. Assembler tedious long and error prone.
- A new language ``B'' a second attempt. c. 1970.
- A totally new language ``C'' a successor to ``B''. c. 1971
- By 1973 UNIX OS almost totally written in ``C''.

Characteristics of C

We briefly list some of C's characteristics that define the language and also have lead to its popularity as a programming language. Naturally we will be studying many of these aspects throughout the course.

- Small size
- Extensive use of function calls
- Loose typing -- unlike PASCAL
- Structured language
- Low level (BitWise) programming readily available
- Pointer implementation - extensive use of pointers for memory, array, structures and functions.

C has now become a widely used professional language for various reasons.

- It has high-level constructs.
- It can handle low-level activities.
- It produces efficient programs.
- It can be compiled on a variety of computers.

Its main drawback is that it has poor error detection which can make it off putting to the beginner. However diligence in this matter can pay off handsomely since having learned the rules of C we can break them.

19.5 C Program Structure

A C program basically has the following form:

- Pre-processor Commands
- Type definitions
- Function prototypes -- declare function types and variables passed to function.
- Variables
- Functions

We must have a *main()* function.

A function has the form:*type*function_name (***parameters***)

{

local variables

```
}
```

If the type definition is omitted C assumes that function returns an integer type.

NOTE: This can be a source of problems in a program.So returning to our first C program:

```
/* Sample program */


main()

                {


                printf( "I Like C \n");

                exit ( 0 );


                }
```

NOTE:

- C requires a semicolon at the end of **every** statement.
- printf is a ***standard*** C function -- called from main.
- \n signifies newline. **Formatted output** -- more later.

- exit() is also a standard function that causes the program to terminate. Strictly speaking it is not needed here as it is the last line of main() and the program will terminate anyway.

Let us look at another printing statement: printf(".\n.1\n..2\n...3\n");

The output of this would be:

.

.1

..2

...3

Variables: C has the following simple data types:

The Pascal Equivalents are:

On UNIX systems all ints are long ints unless specified as short int explicitly.

NOTE: There is NO Boolean type in C -- you should use char, int or (better) unsigned char.

Unsigned can be used with all char and int types.

To declare a variable in C, do: var_type ***list variables***;

e.g. inti,j,k;

float x,y,z;

char ch;

Defining Global Variables

Global variables are defined above main() in the following way:-

short number,sum;

intbignumber,bigsum;

char letter;

main()

{

}

It is also possible to pre-initialise global variables using the = operator for assignment.

NOTE: The = operator is the same as := is Pascal.

For example:-

```
float sum=0.0;

        intbigsum=0;

        char letter=`A';


        main()

                {


                }
```

This is the same as:-

```
float sum;

        intbigsum;

        char letter;
```

```
main()
{

sum=0.0;
bigsum=0;
letter=`A';

}
```

...but is more efficient.

C also allows multiple assignment statements using =, for example:

```
a=b=c=d=3;
```

...which is the same as, but more efficient than:

```
a=3;
b=3;
c=3;
d=3;
```

This kind of assignment is only possible if all the variable types in the statement are the same.

You can define your own types use typedef. This will have greater relevance later in the course when we learn how to create more complex data structures.

As an example of a simple use let us consider how we may define two new types real and letter. These new types can then be used in the same way as the pre-defined C types:

typedef real float;

typedef letter char;

Variables declared:

real sum=0.0;

letter nextletter;

Printing Out and Inputting Variables

C uses formatted output. The printf function has a special formatting character (%) -- a character following this defines a certain format for a variable:

%c -- characters

%d -- integers

%f -- floats

e.g. printf("%c %d %f",ch,i,x);

NOTE: Format statement enclosed in ``...", variables follow after. Make sure order of format and variable data types match up.

scanf() is the function for inputting values to a data structure: Its format is similar to printf: ***i.e.*** scanf("%c %d %f",&ch,&i,&x);

NOTE: & before variables. Please accept this for now and remember to include it.

Constants

ANSI C allows you to declare constants. When you declare a constant it is a bit like a variable declaration except the value cannot be changed.

The const keyword is to declare a constant, as shown below:

intconst a = 1;

constint a =2;

Note:You can declare the const before or after the type. Choose one an stick to it.It is usual to initialise a const with a value as it cannot get a value any other way.

The preprocessor #define is another more flexible (see Preprocessor Chapters) method to define constants in a program.

You frequently see const declaration in function parameters. This says simply that the function is not going to change the value of the parameter.

The following function definition used concepts we have not met (see chapters on functions, strings, pointers, and standard libraries) but for completenes of this section it is is included here:

void strcpy(char *buffer, char const *string)

The second argument string is a C string that will not be altered by the string copying standard library function.

"Expressions and Assignment Statements"

Expressions are the fundamental means of specifying computations in a programming language.

Arithmetic Expressions

Their evaluation was one of the motivations for the development of the first programming languages.Most of the characteristics of arithmetic expressions in programming languages were inherited from conventions that had evolved in math.Arithmetic expressions consist of operators, operands, parentheses, and function calls.The operators can be unary, or binary. C-based languages include a ternary operator.The purpose of an arithmetic expression is to specify an arithmetic computation.

An implementation of such a computation must cause two actions:

- Fetching the operands from memory
- Executing the arithmetic operations on those operands.

Design issues for arithmetic expressions:

1. What are the operator precedence rules?

2. What are the operator associativity rules?

3. What is the order of operand evaluation?

4. Are there restrictions on operand evaluation side effects?

5. Does the language allow user-defined operator overloading?

6. What mode mixing is allowed in expressions?

Operator Evaluation Order

Precedence

1. The operator precedence rules for expression evaluation define the order in which “adjacent” operators of different precedence levels are evaluated (“adjacent” means they are separated by at most one operand).

2. Typical precedence levels:

    1. Parentheses

    2. unary operators

    3. ** (if the language supports it)

    4. *, /

    5. +, -

3. Many languages also include unary versions of addition and subtraction.

4. Unary addition is called the identity operator because it usually has no associated operation and thus has no effect on its operand.

5. In Java, unary plus actually does have an effect when its operand is short or byte. An implicit conversion of short and byte operands to int type takes place.

Ex:

A + (- B) * C // is legal

A + - B * C // is illegal

Associativity

The operator associativity rules for expression evaluation define the order in which adjacent operators with the same precedence level are evaluated. “An operator can be either left or right associative.”

Typical associativity rules:

- Left to right, except **, which is right to left
- Sometimes unary operators associate right to left (e.g., FORTRAN)

Ex: (Java)

a – b + c // left to right

Ex: (Fortran)

A ** B ** C // right to left

(A ** B) ** C // In Ada it must be parenthesized

Language	**Associativity Rule**
FORTRAN	**Left: * / + -**
	Right: **
C-BASED LANGUAGES	**Left: * / % binary + binary -**
	Right: ++ -- unary – unary +
ADA	**Left: all except ****
	Non-associative: **

APL is different; all operators have equal precedence and all operators associate right to left.

Ex:

A X B + C // A = 3, B = 4, C = 5 ➔ 27

Precedence and associativity rules can be overridden with parentheses.

Parentheses

Programmers can alter the precedence and associativity rules by placing parentheses in expressions.

A parenthesized part of an expression has precedence over its adjacent un-parenthesized parts.

Ex: (A + B) * C

Conditional Expressions

Sometimes **if-then-else** statements are used to perform a conditional expression assignment.

```
if (count == 0)
   average = 0;
else
   average = sum / count;
```

In the C-based languages, this can be specified more conveniently in an assignment statement using a conditional expressions

```
average = (count == 0) ? 0 : sum / count;
```

Operand evaluation order

The process:

1. Variables: just fetch the value from memory.

2. Constants: sometimes a fetch from memory; sometimes the constant is in the machine language instruction.

3. Parenthesized expressions: evaluate all operands and operators first.

Side Effects

A **side effect** of a function, called a **functional side effect**, occurs when the function changes either one of its parameters or a global variable.

Ex:a + fun(a)

If fun does not have the side effect of changing a, then the order of evaluation of the two operands, a and fun(a), has no effect on the value of the expression.

However, if fun changes a, there is an effect.

Ex:Consider the following situation: fun returns the value of its argument

divided by 2 and changes its parameter to have the value 20, and:

a = 10;

b = a + fun(a);

- If the value of a is returned first (in the expression evaluation process), its v alue is 10 and the value of the expression is 15.

- But if the second is evaluated first, then the value of the first operand is 20 and the value of the expression is 25.

The following shows a C program which illustrate the same problem.

int a = 5;

intfun1() {

```
  a = 17;
return 3;
}
voidfun2() {
  a = a + fun1();
}
void main() {
fun2();
}
```

The value computed for a in fun2 depends on the order of evaluation of the operands in the expression a + fun1(). The value of a will be either 8 or 20.

Two possible solutions:Write the language definition to disallow functional side effects

- No two-way parameters in functions.
- No non-local references in functions.

Type Conversions

- A **narrowing conversion** is one that converts an object to a type that cannot include all of the values of the original type e.g., **float** to **int**.

- A **widening conversion** is one in which an object is converted to a type that can include at least approximations to all of the values of the original type e.g., **int** to **float**.

Coercion in Expressions

- A **mixed-mode expression** is one that has operands of different types.

- A **coercion** is an implicit type conversion.

Disadvantage of coercions:

1. They decrease in the type error detection ability of the compiler

2. In most languages, all numeric types are coerced in expressions, using widening conversions.

3. Language are not in agreement on the issue of coercions in arithmetic expressions.

4. Those against a broad range of coercions are concerned with the reliability problems that can result from such coercions, because they eliminate the benefits of type checking.

5. Those who would rather include a wide range of coercions are more concerned with the loss in flexibility that results from restrictions.

6. The issue is whether programmers should be concerned with this category of errors or whether the compiler should detect them.

Ex:**void**mymethod() {

int a, b, c;

float d;

…

a = b * d;

…

}

7. Assume that the second operand was supposed to be c instead of d.

8. Because mixed-mode expressions are legal in Java, the compiler wouldn't detect this as an error. Simply, b will be coerced to **float**.

Explicit Type Conversions

Often called casts in C-based languages.Ex: Ada:

FLOAT(INDEX)--INDEX is INTEGER type

Java:

(int)speed /*speed is float type*/

Errors in Expressions

- Caused by:

a. Inherent limitations of arithmetic e.g. division by zero

b. Limitations of computer arithmetic e.g. overflow or underflow

Such errors are often ignored by the run-time system.

Relational and Boolean Expressions

Relational Expressions: has two operands and one relational operator.The value of a relational expression is Boolean, unless it is not a type included in the language.

– Use relational operators and operands of various types.

– Operator symbols used vary somewhat among languages **(!=, /=, .NE., <>, #)**

- The syntax of the relational operators available in some common languages is as follows:

Operation	***Ada***	***C-Based Languages***	***Fortran 95***
Equal	=	==	**.EQ. or ==**
Not Equal	/=	**!=**	**.NE. or <>**
Greater than	>	>	**.GT. or >**
Less than	<	<	**.LT. or <**
Greater than or equal	>=	>=	**.GE. or >=**
Less than or equal	<=	<=	**.LE. or >=**

Boolean Expressions:- Operands are Boolean and the result is Boolean.

FORTRAN 77	FORTRAN 90	C	Ada

.AND.	and	&&	and
.OR.	or	||	or
.NOT.	not	!	not

Versions of C prior to C99 have no Boolean type; it uses int type with 0 for false and nonzero for true.

One odd characteristic of C's expressions: **a < b < c** is a legal expression, but the result is not what you might expect.The left most operator is evaluated first b/c the relational operators of C, are left associative, producing either 0 or 1.Then this result is compared with var c. There is never a comparison between b and c.

Short Circuit Evaluation

A **short-circuit evaluation** of an expression is one in which the result is determined without evaluating all of the operands and/or operators.

Ex:(13 * a) * (b/13 – 1) // is independent of the value (b/13 – 1) if a = 0, b/c 0*x = 0.

So when a = 0, there is no need to evaluate (b/13 – 1) or perform the second multiplication.However, this shortcut is not easily detected during execution, so it is never taken.

The value of the Boolean expression:

(a >= 0) && (b < 10) // is independent of the second expression if a < 0, b/c (F && x)

is False for all the values of x.

So when a < 0, there is no need to evaluate b, the constant 10, the second relational expression, or the && operation.Unlike the case of arithmetic expressions, this shortcut can be easily discovered during execution.

Short-circuit evaluation exposes the potential problem of side effects in expressions

(a > b) || (b++ / 3) // b is changed only when a <= b.

If the programmer assumed b would change every time this expression is evaluated during execution, the program will fail.

C, C++, and Java: use short-circuit evaluation for the usual Boolean operators (**&&** and ||), but also provide bitwise Boolean operators that are not short circuit (**&** and |)

Assignment Statements

Simple Assignments

The C-based languages use == as the equality relational operator to avoid confusion with their assignment operator.

The operator symbol for assignment:

1. = FORTRAN, BASIC, PL/I, C, C++, Java

2. := ALGOL, Pascal, Ada

Conditional Targets

Ex:

flag ? count 1 : count2 = 0; ⇔ **if** (flag)

```
                                    count1 = 0;
                                    else
                                    count2 = 0;
```

Compound Assignment Operators

A compound assignment operator is a shorthand method of specifying a commonly needed form of assignment.

The form of assignment that can be abbreviated with this technique has the destination var also appearing as the first operand in the expression on the right side, as in

a = a + b

The syntax of assignment operators that is the catenation of the desired binary operator to the = operator.

sum += value; ⇔ sum = sum + value;

Unary Assignment Operators

C-based languages include two special unary operators that are actually abbreviated assignments.They combine increment and decrement operations with assignments.

The operators ++ and -- can be used either in expression or to form stand-alone single-operator assignment statements. They can appear as prefix operators:

sum = ++ count; ⇔ count = count + 1; sum = count;

If the same operator is used as a postfix operator:

sum = count ++; ⇔ sum = count; count = count + 1;

Assignment as an Expression

This design treats the assignment operator much like any other binary operator, except that it has the side effect of changing its left operand.

Ex:while ((ch = getchar())!=EOF)

{…} // why ( ) around assignment?

The assignment statement must be parenthesized b/c the precedence of the assignment operator is lower than that of the relational operators.

Basics of Formatted Input/Output in C

Concepts

I/O is essentially done one character (or byte) at a time

Stream -- a sequence of characters flowing from one place to another

1. *input stream*: data flows from input device (keyboard, file, etc) into memory

2. *output stream*: data flows from memory to output device (monitor, file, printer, etc)

Standard I/O streams (with built-in meaning)

1. stdin: standard input stream (default is keyboard)

2. stdout: standard output stream (defaults to monitor)

3. stderr: standard error stream

4. stdio.h -- contains basic I/O functions

5. scanf: reads from standard input (stdin)

6. printf: writes to standard output (stdout)

There are other functions similar to printf and scanf that write to and read from other streams

How to include, for C or C++ compiler

```
#include <stdio.h>          // for a C compiler
#include <cstdio>           // for a C++ compiler
```

Formatted I/O -- refers to the conversion of data to and from a stream of characters, for printing (or reading) in plain text format

- All text I/O we do is considered *formatted* I/O
- The other option is reading/writing direct binary information (common with file I/O, for example)

Output with printf

Recap

The basic format of a **printf** function call is: printf (*format_string*, *list_of_expressions*);where:

- *format_string* is the layout of what's being printed
- *list_of_expressions* is a comma-separated list of variables or expressions yielding results to be inserted into the output

To output string literals, just use one parameter on printf, the string itself

- printf("Hello, world!\n");
- printf("Greetings, Earthling\n\n");

Conversion Specifiers

A conversion specifier is a symbol that is used as a placeholder in a formatting string. For integer output (for example), %d is the specifier that holds the place for integers.

Here are some commonly used conversion specifiers (not a comprehensive list):

%d int (signed decimal integer)

%u unsigned decimal integer

%f floating point values (fixed notation) - float, double

%e floating point values (exponential notation)

%s string

%c character

Printing Integers

To output an integer, use %d in the format string, and an integer expression in the *list_of_expressions*.

intnumStudents = 35123;

printf("FSU has %d students", numStudents);

// Output:

```
// FSU has 35123 students
```

We can specify the field wicth (i.e. how many 'spaces' the item prints in). Defaults to right-justification. Place a number between the % and the d. In this example, field width is 10:

```
printf("FSU has %10d students", numStudents);

// Output:

// FSU has      35123 students
```

To left justify, use a negative number in the field width:

```
printf("FSU has %-10d students", numStudents);

// Output:

// FSU has 35123      students
```

If the field width is too small or left unspecified, it defaults to the minimum number of characters required to print the item:

```
printf("FSU has %2d students", numStudents);

// Output:

// FSU has 35123 students
```

Specifying the field width is most useful when printing multiple lines of output that are meant to line up in a table format

Printing Floating-point numbers

Use the %f modifer to print floating point values in fixed notation:

```
double cost = 123.45;
```

```
printf("Your total is $%f today\n", cost);

 // Output:

 // Your total is $123.450000 today
```

Use %e for exponential notation:

```
printf("Your total is $%e today\n", cost);

 // Output:

 // Your total is $1.234500e+02 today
```

Note that the e+02 means "times 10 to the 2nd power"
You can also control the decimal precision, which is the number of places after the decimal. Output will round to the appropriate number of decimal places, if necessary:

```
printf("Your total is $%.2f today\n", cost);


 // Output:

 // Your total is $123.45 today
```

Field width can also be controlled, as with integers:

```
printf("Your total is $%9.2f today\n", cost);

 // Output:

 // Your total is $    123.45 today
```

In the conversion specifier, the number before the decimal is field width, and the number after is the precision. (In this example, 9 and 2).%-9.2 would left-justify in a field width of 9, as with integers

Printing characters and strings

Use the formatting specifier %c for characters. Default field size is 1 character:

```
 char letter = 'Q';

printf("%c%c%c\n", '*', letter, '*');

 // Output is:  *Q*
```

Use %s for printing strings. Field widths work just like with integers:

```
printf("%s%10s%-10sEND\n", "Hello", "Alice", "Bob");

 // Output:

 // Hello     AliceBob       END
```

scanf

To read data in from standard input (keyboard), we call the **scanf** function. The basic form of a call to scanf is:

scanf(*format_string*, *list_of_variable_addresses*);

The format string is like that of printf

But instead of expressions, we need space to store incoming data, hence the list of variable addresses

If **x** is a variable, then the expression **&x** means "address of x"

scanf example:

```
int month, day;

printf("Please enter your birth month, followed by the day: ");

scanf("%d %d", &month, &day);
```

Conversion Specifiers

Mostly the same as for output. Some small differences, Use %f for type float, but use %lf for types double and long double. The data type read, the conversion specifier, and the variable used need to match in type. White space is skipped by default in consecutive *numeric* reads. But it is *not* skipped for character/string inputs.

Example

```
#include <stdio.h>

int main()

{

int i;

 float f;

 char c;

printf("Enter an integer and a float, then Y or N\n> ");

scanf("%d%f%c", &i, &f, &c);

printf("You entered:\n");

printf("i = %d, f = %f, c = %c\n", i, f, c);

}
```

Sample run #1

User input underlined, to distinguish it from program output

Enter an integer and a float, then Y or N

>34 45.6Y

You entered:

i = 34, f = 45.600, c = Y

Sample Run #2

Enter an integer and a float, then Y or N

>12 34.5678 N

You entered:

i = 12, f = 34.568, c =

Note that in this sample run, the character that was read was **NOT** the letter 'N'. It was the space. (Remember, white space not skipped on character reads).

This can be accounted for. Consider if the scanf line looked like this:

scanf("%d%f %c", &i, &f, &c);

There's a space betwen the %f and the %c in the format string. This allows the user to type a space. Suppose this is the typed input:

12 34.5678 N

Then the character variable c will now contain the 'N'.

Interactive Input

You can make input more interactive by prompting the user more carefully. This can be tedious in some places, but in many occasions, it makes programs more user-friendly. Example:

```
int age;
  double gpa;
  char answer;
printf("Please enter your age: ");
scanf("%d", &age);
printf("Please enter your gpa: ");
scanf("%lf", %gpa);
printf("Do you like pie (Y/N)? ");
scanf("%c", %answer);
```

A good way to learn more about scanf is to try various inputs in various combinations, and type in test cases -- see what happens!

printf/scanf with C-strings

An entire C-style string can be easily printed, by using the %s formatting symbol, along with the name of the char array storing the string (as the argument filling in that position):

```
  char greeting[] = "Hello";
printf("%s", greeting);     // prints the word "Hello"
```

Be careful to **only** use this on char arrays that are being used as C-style strings. (This means, only if the null character is present as a terminator).

Similarly, you can read a string into a char array with scanf. The following call allows the entry of a word (up to 19 characters and a terminating null character) from the keyboard, which is stored in the array word1:

```
char word1[20];

scanf("%s", word1);
```

Characters are read from the keyboard until the first "white space" (space, tab, newline) character is encountered. The input is stored in the character array and the null character is automatically appended.

Note also that the & was not needed in the scanf call (word1 was used, instead of &word1). This is because the name of the array by itself (with no index) actually IS a variable that stores an address (a *pointer*).

Flow Control Statements:- C provides two styles of flow control:

- Branching
- Looping

Branching is deciding what actions to take and looping is deciding how many times to take a certain action.Branching is so called because the program chooses to follow one branch or another.

if statement

This is the simplest form of the branching statements.

It takes an expression in parenthesis and an statement or block of statements. if the expression is true then the statement or block of statements gets executed otherwise these statements are skipped.

NOTE: Expression will be assumed to be true if its evaulated values is non-zero.

if statements take the following form:

```
 if (expression)
  statement;
```

or

```
if (expression)
  {
    Block of statements;
  }
```

or

```
if (expression)
  {
    Block of statements;
  }
else
  {
    Block of statements;
  }
```

or

```
if (expression)
```

```
{
  Block of statements;
}
else if(expression)
{
  Block of statements;
}
else
{
  Block of statements;
}
```

Operator? :

The Operator is just like an if ... else statement except that because it is an operator you can use it within expressions.

? : is a ternary operator in that it takes three values, this is the only ternary operator C has.

? : takes the following form:

if condition is true ? then X return value : otherwise Y value;

switch statement:

The switch statement is much like a nested if .. else statement. Its mostly a matter of preference which you use, switch statement can be slightly more efficient and easier to read.

```
switch( expression )
   {
     case constant-expression1:     statements1;
     [case constant-expression2:    statements2;]
     [case constant-expression3:    statements3;]
     [default : statements4;]
   }
```

Using break keyword:

If a condition is met in switch case then execution continues on into the next case clause also if it is not explicitly specified that the execution should exit the switch statement. This is achieved by using *break* keyword.

What is default condition:

If none of the listed conditions is met then default condition executed.

Looping

Loops provide a way to repeat commands and control how many times they are repeated. C provides a number of looping way.

2 while loop

The most basic loop in C is the while loop.A while statement is like a repeating if statement. Like an If statement, if the test condition is true: the statements get

executed. The difference is that after the statements have been executed, the test condition is checked again. If it is still true the statements get executed again. This cycle repeats until the test condition evaluates to false.

Basic syntax of while loop is as follows:

```
while ( expression )
{
  Single statement
  or
  Block of statements;
}
```

2. for loop

for loop is similar to while, it's just written differently. for statements are often used to proccess lists such a range of numbers:

Basic syntax of for loop is as follows:

```
for( expression1; expression2; expression3)
{
  Single statement
  or
  Block of statements;
}
```

In the above syntax:

- expression1 - Initialises variables.
- expression2 - Conditional expression, as long as this condition is true, loop will keep executing.
- expression3 - expression3 is the modifier which may be simple increment of a variable.

3. do...while loop

do ... while is just like a while loop except that the test condition is checked at the end of the loop rather than the start. This has the effect that the content of the loop are always executed at least once.

Basic syntax of do...while loop is as follows:

```
do
{
  Single statement
  or
  Block of statements;
}while(expression);
```

break and continue statements

C provides two commands to control how we loop:

- break -- exit form loop or switch.
- continue -- skip 1 iteration of loop.

You already have seen example of using break statement. Here is an example showing usage of**continue** statement.

```
#include

main()

{

int i;

int j = 10;


   for( i = 0; i <= j; i ++ )

   {

     if( i == 5 )

     {

       continue;

     }

printf("Hello %d\n", i );

   }

}
```

This will produce following output:

```
Hello 0

Hello 1
```

Hello 2

Hello 3

Hello 4

Hello 6

Hello 7

Hello 8

Hello 9

Hello 10

19.6 Review Questions

1 Define Levels of Language

2 Explain looping in C language.

19.7 References

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Unit – 20 : LOGICAL variables

Structure of the Unit:

20.0 Objective

At the end of the unit learner will be able to

- Understand the Logical Variables
- Know the importance of Double precession variables
- Learn the Subscripted variables and their Dimension
- Understand the importance of DO statement, COMMON and DATA statement
- Get the knowledge of Function and Subroutine

20.1 Introduction

This chapter gives a quick introduction to the most common features of the programming language like Fortran 77. FORTRAN (FORmula TRANslation), introduced in 1956, was the first high level language. It has since been revised several times. Fortran 77, though not the latest version, is widely available and is compatible with later versions.

High level language instructions are not executable. Instead, a high level language source program is read as input by a program called a compiler, which checks its syntax and, if it is free from errors, compiles an equivalent machine code object program. (If the source program contains syntax errors, the compiler outputs a number of messages indicating the nature of the errors and where they occur.)

Although it is in machine code, the object program is incomplete because it includes references to subprograms which it requires for such common tasks as reading input, producing output and computing mathematical functions. These subprograms are grouped together in libraries which are available for use by all object programs. To create an executable program, the object program must be linked to the subprogram libraries it requires. The executable program may then be loaded into memory and run.

A FORTRAN program is just a sequence of lines of plain text. This is called the *source code*. The text has to

follow certain rules (syntax) to be a valid FORTRAN program. We start by looking at a simple example:

```
program circle
real r, area, pi
c This program reads a real number r and prints
c the area of a circle with radius r.
write (*,*) 'Give radius r:'
read (*,*) r
pi = atan(1.0e0)*4.0e0
area = pi*r*r
```

write (*,*) 'Area = ', area

end

A FORTRAN program generally consists of a main program and possibly several subprograms (*i.e*., functions or

subroutines). The structure of a main program is:

program *name*

declarations

statements

end

Column position rules

Fortran 77 is *not* a free-format language, but has a very strict set of rules for how the source code should be formatted. The most important rules are the column position rules:

Col. 1: Blank, or a "c" or "*" for comments

Col. 1-5: Blank or statement label

Col. 6: Blank or a "+" for continuation of previous line

Col. 7-72: Statement

When you have written a FORTRAN program, you should save it in a file that has the extension **.f,** before you can execute the program; you need to translate source code into machine readable form. This is done by a special program called the *compiler*. The UNIX command that typically runs the Fortran 77 compiler is f77. (Note: The FORTRAN compiler used on cgate, however, is invoked by the command xlf.) The compiler translates source code into *object code* and the linker/loader makes this into an *executable*. The default output from the compilation is given the somewhat cryptic name a.out, but you can choose another name if you wish using the -o option. For example, f77 circle.f -o circle.out will compile the file *circle.f* and save the executable in the file *circle.out* (rather than the default *a.out)*

Chapter deals with the use of Logical Variables which is used in the conditional statements and iterative statements. There is also an idea of Double Precision Variables which are used when single precision is not adequate to express the

precision required. Chapter also deals in subscripted variables (Arrays) and there DIMENSION.

The learner will also be able to get the knowledge and importance of subprograms in Fortran which are called Functions and Subroutines. There is also knowledge of DO statement which is used widely. Common and Data Statements are also used so a brief about the Common and Data statements is also provided in this chapter.

20.2. LOGICAL variables

A variable is a unique name which applies to a word of memory and uses to refer to it. A variable consists of one to six upper case alphabetic characters and decimal digits, beginning with an alphabetic character.

Examples:

VOL TEMP A2 COLUMN

Spaces are ignored.

The value of a variable is the constant stored in the word to which it refers. Each variable has a type, which denotes the type of value it may have. The type of a variable may be specified explicitly, or assigned implicitly (by default).

Explicit typing:

The type of a variable may be assigned explicitly by a type specification statement. This has the form:

type variable_list

where *type* is the name of a type

and variable_list is a single variable or a list of variables, separated by commas. The statement assigns the given type to all the variables in the list.

Examples:

INTEGER size

REAL number,i

Type specification statements are not compiled into executable machine code instructions. Instead the compiler records the names and types of the

variables and reserves storage for them. Such non-executable statements must be placed at the beginning of a program, before the first executable

statement.

The most common declarations are:

Integer	list of variables
real	list of variables
double precision	list of variables
complex	list of variables
logical	list of variables
character	list of variables

Implicit (or default) typing:

If a variable is used without being included in a type specification, its type is assigned implicitly (by default) according to the following *rule:*

If the variable begins with a character from I to N, its type is INTEGER. Otherwise, it is REAL.

Thus TEMP is a REAL variable, while ITEMP is an INTEGER.

Note: because a variable can be used without first being declared in a type specification, a misspelled variable is not in general detected as an error by the compiler. The program may compile and run, but produce incorrect results. Care should therefore be taken to get variable names right, and if unexpected results are obtained, variable names are one of the first things to check.

Assigning a value:

Before a variable can be used in computation, it must be assigned an initial value. This may be done by reading a value from input or by using an assignment statement.

The READ statement is used to assign values to variables by reading data from input. The simplest form of the READ statement is:

READ *variable_list*

where *variable_list* is a single variable or a list of variables separated by commas.

This statement reads constants from the terminal, separated by spaces, commas, or new lines, and assigns them in sequence to the variables in the list.

Execution of the program stops until the right number of constants has been entered.

Example:

READ *, VAR1, VAR2, VAR3

waits for three constants to be entered and assigns them in sequence to the variables VAR1, VAR2 and VAR3.

The assignment statement

The simplest form of assignment statement is:

variable = constant

This means that the constant is assigned as a value to the variable on the left-hand-side. Note that the '=' sign has a different meaning than in algebra. It does not indicate equality, but is an assignment operator.

Examples:

len = 74.5

Ilen= 100

The LOGICAL type:

There are two LOGICAL constants, defined as .TRUE. and .FALSE..

A LOGICAL variable can be assigned either of these values. It may not be assigned a value of any other type. Each LOGICAL variable must be declared in a LOGICAL type specification statement, which must occur, like all other type specifications, before the first executable statement.

Example: the LOGICAL variable ERROR could be declared and initialised by the statements:

LOGICAL error

error = .false.

Logical expressions:

A logical expresssion is one which evaluates to one of the LOGICAL constants .TRUE. or .FALSE..

Thus the simplest logical expressions are the

LOGICAL constants themselves, and LOGICAL variables.

Variable names in Fortran consist of 1-6 characters chosen from the letters a-z and the digits 0-9. The first character must be a letter. Upper and lower case are same means it is case insensitive, in fact, it assumes all input is upper case. However, nearly all Fortran 77 compilers will accept lower case.

Reserved words cannot be used as names of variable.

LOGICAL variables and assignment:

Example:

```
LOGICAL i, j
i = .TRUE.
j = i .AND. 3 .LT. 5/2
```

The order of precedence is important, as the above example shows. The rule is that arithmetic expressions are evaluated first, then relational operators, and finally logical operators. Hence j will be assigned .FALSE. in the example above. Among the logical operators the precedence (in the absence of parenthesis) is that .NOT. is done first, then .AND., then .OR. is done last.

Relational expressions

A relational expression is a logical expression which states a relationship between two expressions, evaluating to .TRUE. if the relationship applies

or .FALSE. otherwise. For the present, we shall consider only relationships between arithmetic expressions.

A relational expression has the form:

arithmetic_expression relational_operator arithmetic_expression

The relational operators are:	Meaning
.LT.	Less than
.LE.	Less than or equal to
.EQ.	Equal to

.NE.	Not equal to
.GE.	Greater than or equal to
.GT.	Greater than

Thus examples of relational expressions are:

N.GE.0

X.LT.Y

Note:

1. Relational operators have lower precedence than arithmetic operators. Therefore, in evaluating a relational expression, the arithmetic expressions are evaluated before the comparison indicated by the relational operator is made.
2. The two arithmetic expressions may be of different type (i.e. one INTEGER and one REAL). In this case, the INTEGER expression is converted to REAL form before the comparison is made.

Composite logical expressions

It is often necessary to express a condition which combines two or more logical expressions. For example, to check that the value of a variable lies

within a given range, we should have to check that it is greater than the lower limit AND less than the upper limit. Such conditions are expressed in Fortran by composite logical expressions, which have the form:

L1 logical_operator L2

where *L1* and *L2* are logical expressions (relational or composite). The logical operators and their meanings are shown below. The second column

indicates the conditions under which a composite logical expression as above evaluates to .TRUE..

.AND.	Both *L1* and *L2* are	.TRUE.
.OR.	Either *L1* or *L2* or both are	.TRUE.
.EQV.	Both *L1* and *L2* have the same value	(.TRUE. or FALSE.)
NEQV.	*L1* and *L2* have different values	(one .TRUE. and one .FALSE.)

There is one further logical operator .NOT., which unlike the others, takes only one operand, which it precedes. The expression .NOT.*L* is .TRUE. if the logical expression *L* is .FALSE. and vice versa.

As with arithmetic operators, precedence rules are required to define the interpretation of expressions like:

.NOT. *L1* .OR. *L2*

which could evaluate to .TRUE. under either of the following conditions, depending on the order of evaluation:

1. *L1* is .FALSE. or *L2* is .TRUE.

2. *L1* and *L2* are both .FALSE.

Logical assignment

The value of a logical expression can be assigned to a variable of type LOGICAL, e.g.

```
LOGICAL VALID
VALID = X.GT.MIN .AND. X.LT.MAX
```

Logical expressions are more commonly used in logical IF statements and structures.

20.3 Double precision variables

A REAL variable or constant occupies one word of storage and this limits its accuracy. When greater accuracy is required, DOUBLE PRECISION variables and constants may be used. These occupy two words of storage and can store a greater number of significant digits.

DOUBLE PRECISION constants

DOUBLE PRECISION constants are written in exponential form, but

with the letter 'D' in place of 'E', e.g.

```
3D-7
54713D-3
72.7192D0
1.413D5
```

DOUBLE PRECISION variables

DOUBLE PRECISION variables must be declared in a type specification

of the form:

DOUBLE PRECISION *variable_list*

where *variable_list* is a list of variables, separated by commas.

In many calculations, particularly those involving iteration or long sequences of calculations, single precision is not adequate to express the precision required. To overcome this limitation , FORTRAN provides the double precision data type. Each double precision is stored in two memory locations, thus providing twice as many significant digits.

Keep the following considerations in mind:

- Double precision provides greater range and precision than single precision
- Computations that mix single and double operands are performed in double precision, which requires conversion of the single-precision operands to double-precision. These conversions do not affect performance.
- Double-precision values that are converted to single-precision require rounding operations.

20.4 Subscripted Variable and DIMENSION

The Fortran variables considered so far were single entities where each variable name could store one number. There is another type of variable called a ***subscripted variable*** which refers to an array or a group of quantities by a single name. Each member in the group is referred to by its position in the group. For Example: assume the following group. For example: assume the following group of numbers named GRP.

GRP = {3.5 4.31 6.42 7.87 9.92}

Third member is referred as GRP (3), where the number 3 is called the subscript and is enclosed in parenthesis. In general GRP (I) is used to refer any element where I may take the values from 1 to 5.

Such arrays are useful as they are stored in the memory as a group and any member of the group may be referred by subscript attached to the array name. The subscripts may be used as indices in DO loops which enhance the flexibility of DO loops.

Consider the following statement:

DIMENSION MARKS (50)

It is a non executable statement which provides information to the compiler that MARKS is a Subscript variable with 50 components and each component is of type integer since MARKS is an integer variable name. Thus 50 locations in memory would be reserved for MARKS and its components stored in contiguous locations.

The first number is assigned to MARKS (1), the second to MARKS (2) and the ones in the succeeding lines to succeeding components of MARKS.

The rule for writing a subscripted variable is given below:

The general form of a subscript variable is an integer or a real variable name followed by subscripts enclosed within the parenthesis. The subscripts are separated by commas.

A *subscripted variable* is the combination of the array name and a subscript.You can use a subscripted variable anyplace an ordinary variable can go.

- Two Dimensional arrays called matrices often occur in practice. Let A is a 2D array .Each element of it is identified by using two subscripts. Thus the element in the second row and third column may be identified by attaching the subscripts (2,3) to the array name. In general, an element is identified as A(I,J) where I is the row subscript and J is the column subscript.

DIMENSION statement

When subscript variable are used, a DIMENSION statement is required to inform the compiler that a particular variable is a subscript variable so that the required amount of storage is allocated to the variable. The general form of the DIMENSION statement is

DIMENSION *var(integer constant)*

Where *var* is a variable name and *positive integer constant* specifies the upper limit of the subscript variable)

Example: DIMENSION BAL (10, 30), Cost (10)

DIMENSION statement may contain any number of variables. The variables are separate by commas. The DIMENSION statement provides information to the compiler to enable it to reserve memory locations for arrays. It is thus called a specification statement. It is not executable. All the specification statements such as INTEGER, REAL, DIMENSION must be placed at the beginning of the program before all executable statements. The dimensions specified in the DIMENSION statement must be the maximum values that will be ever reached by the subscripts of the variable in the program. The dimension specification of an array can appear only once in a program unit. The name of an array declared in a DIMENSION statement can appear in a type statement or a COMMON statement without dimensioning information.

DIMENSION example

The following DIMENSION statement declares z as an array of 25 elements, a as an array of 36 elements (6 x 6), and ams as an array of 50 elements

(2 x 5 x 5).

DIMENSION z(25), a(6,6), ams(2,5,5)

20.5 DO Statement

A DO loop is a sequence of statements beginning with a DO statement. This has the form:

DO *label*, *var = e1, e2,* [,*e3*]

the square brackets indicating that ',*e3'* may be omitted.

label is the label of an executable statement sequentially following the DO statement called the terminal statement of the DO loop.

var is an INTEGER or REAL variable called the loop control variable.

e1, e2 and *e3* are arithmetic expressions (i.e. INTEGER or REAL constants, variables or more complex expressions).

The sequence of statements beginning with the statement immediately following the DO statement and ending with the terminal statement is called the range of the DO loop.

Execution

A DO loop is executed as follows:

1. The expressions *e1*, *e2* and *e3* are evaluated and if necessary converted to the type of *var*. If *e3* is omitted, a value of 1 is used. The resulting values are called the parameters of the loop. We shall call them *initial*, *limit* and *increment* respectively.

2. *initial* is assigned as a value to *var*.

3. *var* is compared with *limit*, the test depending on the value of *increment* as follows:

Condition tested:

increment > 0 ---> *var* <= *limit*

increment < 0 ---> *var* >= *limit*

If the condition tested is "true", then:

1. the range of the DO loop is executed,

2. *var* is incremented by *increment*,

3. control returns to step 3.

Otherwise: iteration stops and execution continues with the statement following the terminal statement.

Examples:

DO 10, I = 1,5

causes the range of statements beginning with the next and ending with the statement labelled 10 to be executed 5 times.

DO 10, I = 0,100,5

causes the range to be executed 21 times for values of I of 0,5,10...100.

Restrictions

To protect the integrity of the loop structure, there are various restrictions affecting DO loops.

1. *Increment* must not be zero.
2. The terminal statement must be one which is self-contained and allows execution to continue at the next statement. This rules out STOP, END and another DO statement. It is often convenient to end a DO loop with a CONTINUE statement, which has no effect whatever, serving only to mark the end of the loop.
3. The range of a DO loop can be entered only via the initial DO statement. Thus a GOTO cannot cause a jump into the range of a DO loop. However, GOTOs can be included in the range to jump to statements either inside or outside it. In the latter case, this can cause iteration to stop before the control variable reaches the limiting value.
4. The control variable can be freely used in expressions in the range of the loop but it cannot be assigned a value.
5. The loop parameters are the *values* of the expressions *e1, e2* and *e3* on entry to the loop. The expressions themselves are not used. Therefore

if any of *e1, e2* and *e3* are variables, they can be assigned values within the loop without disrupting its execution.

The control variable

As explained under 'Execution' the control variable is incremented and tested at the end of each iteration. Thus, unless iteration is interrupted by a GOTO, the value of the control variable after execution of the loop will be the value which it was assigned at the end of the final iteration. For example, in a loop controlled by the statement:

DO 10, I = 0,100,5

the control variable I is incremented to exactly 100 at the end of the 20th iteration. This does not exceed *limit*, so another iteration is performed. I is then incremented to 105 and iteration stops, with I retaining this value.

If the control variable is REAL, inconsistent results may be obtained unless allowance is made for approximation.

Nested DO loops

DO loops, can be nested, provided that there is no overlapping. (i.e. that the range of each nested loop is entirely within the range of any loop in which it is nested).

- Here is a simple example that prints the cumulative sums of the integers 1 through 10:

```
integer i, n, sum
sum = 0
n = 10
do i = 1, n
                                        sum = sum + i
                                    write(*,*) 'i =', i
                                write(*,*) 'sum =', sum
enddo
```

20.6 Functions and subroutines

Very often, a program has to perform a computation several times using different values, producing a single value each time. In Fortran, such a computation can be defined as a function and referred to by a name followed by a list of the values (called arguments) which it uses, in parentheses, i.e.

name([*argument_list*])

where *argument_list* is an optional list of arguments separated by commas. Note that the parentheses must be included even if a*rgument_list* is omitted, i.e.

name()

Such a function reference can be used in the same way as a variable or array element, except that it cannot be the object of an assignment. Like a variable or array element, a function reference is evaluated and the value obtained is substituted for it in the expression in which it appears. The type of a function is the type of the value so obtained.

The definition of a function must include a definition of its type and the number and types of its arguments. In a function reference the number and type of the arguments must be as defined.

A function reference has an identical form to an array element, and may be used in a similar context. Fortran distinguishes between the two by checking whether the name has been declared as an array, and assuming that it is a function if it has not.

Intrinsic functions

Fortran provides a wide range of intrinsic functions, which are defined as part of the language. Many of them have an argument, or list of arguments, which may be of different types in different references. Most, though not all, of these return a value of the same type as that of their arguments in any reference. For example, the function ABS returns the absolute value of its argument, which may be REAL or INTEGER. Thus ABS(X) returns the absolute value of the REAL variable X as a REAL value, while ABS(N) returns the absolute value of the INTEGER variable N as an INTEGER value

A function of this kind is called a generic function.

External functions

As well as using the intrinsic functions provided by the language,a programmer may create and use his/her own external functions. These functions may be included in the same source file as a program which uses them and compiled along with it, or may be written and compiled separately to obtain separate object files which are then linked to the object version of the program to obtain an executable program, in the same way as the library subprograms.. In either case, the program and functions are entirely independent program units.

The FUNCTION statement

An external function must begin with a FUNCTION statement. This has the form:

[*type*] FUNCTION *name*([*argument_list*])

As before, square brackets indicate that an item is optional.

Example:

FUNCTION AVRAGE(A,B,C)

Type

Each function has a type corresponding to the type of value returned by a reference to it. As for variables, the type of a function may be specified explicitly or assigned implicitly according to the first letter of the function name. For example, the function:

FUNCTION FUN1(*arg1,...*) returns a value of type REAL,

but INTEGER FUNCTION FUN1(*arg1,...*) returns a value of type INTEGER.

The argument list

argument_list is an optional list of dummy arguments, separated by commas. Each dummy argument is a name similar to a variable or array name, which represents a corresponding actual argument used in a function reference. Dummy arguments, and variables used in a function, are defined only within it. They may therefore be identical to variable or array names used in any other program unit. If a dummy argument represents an array, it must appear in a type specification or DIMENSION statement in the function. If it represents a variable, it may appear in a type specification, or may be typed by default.

A function may have no arguments, e.g.

FUNCTION NOARGS()

The function reference

As we have seen, a function reference has the form:

name(*argument_list*)

argument_list is a list of actual arguments, which must match the list of dummy arguments in the FUNCTION statement with respect to the number of arguments and the type of each argument.

For example:

```
REAL X(100)
. . .
RESULT = FUN1(X,J,10)
```

would be a valid reference to the function FUN1(A,B,N) shown above.

If a dummy argument is a variable name, the corresponding actual argument may be any expression of the same type, i.e. a constant, variable, array element or more complex arithmetic expression. If a dummy argument is an array name, the actual argument may be an array or array element. The dimensions of the dummy array may be variable if they are also dummy arguments.

Example:

```
REAL X(5,10)
. . .
Y = FUN(X,5,10)
. . .
END
FUNCTION FUN(A,M,N)
REAL A(M,N)
```

Actual and dummy arguments

The dummy arguments and corresponding actual arguments provide a means of exchanging information between a program unit and a function.

Each actual argument refers to a word or other unit of storage. However, no storage is reserved for a dummy argument; it is simply a name. When a function reference is evaluated, the address of each actual argument is passed to the function, and the corresponding dummy argument is set to refer to it. The dummy argument may therefore be used in the function as a variable or array referring to the same unit of storage as the actual argument.

Thus if a dummy argument represents a variable, its value on entry to the function is that of the corresponding actual argument when the function is referenced. If its value is changed in the function by an assignment or READ statement, the actual argument will be correspondingly changed after the function reference has been evaluated.

Arrays as arguments

If a dummy argument is an array, the corresponding actual argument may be an array or array element. In the former case, the elements of the dummy array correspond to the elements of the actual array in the order of their storage in

memory. This, however, does not imply that the subscripts are identical, or even that the two arrays have the same number of subscripts.

For example, suppose that the function:

```
FUNCTION FUN(A)
REAL A(9,6)
. . .
END
```

is referenced by program MAIN as follows:

```
PROGRAM MAIN
REAL X(100),Y(0:5,-10,10)
. . .
F1 = FUN(X)
F2 = FUN(Y)
. . .
END
```

Evaluation of a function

Once the dummy arguments have been initialized as described above, the statements comprising the body of the function are executed. Any statement other than a reference to the function itself may be used. At least one statement must assign a value to the function name, either by assignment, or less commonly, by a READ statement. Execution of the function is stopped, and control returned to the program unit containing the function reference, by a RETURN statement, written simply as:

```
RETURN
```

The value of the function name when RETURN is executed is returned as the function value to the program unit containing the function reference.

Statement functions

If a function involves only a computation which can be written as a single statement, it may be declared as a statement function in any program unit which refers to it. The declaration has the form:

name(*argument_list*) = *expression*

where:

name is the name of the statement function.

argument_list is a list of dummy arguments.

expression is an expression which may include constants, variables and array elements defined in the same program unit, and function references.

The declaration must be placed after all type specifications, but before the first executable statement.

Example:

Function DGTORD might be declared as a statement function in the program ANGLES:

DGTORD(DEGREE) = DEGREE*ATAN(1.0)/45.0

Subroutines

A SUBROUTINE is a subprogram similar in most respects to a function. Like a function, a subroutine has a list of dummy arguments used to exchange information between the subroutine and a program unit referring to it. Unlike a function, a subroutine does not return a value via its name (and therefore has no type), but it may return one or more values via its arguments. A subroutine subprogram begins with a SUBROUTINE statement and ends with END. The SUBROUTINE statement has the form:

SUBROUTINE *name*[(*argument_list*)]

where *name* and *argument_list* have the same meanings as in the FUNCTION statement.

The square brackets indicate that the item (*argument_list*) is optional, i.e. a subroutine may have no arguments, in which case the SUBROUTINE statement is simply:

SUBROUTINE *name*

As for a function, a subroutine must include at least one RETURN statement to return control to the program unit referring to it.

A subroutine is referenced by a CALL statement, which has the form:

CALL *name*[(*argument_list*)]

where *argument_list* is a list of actual arguments corresponding to the dummy arguments in the SUBROUTINE statement. The rules governing the relationship between actual and dummy arguments are the same as for functions. Functions (intrinsic and external) and subroutines are often called procedures.

Procedures as arguments

A program unit can pass the names of procedures as arguments to a function or subroutine. The calling program unit must declare these names in an EXTERNAL statement for external procedures (functions or subroutines), or INTRINSIC statement for intrinsic functions. The statements have the form:

EXTERNAL *list.*

INTRINSIC *list*

respectively, where *list* is a list of external procedures, or intrinsic functions respectively. If an actual argument is a procedure name, the corresponding dummy argument may be:

1. used as a procedure in a CALL statement or function reference,

   or:

2. passed as an actual argument to another procedure. In this case, it must be listed in an EXTERNAL statement.

In this way, a procedure name can be passed from one procedure to another for as many levels as required.

20.7 COMMON and DATA Statement

The **COMMON** statement specifies blocks of physical storage, called common blocks that may be accessed by any of the functions or subroutines of a program. Thus, the COMMON provides a global facility

based on storage association.

The common blocks may be named and are called named common blocks, or may be unnamed and are called blank common.

Lengthy argument lists in subroutines and user-defined functions can occur as modularised programs grow ever larger, requiring more and more information to

be passed between program units. The COMMON block, a piece of shared memory in the computer, is another method for passing information between program units.

Data stored in a COMMON block is not passed between program units via argument lists, but through the COMMON statement near the beginning of each program unit.

There are two types of COMMON blocks: blank and named. A program may contain only one blank COMMON

block but any number of named COMMON blocks. Every COMMON block must be declared in every program unit in which the information stored therein is needed. In addition, the unique blank COMMON block must be declared in the main program. The blank COMMON block is set up with the statement

COMMON *variable-list*

and the named COMMON block is declared by

COMMON /*name*/ *variable-list*

where the *name* between the forward slashes is the name of the named COMMON block.

Every subroutine or user-defined function that uses data stored in the COMMON block, blank or named, must have a similar statement to those above. The variable names do not need to match between program units but it is vital that their types and the order in which they appear in the list are identical.

Blank Versus Named

Declaration

Blank COMMON blocks must be declared in the main program. It is not necessary to declare named COMMON blocks in the main program unless they are used there.

Length

Blank COMMON blocks need not be the same length in different program units. However, a named COMMON block must be exactly the same length wherever it appears. This means that some knowledge about how the computer stores

information is necessary. That is, the programmer must know how much storage each variable or array takes in order to ensure that the named COMMON blocks are the same length.

Initialization

Variables in blank COMMON blocks may be initialized with READ or assignment statements but not with a DATA statement. The same restrictions apply to named COMMON blocks with one important difference: named COMMON blocks may be initialised in a special nonexecutable subroutine called a BLOCK DATA.

Thus the COMMON statement declares variables and arrays so that they are put in a storage area that is accessible to multiple program units, thus allowing program units to share data without using arguments.

A storage sequence, composed of a series of storage units that are shared between program units, is referred to as *common storage*. For each common block, a common block storage sequence is formed consisting of the storage sequences of all entities in the list of variables and arrays for that common block. The order of the storage sequence is the same as its order of appearance in the list.

COMMON examples

The following equivalent statements define a blank common block. Note that these two COMMON statements cannot appear in the same program unit.

COMMON //F,X,B(5)

COMMON F,X,B(5)

The following declaration:

COMMON /LABEL/NAME,AGE,DRUG,DOSE//Y(33),

Z,/RECORD/,DOC, 4 TIME(5), TYPE(8)

makes the following COMMON storage assignments:

NAME, AGE, DRUG, and DOSE are placed in common block LABEL.

Y and Z are placed in a blank common block.

DOC, TIME, and TYPE are placed in a common block RECORD

The DATA statement

The **DATA** statement is a non-executable statement used to initialize variables. It is particularly useful for initializing arrays.

It has the form:

DATA *variable_list*/*constant_list*/ [,*variable_list*/*constant_list*/] ...

(The square brackets and ellipsis have their usual meaning.)

Each *variable_list* is a list of variables, and each *constant_list* a list of constants, separated by commas in each case. Each *constant_list* must

contain the same number of items as the preceding *variable_list* and corresponding items in sequence in the two lists must be of the same type.

The DATA statement assigns to each variable in each *variable_list* a value equal to the corresponding constant in the corresponding

constant_list. For example:

DATA A,B,N/1.0,2.0,17/

assigns the values 1. and 2. respectively to the REAL variables A and B, and 17 to the INTEGER variable N.

A constant may be repeated by preceding it by the number of repetitions required (an integer) and an asterisk. Thus:

DATA N1,N2,N3,N4/4*0/

assigns a value of zero to each of the variables N1,N2,N3 and N4.

Items in a *variable_list* may be array elements. Thus, if A is an array of dimension 20, the DATA statement:

DATA A(1),A(2),A(3),A(4)/4*0.0/,A(20)/-1.0/

assigns a value of zero to the first four elements, -1.0 to the last element, and leaves the remaining elements undefined.

DATA statements can be placed anywhere in a program after any specifications. It is probably best to put them immediately before the first executable statement. Wherever they may be, they cause initialisation *when the program is loaded* (before execution begins). Therefore they can only be used to *initialise* variables and not to re-assign values to them throughout execution of the program. For this purpose, assignment statements or READ statements must be used.

20.8 Summary

Logical Variables : There are two LOGICAL constants, defined as .TRUE. and .FALSE..A LOGICAL variable can be assigned either of these values. It may not be assigned a value of any other type.

Double precision variables: A REAL variable or constant occupies one word of storage and this limits its accuracy. When greater accuracy is required, double precision variables and constants may be used. These occupy two words of storage and can store a greater number of significant digits.

Subscripted variables and their DIMENSION: A *subscripted variable* is the combination of the array name and a subscript. The DIMENSION statement specifies the symbolic names and dimension specifications of arrays.

COMMON and DATA statement : The COMMON statement specifies blocks of physical storage, called common blocks that may be accessed by any of the functions or subroutines of a program. Thus, the COMMON provides a global facility based on storage association. The DATA statement is a non-executable statement used to initialize variables.

DO statement:A DO loop is a sequence of statements beginning with a DO statement.

Function and Subroutine: Functions and subroutines are procedures. Functions and subroutines are FORTRAN's subprograms. Most problems that require a computer program to solve them are too complex to sit down and work all the way through them in one go. Using subprograms allows you to tackle bite size pieces of a problem individually. Once each piece is working correctly you then put the pieces together to create the whole solution. To implement functions and subroutines, first write a main program that references all of the subprograms in the desired order and then start writing the subprograms. The purpose of a function is to take in a number of values or arguments, do some calculations with those arguments and then return a single result.

20.9 Review Questions

1. Define Function and subroutine.
2. Give the differences between function and subroutine.
3. Describe how logical variables are used.

4. What is the use of Double Precision Variables?
5. Show how the DO loop is executed.
6. What do you mean by Subscripted Variables?
7. Describe the use of Dimension statement.
8. Explain how Common and Data Statements are used.

2.10 References

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Unit - 21: Programming in Chemistry I

Structure of Unit:

21.0 Objectives

After complete study and understanding of this unit, you should be able to :

- Understand the technique of writing BASIC programs for some chemistry applica tions
- Able to write BASIC language programs for many more chemistry applications
- Understand the technique of writing C programs for some chemistry application

- Able to write C language programs for many more chemistry applications

21.1 Introduction

In order to gain skills in the BASIC language programming for chemical applications, the first step is to study existing programs for some typical applications. It is with this intention, six typical applications are selected and BASIC language programs are developed for these applications. A study of these programs will help the student to develop skills for writing BASIC programs for similar applications.

Developing C language programs requires acquiring I 'ogramming skills. these skills can be acquired by studying existing programs for some typical applications. It is with this intention, C language programs are developed for six applications in chernistr '. AlSO the. e pro- grams are explained with some practical problems and the steps involved in the program execution to obtain the desired results.

Examples of some program code in BASIC language

21.1 Determine of Lattice Energy of A Crystal

The Lattice Energy of a crystal is calculated by the Born-Lande expression as given below.

$$E = \frac{N_A . A Z^2 . e^2 (1 - 1/n)}{4 P e_0 r}$$

where E = Lattice Energy

N_A = Avagadro number

A = Modeling constant

Z = charge of the ion

e = charge of electron

n = Born exponent

r_0 = Internuclear distance in the crystal

4P e_o = 1.121 x 10-10 N-1 m? c2

Example

Calculate the Lattice Energy of NaCI with the following values,

N_A = 6.023 x 10^{23} per mole

A = 1.74756, Z =1, r_o = 0.2814, n =8

Enter the following data

e = 1.602 x10 $^{-19}$, 4P e_o = 1.121 x 10^{-10}

The following is the BASIC Language program, which calculates the lattice energy

```
10 REM CALCULATION OF LATTICE ENERGY OF A CRYSTAL
20 LET NA=6.023e23
30 LET A=1.74756
40 LET C= 1.121e-l 0
50 PRINT "ENTER CHARGE OF ION, CHARGE OF ELECTRON"
60 INPUT Z,E
70 PRINT "ENTER BORN EXPONENT, INTERNUCLEAR DISTANCE"
80 INPUT N,RO
90 LET LE=(NA*A*Z-2*E-2(1-1IN))/C
100 PRINT "LATTICE ENERGY OF THE CRYSTAL =";LE
110 STOP
120 END
```

When the program is compiled and executed, the following message appears on the screen

Enter the charge of ion, charge of electron

Enter the following values

1,1.602e-19

and press Enter Button

Next the following message appears on the screen

Enter Born Exponent, ion nuclear distance

8,0.2814

Then the program calculates and displays the result:

Lattice Energy of the crystal:

Note:

The above program is a general purpose program and can be used to calculate the Lattice Energy of any crystal

21.2 Calculation of Critical Constants of Vander Waals'gases

The critical constants Tc, Pc and Vc can be calculated from the Van Der Waals constants a and b by the following expressions:

Critical Temperature Tc = 8a127Rb Critical Pressure Pc = a/27b2

Critical Volume Vc = 3b

The following is the BASIC language program to calculate the critical constants Tc, Pc and Vc from the Van Der Waals constants a and b:

```
10 REM CALCULATION OF CRITICAL CONSTANTS OF
20 REM VAN DER WAALS GASES
30 PRINT "ENTER THE GAS NAME"
40 INPUT NAME$
```

```
50 PRINT "ENTER THE VAN DER WAALS CONSTANTS A AND B"

60 INPUT A, B

70 R= 0.082

80 Vc = 3 * B

90 Tc = (8* A)/(27*R *8)

100 Pc = A/(27*W  Λ2)

110 Vc=3*B

120 "PRINT "CRITICAL VOL OF GAS ="; Vc

130 PRINT "CRITICAL TEMP. OF GAS ="; Tc

140 PRINT "CRITICAL PRES. OF GAS = "; Pc

150 STOP

160 END
```

Example

Find the critical constants V c, Tc, and Pc for the acetylene gas whose Van Der Waals constant a and b are a = 4.400, b = 0.0515

Program Execution

When the above program is compiled and executed, the following message will appear on the screen:

Enter the Gas Name:

Enter the data

ACETYLENE

and press the enter button

Then the following message will appear on the Sceen

Enter the Van Der Waals constants A and B

Enter the following data

4.400 0.0515

and press the Enter Button

Then the program calculates and displays the following results

Critical Vol. Of Gas = 0.1545

Critical Temp. of Gas = 308.7151

Critical Pres. of Gas = 61.44329

Examples of some program code in C language

21.3 Van Der Waals Equation For Gases

For real gases the Pressures, Volume, Temperature and moles of the gas are related by the following equation

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

Where P = Pressure

V=Volume

T = Temperature

n = No. of moles

R =: Ideal gas law constant

a and b ale called Van Der Waals constant

$$P=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$$

The following is the C language program which calculates the pressure of a gas, when all the other quantities are known:

```
# include < stdio.h>

main ()

{

float p,n,r,t, v,a,o;

printf{"Enter the values for Volume, Temperature and moles of the gas\n");

Scanf("%f%f%f", &v,&t,&n );

printt"Enter the values r Gas Law constant, Van Der Waal Constant a and Van Der Waals

constant b\n");

scanf("%f%f%f", &r,&a,&b);

p= (n*r*t)/(v-n*b) - (n*r*a}/(n*v);

printf(“pressure of the gas ==%f atm",p);

}
```

Example

We can calculate the pressure of 2.00 moles of carbondioxide gas at 298 K in a 5.00 L

container. The Van Der vaals constants for carbondioxide are:

a - 3.5 92 L^2 ahm/mol^2 and b = 0.04217 L/mol. the Ideal gas law constant (R) being 0.082/L. atm

From the above problem we have

n =2, T = 298, V = 5

a = 3.592, b = 0.04217, R =.00821

Program Execution

When the above program is compiled and executed, 'he following message will appear on the screen.

Enter the values for Volume, Temperature and moles of the gas

Enter the data of the above problem as given below:

5 298 2

and press Enter Button

Then the next message will appear on the screen as given below:

Enter the value for Gas constant,

Now enter these value as given below:

0.0821 3.592 0.04217

and press Enter Button.

The program now calculates the pressure (If the gas and The pressure of the gas = 9.77 atm

Note:

The above program is a general program for calculating the pressure of gas, when known the other six quantities.

21.4 Calculation of Lattice Energy of Crystals

Born and Lande provided the following formula for the calculation of Lattice Energies of crystals.

$$\Delta U_{Latice} = \frac{N_A A Z^2 e^2 (1 - 1/n)}{4\pi\varepsilon_0 r_0}$$

where NA = Avagadros Numbers

A = Maldelung constant

Z = Ionic charge number

e = Electronic charge

$4\pi\varepsilon_0 r_0 = 1.1126 \times 10^{-10} N^{-1} m^{-2} c^2$

r = Distance of Separation of ions in the crystal

n = Born exponent

The following is the C Language program, which calculates the Lattice Energy of crystals, when all the quantities on the right hand side of the above expression are-known.

```
# include < stdio.h>

main ( )

{double lattice, na, a, z,e,ro, n;

printfi=Enter the values of Avagadro Number, Model ing constant, Dist of separation of ions in

the crystalm");

scanf("%f%f%f", &na,&a,&ro);

printf("Enter the values of Born Exponent, Electronic charge and Ionic charge\n");

scanf("%f%f%f" , &n,&e,&z);

lattice = (na*a*z*z*e*e )*(1-1 /n)/(( 1.1126e-10)*ro);

printf("Lattice Energy of the given crystal = %fKjmol-1", lattice);

}
```

Example

Calculate the lattice energy of NaCI, with the following values:

Avagadros Number A = 6.023 x 1023 per mole

Madelung constant A = 1.748

Distance of Separation of ions in the crystal r_o = 0.2814 nm

Born exponent n = 8

$4P\hat{I}_0 r_0 = 1.1126 \times 10^{-10} N^{-1} m^{-2} c^2$ Electronic charge e = 1.602 ' 10 -19 C

Electronic chagre e = 1.602 X 10^{-19}C

Ionic charge no. Z = 1

Program Execution

When the above program is compiled and executed, the following message will appear on the screen:

Enter the values of Avagadro Number, Madelung constant, Distance of separation of ions in the crystal:

Enter the data of the above example as given below:

6.023 E23 1.748 0.2814

and press Enter Button

Then the next message will appear on the screen as given below:

Enter the values of Born Exponent, Electronic charge and Ionic charge

Enter the values as given below:

8 1.602E-19 1

and press Enter Button

The program now calculates the Lattice energy for NaCl and displays the result as given below: '

Lattice energy of the given crystal = 756 Kjmol^{-1}

21.5 First Order Rate Constant From Kinetic Data

The first order rate constant K is generally expressed as

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

where K = First order rate constant

t = Temperature

a = Initial concentration of the reactant A

x = moles of A already converted to the product after time t

The following is the C program, which calculates the first order rate constant from the kinetic data

```
<stdio.h>

main ( )

{

double t[10], u[10], K, vmax;

int i, n;

printf("Enter the number of observations\n");

scanf("%d",&n);

printf("Enter the values of Temperature and Volume respectively\n");

for(i=<n;i++) ,

{

scanf("%f",&t[I],&v[I]);

}

vmax = v[n-I];

printf("temp\t k\n\n");

for(i=O;i‹n-I), i++)

K=(2.303/t[i])* log (vmax/(vmax-v[i]));

printf("%f\t%f\n", t[i],K);
```

}

}

Example

Decomposition of diazobenzone chloride was followed at constant temperature by mea- suring the volume of nitrogen evolved at suitable intervals. The readings thus, obtained are given below:

Time from start:	0	20	55	70	8	minutes
Volume of N_2:		0	10	15	33	162 ml

Calculate the rate constant and order of the reaction

Program Execution

When the above program is compiled and executed, the following message will appear on the screen:

Enter the number of observations

Enter the following data

5

and press the Enter Button

Then the next message will appear on the screen as given below:

Enter the values of Temperature and Volume respectively

Enter the data as follows:

0,0

20,10

55,15

70,33

9999,162

and press the Enter Button

Then the program will calculate the rate constant for different times and displays tl' results as follows:

Time	K
0	-
20	3.22e-3
50	3.36e-3
70	3.26e-3

Note

the above program is a general program and can be used for any kinetic data consisting of Time and Volume.

21.6 Calculatin of The Average Value of The Rate Constant For A Second Order Reaction

The average rate constant of a second order reaction involving equal initial concentrations of reactions is given by

$$K = \frac{1}{n}\left[\sum_{i=1}^{n}(1/at_1)\frac{X_i}{a - X_i}\right]$$

where K, is the Average Rate Constant, t; is the time for which the reaction has taken place to consume x amount of the reactant and a is the initial concentrating the reactant

The above equation can be written as

$$K = \frac{1}{n}\left[\sum_{i=1}^{n}(1/at_1)\left(\frac{X_i}{a}\right)\left(1-\frac{X_i}{a}\right)\right]$$

where x_i/a is the fraction reacted

The following is the C language program for the calculation of the Average value of the rate constant for a second order reaction

```
#include<stdio.h>

main ( )

{

double y[20], p[20], r[20], i[20], p[20], incon, s=0

int n,l;

printf("Enter the Name of the reaction\n");

scanf("%s", n$);

printf("Enter initial concentration\n");

scanf("%d," &incon) ,

printf("Enter No of observations\n");'

scanf("%f" ,&n);

for(i<0;i<n;i++)

{

printf("Enter fraction of reactants consumed");

scanf("%f',&y[i]);

}
```

```
for(i=0;i<n;i++)
{
printf("Enter Time for which reaction has taken");
scanf("%f' ,&t[I]);
for(i=0;i<n;i++)
{
p[i]=incon*t[i];
1[i]= 1-y[i];
r[i]=y[i]/(p[i]*I[i]);
s=s+r[i];
}
ratecons=s/n;
printf("Average Rate Constant for the second order reaction =%f\n",ratecons):
printf("LITER/MOLE/SEC"):
}
}
```

Example

Calculate the average rate constant for the second order reaction of Alkaline hydrolysis of ethyl nitrobenzoate with the following data:

Initial concentration = 0.01

Fraction of reactants consumed	Time of Reaction
0.3295	120
0.488	240

0.690	530
0.7035	600

Program Execution

When the above program is executed, the following message will appear on the screen:

Enter the Name of the Reaction:

Enter the data

Alkaline hydrolysis of Ethyl nitrobenzoate

And press the Enter Button

Next the following message appears on the screen

Enter no. of observations

Enter the data

4

and press Enter Button

Next the following message appears on the screen:

Enter fraction of Reactants consumed

Enter the following data

0.3295

0,488

0.690

0.7035

and press the Enter Button

Next the following message appears on the screen

Enter the Time for which the reaction has taken

Enter the following data

120

240

530

600

and press Enter Button

The program then calculates and displays the following results

Average Rate constant for second order reaction = 0.0811033 LITER/MOLE/SEC

21.7 Calculation of Dissociation Constant of A Weak Acid

The dissociation constant of a weak acid is given by the expression

$K = \alpha^2 C(1- \alpha)$

Where a is the degree of dissociation and

C is the concentration

The following is the C language program, which calculates the dissociation constant from the degree of dissociation and concentration data.

```
#include<stdio.h>

main ( )

{

double al[10], c[ 10], sum = 0.0, discon;

int i;

char name[80];

printf("Enter the Name of the electrolyte\n");
```

```
scanf("%s",name);
printf(" Enter five degree of dissociation and concentration Values\n");
for(i=0ii<5; i++)
{
scanf("%f%f",&al[i],&c[i]);
sum=sum+al[i] *al[i] *c[i]/(1-al[i]);
}
discon=sum/5.0;
printf("The Average Value of Dissociation Constant for");
pri ntf("%s=%f\n" ,name,discon);
}
```

Example

Calculate the dissociation constant for acetic acid from the following data

Program Execution

When the program is executed, the following message appears on the screen

Enter the Name of the Electrolyte

Enter

Acetic Acid

And press Enter Button

Next the following message appears on the screen

Enter five deg. of dissociation and cone. Values'

Enter five values and press Enter Button

Then the program calculates and displays the Average Value of Dissociation Constant

21.8 Summary

An attempt is made in this unit to write BASIC language programs for simple applications like summation of series, least square fit of XY data to a straight line, calculation of activation energy using Arrhenius equation by least square fitting, determination of lattice energy of a crystal, determination of equivalent conductivity of an electrolyte at a definite concen-tration, calculation of critical constants of Van Der Waals gases etc. A thorough understanding of these programs will help the student to develop BASIC programs for many other chemical applications. In this unit, C Language programs are developed for some typical applications like Van Der Waals equation for real gases, calculation of energy of activation, calculation of lattice energy of crystals first order rate constant from kinetic data, calculation of rate constant for a second order reaction. Calculation of dissociation constant of a acid. Thorough under- standing of these program" skill helps the student to acquire skill. Develop C language programs for similar applications.

21.9 Review Questions

1. Write the program for the calculation of critical controls of van der Waals Gases using BASIC language.
2. Write the program for the calculation of lattice energy of a crystal using BASIC language.
3. Write a flow chart and a program for the calculation of rate constant of a first order using C language.
4. Write a flow chart and a program for the calculation of rate constant of a second order using C language.
5. Write the program for the calculation of lattice energy of a crystal using C language.
6. Write the program for the calculation of dissociation constant of a weak acid using C language.

7. Write a program to find the maximum among three numbers using C language

21.10 References

Unit 22 Programming in ChemistryII

Structure of Unit

22.0 Objective

After complete study and understanding of this unit, you should be able to :

- Understand Hckel Molecular Orbital Theory
- Knowledge of computer progremme codes for Hückel Molecular Orbital Theory
- Deep understanding of Chemical database
- Cambridge structure database
- Knowledge about chemspider

22.1 Introduction

The unit deals with the Hückel Molecular Orbital Theory. In the 1930's a theory was devised by Huckel to treat the electrons of aromatic hydrocarbon systems such as benzene and naphthalene. This theory can also be applied to conjugated systems. Huckel theory can lead to some interesting, valuable predictions even though it is not a quantitative theory. The underlying premise is that the reactive properties of molecules result from the character of the highest energy electrons, which are, in the case of conjugated molecules, the electrons. The unit describe the computer programme related Hückel molecular orbital theory and some examples are helpful for learners o understand these function then the unit includes the chemical database their types, database related to define structure features, unit describs elementary structures i.e. bond length, bond angle, dihedral angle.

22.2 Diagonalization and Hückel Molecular Orbital Theory

Solving the HMO secular equation for complex molecules can become very difficult by hand.

However, we may enlist the help of the computer. The solutions to the secular equation for

butadiene:

$$\begin{pmatrix} \alpha\text{-}E & \beta & 0 & 0 \\ \beta & \alpha\text{-}E & \beta & 0 \\ 0 & \beta & \alpha\text{-}E & \beta \\ 0 & 0 & \beta & \alpha\text{-}E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0 \qquad 1$$

are E1, E2, …. The energies may also be obtained as the eigenvalues of the equation:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

where we have just rearranged Equation 1 to put the energy term on the right-hand side. The

mathematical procedure for solving Equation 2 is called diagonalization. There are several

efficient ways to diagonalize matrices; our computer program uses Jacobi's method.

Since we don't know the values of α and β, we must rewrite Equation 1 in a slightly different

way. Dividing both sides of Eq. 1 by β gives:

$$\begin{pmatrix} \frac{(\alpha-E)}{\beta} & 1 & 0 & 0 \\ 1 & \frac{(\alpha-E)}{\beta} & 1 & 0 \\ 0 & 1 & \frac{(\alpha-E)}{\beta} & 1 \\ 0 & 0 & 1 & \frac{(\alpha-E)}{\beta} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

We now define xi = (Ei–α)/β . Substituting x into Equation 3 gives:

$$\begin{pmatrix} -x_i & 1 & 0 & 0 \\ 1 & -x_i & 1 & 0 \\ 0 & 1 & -x_i & 1 \\ 0 & 0 & 1 & -x_i \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

Once again, rearranging Equation 4 to put the x terms on the right-hand side gives:

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = x_i \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

where the eigenvalue is x_i

and:

$E_i = \alpha + x_i \beta$

The computer program to diagonalize a matrix is available on the Web at

http://www.colby.edu/chemistry/PChem/eigen.html

one need to do is to input the Hückel matrix with 0's on the diagonal (for carbon; see below

for heteroatoms). The HMO matrix is always symmetric, so we only need to input the lower

triangular part.

Example:

Let's use butadiene as an example: C_A=C_B–C_C=C_D. The input for butadiene is:

0

1 0

0 1 0

0 0 1 0

The output is:

Eigenvector 1: Eigenvalue =1.61803

0.371748

0.601501

0.601501

0.371748

Eigenvector 2: Eigenvalue =0.618034

-0.601501

-0.371748

0.371748

0.601501

Eigenvector 3: Eigenvalue =-0.618034

0.601501

-0.371748

-0.371748

0.601501

Eigenvector 4: Eigenvalue =-1.61803

-0.371748

0.601501

-0.601501

0.371748

Giving the following wavefunctions and energies, from highest energy to lowest:

Eigenvector 4: E= $\alpha - 1.6180\ \beta$

$\Psi_4 = -0.371748\ p_{zA} + 0.601501\ p_{zB} - 0.601501\ p_{zC} + 0.371748\ p_{zD}$

Eigenvector 3: E= $\alpha - 0.618034\ \beta$

$\Psi_3 = 0.601501\ p_{zA} - 0.371748\ p_{zB} - 0.371748\ p_{zC} + 0.601501\ p_{zD}$

Eigenvector 2: E= $\alpha + 0.618034\ \beta$

$\Psi_2 = -0.601501\ p_{zA} - 0.371748\ p_{zB} + 0.371748\ p_{zC} + 0.601501\ p_{zD}$

Eigenvector 1: E= $\alpha + 1.61803\ \beta$

$\Psi_1 = 0.371748\ p_{zA} + 0.601501\ p_{zB} + 0.601501\ p_{zC} + 0.371748\ p_{zD}$

Heteroatoms

Heteroatoms are introduced into the HMO matrix using two parameters, h and k. The diagonal element is the Coulomb integral, which for carbon is α. The off-diagonal elements are the resonance integrals, which for directly bonded carbon atoms are β. The diagonal element for a heteroatom is changed to $\alpha + h\ \beta$ and the off-diagonal element for directly bonded atoms is changed to $k\beta$. A table of h and k is given below.

Atom	Bond Type	π electrons for atom	h	k
C	-C=C-	1	0	1
NFA	-C=N- (pyridine)	1	0.5	1.0
N	=C-N< (pyrrole)	2	1.5	0.8
N	-N=N- (azo)	1	1.0	1.0
O	-C=O (carbonyl)	1	1.0	1.0
O	=C-O- (furan)	2	2.0	0.8
F	=C-F	2	3.0	0.7
Cl	=C-Cl	2	2.0	0.4
Br	=C-Br	2	1.5	0.3
S	=C-S- (thiophene)	2	1.5	0.8

For example, acrolein, $C_A=C_B-C_C=O_D$, has four total pi electrons and the input matrix is:

0

1 0

0 1 0

0 0 1 1

The lowest energy orbital is

Eigenvector 1: E=1.87939

0.228013

0.428525

0.57735

0.656539

The coefficient for oxygen of 0.656539 shows that extra electron density resides on the oxygen,

because of its larger electronegativity.

Another example is vinyl flouride, $C_A=C_B-F_C$, with four total pi electrons and the input matrix:

0

1 0

0 0.7 3

The two bonding MO's are:

Eigenvector 1: E=3.17155

0.0748418

0.237365

0.968533

Eigenvector 2: E=0.890577

0.729234

0.649439

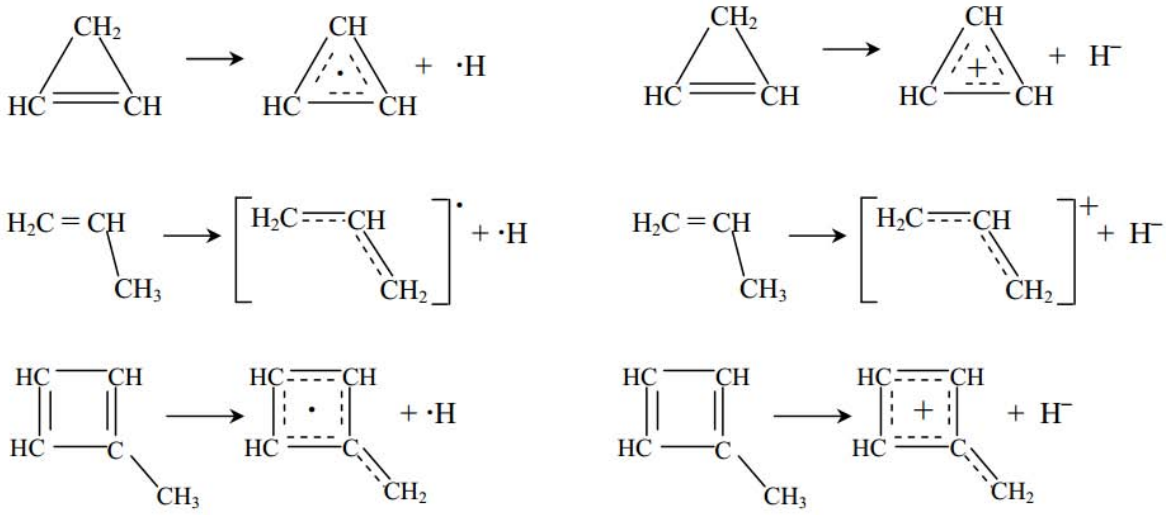
-0.215513

---

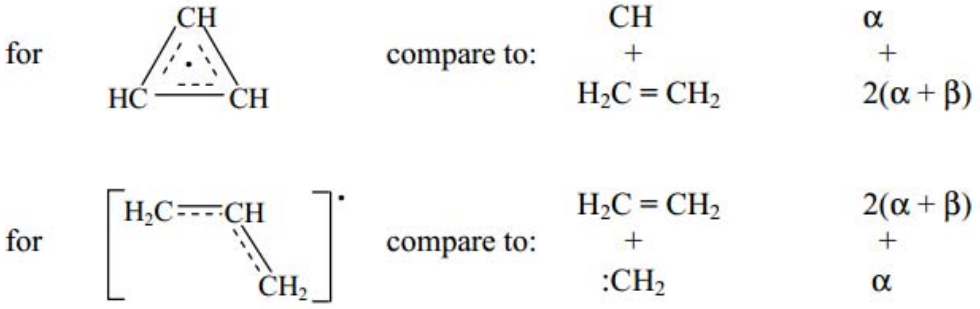
with the lowest energy orbital being primarily a lone-pair on fluorine and the next higher bonding orbital being primarily the double bond on the two carbons.

Ions and Free Radicals

Ions and free radicals can also be studied. Example odd electron radicals are shown at left below, and even electron ions are shown at right.



The only major difference compared to stable closed-shell systems is that the calculation of the π-delocalization energy of an odd-electron species includes a CH2 or CH fragment for the localized reference system. The corresponding energy of the localized fragment is just the energy of a single p-electron in an atomic pz orbital; which is just α. For example:



For the cationic even-electron species the corresponding CH^+ or CH_2^+ fragment does not have a p_z-electron to donate to the π-system. In other words, the contribution of a CH^+ or CH_2^+ fragment is zero. In short, the α part of the difference always cancels out giving the π-delocalization energy as a multiple of β.

22.3 Chemical Database

A chemical database is a database specifically designed to store chemical information. This information is about chemical and crystal structures, spectra, reactions and syntheses, and thermophysical data.

Types of chemical databases

Chemical structures

Chemical structures are traditionally represented using lines indicating chemical bonds between atoms and drawn on paper (2D structural formulae). While these are ideal visual representations for the chemist, they are unsuitable for computational use and especially for search and storage. Small molecules (also called ligands in drug design applications), are usually represented using lists of atoms and their connections. Large molecules such as proteins are however more compactly represented using the sequences of their amino acid building blocks. Large chemical databases for structures are expected to handle the storage and searching of information on millions of molecules taking terabytes of physical memory.

Literature database

Chemical literature databases correlate structures or other chemical information to relevant references such as academic papers or patents. This type of database includes STN, Scifinder, and Reaxys. Links to literature are also included in many databases that focus on chemical characterization.

Crystallographic database

Crystallographic databases store x-ray crystal structure data. Common examples include Protein Data Bank and Cambridge Structural Database.

NMR spectra database

NMR spectra databases correlate chemical structure with NMR data. These databases often include other characterization data such as FTIR and mass spectrometry.

Reactions database

Most chemical databases store information on stable molecules but in databases for reactions also intermediates and temporarily created unstable molecules are stored. Reaction databases contain information about products, educts, and reaction mechanisms.

Thermophysical database

Thermophysical data are information about phase equilibria including vapor–liquid equilibrium, solubility of gases in liquids, liquids in solids (SLE), heats of mixing, vaporization, and fusion. caloric data like heat capacity, heat of formation and combustion, transport properties like viscosity and thermal conductivity

22.4 Chemical structure representation

There are two principal techniques for representing chemical structures in digital databases As connection tables / adjacency matrices / lists with additional information on bond (edges) and atom attributes (nodes), such as:

MDL Molfile, PDB, CML

As a linear string notation based on depth first or breadth first traversal, such as:

SMILES/SMARTS, SLN, WLN, InChI

These approaches have been refined to allow representation of stereochemical differences and charges as well as special kinds of bonding such as those seen in organo-metallic compounds. The principal advantage of a computer representation is the possibility for increased storage and fast, flexible

Substructure

Chemists can search databases using parts of structures, parts of their IUPAC names as well as based on constraints on properties. Chemical databases are particularly different from other general purpose databases in their support for sub-structure search. This kind of search is achieved by looking for subgraph isomorphism (sometimes also called a monomorphism) and is a widely studied application of Graph theory. The algorithms for searching are computationally intensive, often of O (n3) or O (n4) time complexity (where n is the number of atoms involved). The intensive component of search is called atom-by-atom-searching (ABAS), in which a mapping of the search substructure atoms and bonds

with the target molecule is sought. ABAS searching usually makes use of the Ullman algorithm or variations of it (i.e. SMSD. Speedups are achieved by time amortization, that is, some of the time on search tasks are saved by using precomputed information. This pre-computation typically involves creation of bitstrings representing presence or absence of molecular fragments. By looking at the fragments present in a search structure it is possible to eliminate the need for ABAS comparison with target molecules that do not possess the fragments that are present in the search structure. This elimination is called screening (not to be confused with the screening procedures used in drug-discovery). The bit-strings used for these applications are also called structural-keys. The performance of such keys depends on the choice of the fragments used for constructing the keys and the probability of their presence in the database molecules. Another kind of key makes use of hash-codes based on fragments derived computationally. These are called 'fingerprints' although the term is sometimes used synonymously with structural-keys. The amount of memory needed to store these structural-keys and fingerprints can be reduced by 'folding', which is achieved by combining parts of the key using bitwise-operations and thereby reducing the overall length.

Conformation

Search by matching 3D conformation of molecules or by specifying spatial constraints is another feature that is particularly of use in drug design. Searches of this kind can be computationally very expensive. Many approximate methods have been proposed, for instance BCUTS, special function representations, moments of inertia, ray-tracing histograms, maximum distance histograms, shape multipoles to name a few.

Registration systems

Databases systems for maintaining unique records on chemical compounds are termed as Registration systems. These are often used for chemical indexing, patent systems and industrial databases. Registration systems usually enforce uniqueness of the chemical represented in the database through the use of unique representations. By applying rules of precedence for the generation of stringified notations, one can obtain unique/'canonical' string representations such as 'canonical SMILES'. Some registration systems such as the CAS system make use of algorithms to generate unique hash codes to achieve the same objective. A key

difference between a registration system and a simple chemical database is the ability to accurately represent that which is known, unknown, and partially known. For example, a chemical database might store a molecule with stereochemistry unspecified, whereas a chemical registry system requires the registrar to specify whether the stereo configuration is unknown, a specific (known) mixture, or racemic. Each of these would be considered a different record in a chemical registry system. Registration systems also preprocess molecules to avoid considering trivial differences such as differences in halogen ions in chemicals. An example is the Chemical Abstracts Service (CAS) registration system.

Tools

The computational representations are usually made transparent to chemists by graphical display of the data. Data entry is also simplified through the use of chemical structure editors. These editors internally convert the graphical data into computational representations. There are also numerous algorithms for the interconversion of various formats of representation. An open-source utility for conversion is OpenBabel. These search and conversion algorithms are implemented either within the database system itself or as is now the trend is implemented as external components that fit into standard relational database systems. Both Oracle and PostgreSQL based systems make use of cartridge technology that allows user defined datatypes. These allow the user to make SQL queries with chemical search conditions (For example a query to search for records having a phenyl ring in their structure represented as a SMILES string in a SMILESCOL column could be

```
SELECT * FROM CHEMTABLE WHERE SMILESCOL.CONTAINS('c1ccccc1')
```

Algorithms for the conversion of IUPAC names to structure representations and vice versa are also used for extracting structural information from text. However there are difficulties due to the existence of multiple dialects of IUPAC. Work is on to establish a unique IUPAC standard

22.5 List of some Databases of chemical structures

mcule database

free database for virtual screening and compound ordering

Synthesis references database

Aurora Fine Chemicals

eChemPortal, a global portal to information on Chemical Substances

NLM ChemIDplus, biomedical chemicals searchable by name and structure.

Organic synthesis database

ZINC, a free database for virtual screening

ChemSpider, Free access to > 20 Million Chemical Structures, Physical Property Data and Systematic Identifiers

MMsINC, a free web-oriented database of commercially available compounds for virtual screening and chemoinformatic applications

ChemIndustry a free database derived from PubChem data

OpenCDLig a free Web application for host/guest complexes

NCI/CADD Chemical Structure Lookup Service, lookup in which databases a structure occurs (currently > 70 million indexed chemical structures)

ChEBI, the free chemical substance registry for biologically relevant molecules

Chemonaut[dead link] Chemonaut is the world's most comprehensive source of physically available commercial compounds.

Synthesis references database

Jochem database, The joint chemical dictionary

SMILES Chemical Reaction Database[dead link], the SMILES database consists of two million peer-reviewed chemical reaction structures stored as SMILES strings.

chemicalize.org Free, web-based database from ChemAxon, it provides similarity, substructure or full structure searches with web and document (pdf, Microsoft documents etc.) parsing capabilities.

22.6 ChemSpider

ChemSpider is a free chemical structure database providing fast access to over 30 million structures, properties and associated information. By integrating and linking compounds from more than 470 data sources, ChemSpider enables

researchers to discover the most comprehensive view of freely available chemical data from a single online search. It is owned by the Royal Society of Chemistry.

ChemSpider builds on the collected sources by adding additional properties, related information and links back to original data sources. ChemSpider offers text and structure searching to find compounds of interest and provides unique services to improve this data by curation and annotation and to integrate it with users' applications.

ChemSpider SyntheticPages, CS|SP, extends this model to cover reactions, providing quick publication, peer review and semantic enhancement of repeatable reactions.

ChemSpider won three international awards in 2010: the ALPSP Prize for Publishing Innovation, the Bio-IT World "Best Practices" award for Community Contribution, and the iExpo/KM forum "Most Innovative Software" award.

The objectives of ChemSpider

Bring together compound data on the web

Over 30M compounds from over 470 data sources, deduplicated with the original source links provided

Provide easy and powerful search options

Structure and substructure search

Validated synonyms improve accurate text search expansion

Improve the quality of public chemistry data sources

Automated chemistry checking of structures on loading

Manual comment and correction tools offer crowdsourced curation with expert review

Provide a publishing platform for the addition and preservation of data

Registered users can upload their own structure sets online and have their own home page

Registered users can add spectra, additional data, links, videos, audio to compound records

ChemSpider SyntheticPages allows publishing of reactions

Make this data accessible and reusable

ChemSpider mobile view – a mobile-optimized website for access through mobile phone browsers

ChemSpider Mobile – an IOS app available for iPhone and iPad we also provide an app for Android

Downloadable compound sets from search results

Web services to query and deliver data

Tools to embed linked structure images and spectra into web pages and blogs

Integrate with publications

Direct links to an expanding collection of structures in RSC journals

Searching of Google Scholar, PubMed and RSC books, journals and databases via validated chemical name dictionaries expands accurate compound name searching

ChemSpider grows daily with more depositions, more links. You are invited to help build this community for chemists by contributing your structures, spectra, syntheses. You can also actively participate in the curation of the data; registration enables you to become a depositor or curator.

22.7 Cambridge Structural Database

The Cambridge Structural Database (CSD), is a repository for small molecule crystal structures. Scientists use single-crystal x-ray crystallography to determine the crystal structure of a compound. Once the structure is solved, information about the structure is saved in a file (CIF format) and deposited in the CSD. Other scientists can search and retrieve structures from the database. The information consists of the space group symmetry of the crystalline phase, its cell parameters, the relative atomic coordinates of all the atoms in the cell in 3D. Scientists can use the CSD to compare existing data with that obtained from crystals grown in their laboratories. The information can also be used to visualize the structure in a variety of software such as atoms, powdercell etc. It is also possible to calculate what the theoretical powder diffraction pattern of the phase would look like. This option is particularly important for analytical reasons because it facilitates the identification of phases present in a crystalline powder mixture without the need for growing crystals. Many of the small molecules are organic compounds of the sort that could

potentially act as medical drugs, and a very important use of the CSD is for structural comparisons among related molecules that can suggest new leads for drug design. The CSD is compiled and maintained by the Cambridge Crystallographic Data Centre.

Cambridge System Overview

The CSDS is used world-wide by both academic and industrial research groups. It is supported and maintained by Cambridge Crystallographic Data Centre (CCDC) staff in Cambridge, and software packages have been developed for search, retrieval, display and analysis of CSD database information.

This webpage outlines the major components of the CSDS provided by the Chemical Datbase Service. For the latest news and related information see the "Links..." menu. Full details are available via the CCDC website. This page also includes a summary with links to key CCDC webpages likely to be of use to CDS users.

Main components for CDS users

Search, display and analysis of Database

The ConQuest software has been developed for the search, retrieval, display and analysis of CSD information. Mercury offers comprehensive facilities for visualising crystal structures in three dimensions and the exploration of crystal packing. Traditionally Cambridge have provided the VISTA package provide a wide range of functionality which allows the user to manipulate and analyse the geometrical parameters saved from a ConQuest search of the CSD.

VISTA functionally is now available within the Mercury component, and this will be the focus for future developments. All components are currently made available to CDS users via X-Windows interfaces, but the component packages are becoming more closely integrated.

Knowledge Bases

IsoStar is a knowledge base of non-bonded interactions derived from the CSD, the Brookhaven Protein Data Bank (PDB) and molecular orbital calculations. It is now available via an easy-to-use web browser graphical interface.

Mogul is a knowledge base of Molecular Geometry using data derived from the CSD. Mogul is currently only available via an X-Windows interface.

The CDS currently also makes the Cambridge Structural Database available via the CrystalWeb & CrystalWorks web interfaces. Both these system have been developed inhouse and allow searching over the entire range of CDS supported crystallographic databases (currently incl. CSD, ICSD, CrystMet, eCrystals, and the Crystal Data Identification File).

Both packages allow bibliographic (author, journal etc.), formula and cell data searching. Structures can be displayed and the reference is automatically linked to electronic literature giving single click access to online journals. CrystalWorks is under active development with new features being added. It is expected that CrystalWorks will eventually fully supersede CrystalWeb.

22.8 Bond length

In molecular geometry, bond length or bond distance is the average distance between nuclei of two bonded atoms in a molecule. It is a transferable property of a bond between atoms of fixed types, relatively independent of the rest of the molecule. Bond length is related to bond order, when more electrons participate in bond formation the bond will get shorter. Bond length is also inversely related to bond strength and the bond dissociation energy, as (all other things being equal) a stronger bond will be shorter. In a bond between two identical atoms half the bond distance is equal to the covalent radius. Bond lengths are measured in the solid phase by means of X-ray diffraction, or approximated in the gas phase by microwave spectroscopy. A set of two atoms sharing a bond is unique going from one molecule to the next. For example the carbon to hydrogen bond in methane is different from that in methyl chloride. It is however possible to make generalizations when the general structure is the same.

22.9 Bond Angle

Molecules, by definition, are most often held together with covalent bonds involving single, double, and/or triple bonds, where a "bond" is a shared pair of electrons (the other method of bonding between atoms is called ionic bonding and involves a positive cation and a negative anion).

Molecular geometries can be specified in terms of bond lengths, bond angles and torsional angles. The bond length is defined to be the average distance between the centers of two atoms bonded together in any given molecule. A bond angle is the angle formed between three atoms across at least two bonds. For four atoms bonded together in a chain, the torsional angle is the angle between the plane formed by the first three atoms and the plane formed by the last three atoms.

Molecular geometry is determined by the quantum mechanical behavior of the electrons. Using the valence bond approximation this can be understood by the type of bonds between the atoms that make up the molecule. When atoms interact to form a chemical bond, the atomic orbitals are said to mix in a process called orbital hybridisation. The two most common types of bonds are sigma bonds and pi bonds. The geometry can also be understood by molecular orbital theory where the electrons are delocalised. An understanding of the wavelike behavior of electrons in atoms and molecules is the subject of quantum chemistry.

22.10 Dihedral angle

In geometry, a dihedral or torsion angle is the angle between two planes.

The dihedral angle of two planes can be seen by looking at the planes "edge on", i.e., along their line of intersection.

Every polyhedron, regular and irregular, convex and concave, has a dihedral angle at every edge.

A dihedral angle (also called the face angle) is the internal angle at which two adjacent faces meet. An angle of zero degrees means the face normal vectors are antiparallel and the faces overlap each other (Implying part of a degenerate polyhedron). An angle of 180 degrees means the faces are parallel (like a tiling). An angle greater than 180 exists on concave portions of a polyhedron. Every dihedral angle in an edge-transitive polyhedron has the same value. This includes the 5 Platonic solids, the 4 Kepler–Poinsot polyhedra, the two quasiregular solids, and two quasiregular dual solids.

22.11 Dihedral angles of four atoms

The structure of a molecule can be defined with high precision by the dihedral angles between three successive chemical bond vectors. The dihedral angle φ varies only the distance between the first and fourth atoms; the other interatomic

distances are constrained by the chemical bond lengths and bond angles. To visualize the dihedral angle of four atoms, it's helpful to look down the second bond vector , which is equivalent to the Newman projection in chemistry. The first atom is at 6 O'clock, the fourth atom is at roughly 2 O'clock and the second and third atoms are located in the center. The second bond vector is coming out of the page. The dihedral angle φ is the counterclockwise angle made by the vectors b1 (red) and b3 (blue). When the fourth atom eclipses the first atom, the dihedral angle is zero; when the atoms are exactly opposite, the dihedral angle is 180°.

22.12 Example using Cambridge structural database programmes

SHAPES OF MOLECULES: VSEPR MODEL

Introduction

• The shapes of molecules tend to be controlled by the number of electrons in the valence shell of the central atom. The valence-shell electron-pair repulsion (VSEPR) model provides a simple method for predicting the shapes of such species.

• The Cambridge Structural Database contains a wealth of diverse molecular geometries, and provides the ability to visualise and manipulate molecules in three-dimensions. This is vitally important in order to study and understand the shapes adopted by particular molecules.

Objectives

• To investigate shapes of molecules by analysing experimental crystal structure data.

• To understand the factors that determine the preferred shape adopted by particular molecules.

• To use the valence-shell electron-pair repulsion (VSEPR) model to predict the shapes of given molecules.

Getting Started

• Open free Mercury (the free version of Mercury can be downloaded from

• Open the free teaching subset of the CSD (downloadable from free_services/teaching/downloads) by selecting File from the top-level menu, followed by Open in the resulting menu, and then selecting the database file

teaching_subset.ind

• Database reference codes (refcodes) of the structures in the teaching database will appear in a list on the right hand side of the main Mercury window. To view a structure select the corresponding refcode in the list.

• Once the teaching database has been loaded Mercury can then read text files containing lists of database reference codes (refcodes). To read in a file containing just those structures required for this tutorial hit File in the top-level menu, followed by Open, then select the file

vsepr.gcd.

Steps Required

Examine the structures of di-, tri-, and tetrachloro mercury

- Consider the following series of molecules: $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ as move across the series, successively adding a Cl to the central Hg atom. For each structure how would you expect the Cl atoms to arrange themselves around the Hg atom? Sketch each of the structures to show the shape of the molecule you predict.
- Check you answers by inspecting the corresponding crystal structures. The following structures are provided: $HgCl_2$ (refcode OKAJOZ), $HgCl_3^-$ (refcode KUSMAM), and $HgCl_4^{2-}$ (refcode KEYZUK).

To display a structure click on the identifier in the Structure Navigator on the right hand side of the main Mercury window.

To manipulate structures in Mercury

1. Structures can be rotated by moving the cursor in the display area while keeping the left-hand mouse button pressed down.
2. To zoom in and out move the cursor up and down in the display area while keeping the right-hand mouse button pressed down.
3. To translate structures hold down the middle mouse button while moving the cursor in the display area (three-button mouse only). Alternatively,

move the cursor in the display area while keeping both the left-hand mouse button and the keyboard Ctrl key pressed down. 4. At any stage the display area can be returned to the default view by hitting the Reset button at the bottom of the window.

- Do the shapes of the experimentally determined structures agree with your predictions? For each of the three structures measure the Cl-Hg-Cl bond angles in the structure. What does this tell you about the observed geometries?

To measure angles in Mercury

1. Set Picking Mode in the tool bar (near the top of the main Mercury window) to the required parameter type, viz. Measure Distance, Measure Angle or Measure Torsion
2. Geometrical measurements (intramolecular or intermolecular) can now be made by clicking on e.g., two atoms for a distance, three atoms for an angle or four atoms for a torsion angle.
3. To remove all geometrical measurements from the display click on the Clear Measurements button in the tool bar near the top of the main Mercury window.

- $HgCl_2$ is linear with bonds angles of 180 deg., $HgCl_3^-$ exists in a trigonal planar arrangement with bond angles of approximately 120 deg., and $HgCl_4^{2-}$ is tetrahedral with all bond angles approaching 109.5 deg.

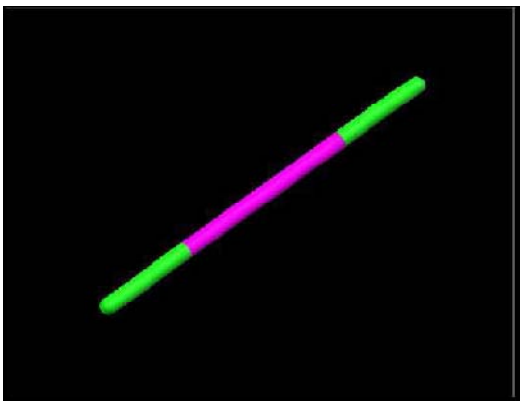


Image: showing $HgCl_2$ (linear)

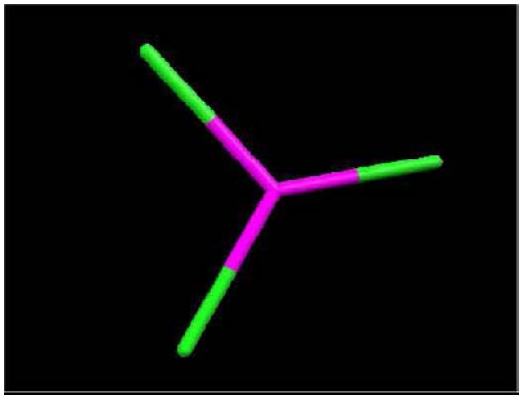


Image: showing $HgCl3^-$ (trigonal planar)

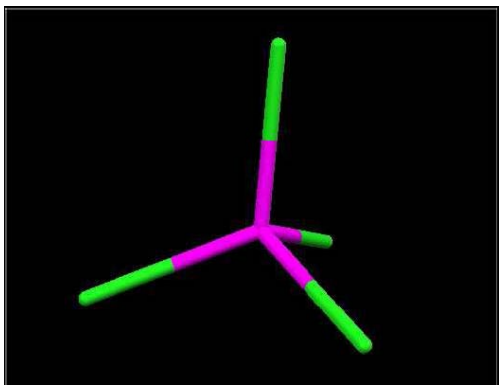


Image: showing $HgCl4^{2-}$ (tetrahedral)

VSEPR model is a main factor that determines the geometry that is adopted

The valence-shell electron pair repulsion (VSEPR) model is used for predicting molecular shape. The primary assumption of the VSEPR model is that regions of enhanced electron density (i.e. bonding pairs, lone pairs and multiple bonds) take up positions as far apart as possible so that the repulsions between them are minimised.

22.13 Summary

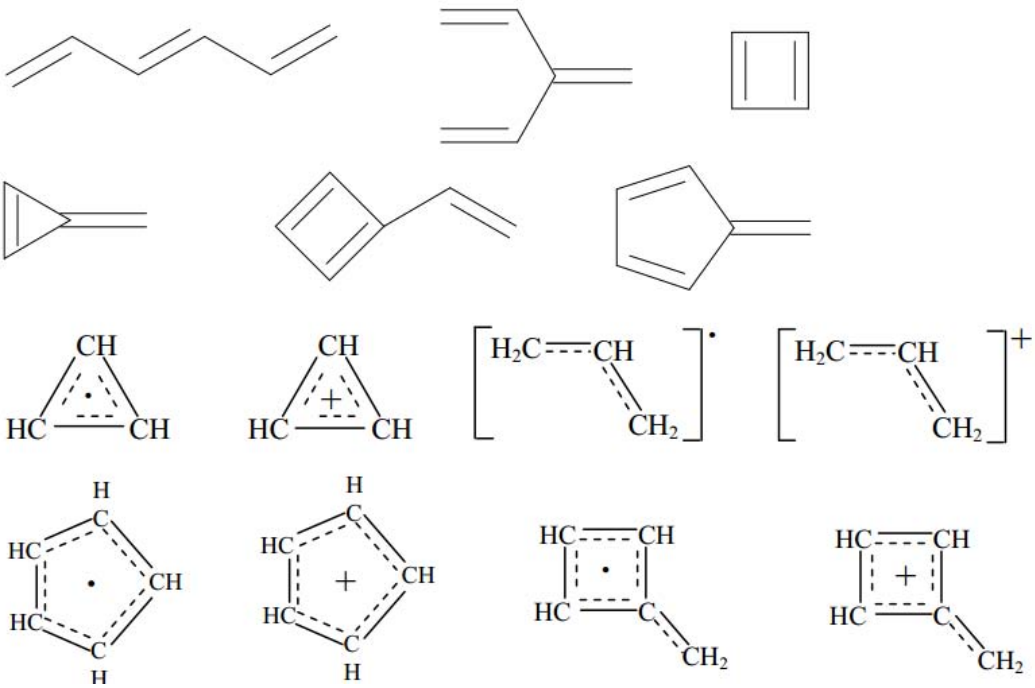
After reading this unit learner will become familiar with Hückel molecular orbital theory and its programme in computer language, solution to secular equation, digonalization, brief detail of chemical databases used worldwide and their types,

database related to define structure features, unit describs elementary structures i.e. bond length, bond angle, dihedral angle.

22.14 Review Questions

1. Define Diagonalization and Hückel Molecular Orbital Theory
2. Calculate wavefunctions and energies using an example of butadiene.

3 You will be assigned one of the following molecules or ions.



Please answer the nine questions that follow.

1. Number the carbon atoms in your molecule. Show the numbering. Give the corresponding Hückel determinant in terms of x's and 1's:
2. Determine the energies and the orbital coefficients using a matrix diagonalization program. List those below or attach a printout.
3. Sketch the orbitals below with the appropriate phase for each p orbital.
4. Give the number of nodes in each wavefunction. Show the nodes in the diagrams, above.

   Classify each orbital as net bonding or anti-bonding.

5. Draw the energy level diagram, below, with a quantitative scale. Give the electron filling.

6. Calculate the π-bond order for each unique bond in the molecule.

$$P_{ij} = \sum_k n_k c_{ki} c_{kj}$$

7. Calculate the π-bond delocalization energy. (Remember for each isolated double bond with two electrons, E = 2(α+β))

8. Calculate the π-electron density on any two atoms of your choosing.

$$P_i = \sum_k n_k c_{ki}^2$$

9. On the energy level in part 5, indicate the lowest energy electronic transition with a vertical arrow. Label the HOMO and LUMO (or SOMO if you have a radical).

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UNIT – 23 : Use of Computer Programs I

Structure of Unit

23.1 Objective

At the end of the unit learner will be able to

- Understand the use of Computer Programs.
- Operating a PC.
- Be able to run Standard Programs and Packages.
- Execute Linear Regression and X-Y Plots.
- Will be able to program numerical integration and differentiation.
- Can find solution of differential equations through programs.

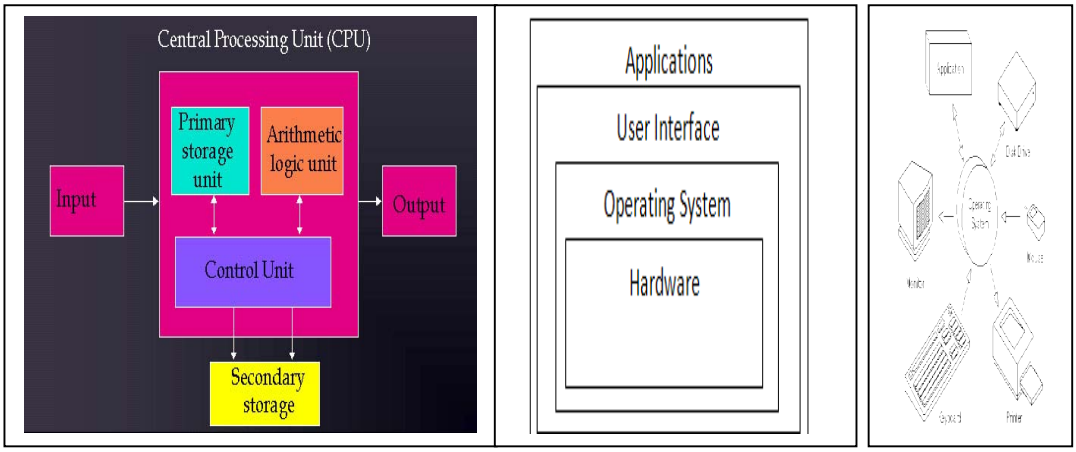
23.2 Introduction

Computer programming is writing list of instructions i.e. creation of *source code* that can be used to solve a given problem. The purpose of computer programming is to find a sequence of instructions that will automate performing a specific task or solve a given problem. It involves understanding, solving problems, verification of its correctness and implementation in a target programming language, testing, debugging, and maintaining the source code.

A **Computer (PC)** is an electronic device that manipulates information, or "data." It has the ability to store, retrieve, and process data.

Computer parts

There are two basic parts of computer Software and Hardware which interacts through an Operating System.



Computer Organisation

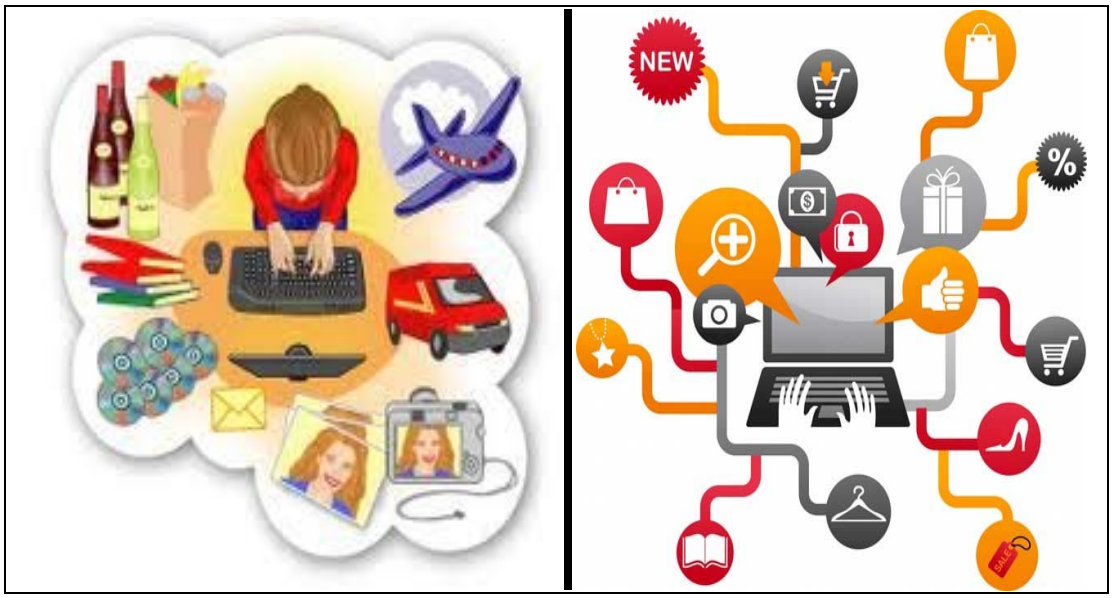
Fig 23.2 (a)Central Processing Unit (b)Layers of Computer System (c)Operating System Process

- **Hardware** is any part of PC that has physical structure, such as monitor, printer or keyboard.

- **Software** is any set of instructions that tells the hardware what to do. It guides the hardware and tells it how to accomplish each task.
- **Operating System** is an interface between Hardware and Software. It manages the computer's **memory**, **processes**, and all of its **software** and **hardware**.

Uses of Computer in Various Fields

- **Education :** Used by school colleges for teaching, Students for working faster, for mathematical problems and other logical problems too. Research scholars get lots of information through internet and can also save data through it.
- **Medical :** Keeping record of patients and the case history, controlling operations in surgery, helps in numerous medical tests, etc
- **Entertainment:** They are used for playing games, making animation, making movies, cutting, editing etc. and also for painting and drawings.
- **Banking, Airlines & Railways :** For online transactions, keeping and fetching records easily anytime anywhere, for reservations sitting at home, etc
- **In offices :** helps to make sheets, documents, letters etc. Helps to connect with other companies and can mail details etc.
- **Defence:** helps in launching missiles, records of the criminals, helps in constructing weapons and controlling of their functions.



Uses of Computer

- **Buildings**: Architects use computer animated graphics to experiment with possible exteriors and to give clients a visual walk-through of their proposed buildings.

- **Departmental Store:** People at the store level, cashiers enter sales data into sale terminals by waving a bar code scanner across a package's bar-coded prices and stock numbers. Bar codes are read by bar code readers, photoelectric scanners that translate the bar code symbols into digital forms
- **Stock Exchange:** Stock markets around the world are in transition. On some trading floors, paper is disappearing. In fact, the trading floor itself is disappearing in some places because many stock markets lunched the computerized system that makes it possible for stockbrokers to do all their trading electronically.

Uses of Programming Language

Computer programming (often shortened to **programming**) is a process that leads from an original formulation of a computing problem to executable programs. It involves activities such as analysis, understanding, and generically solving such problems resulting in an algorithm, verification of requirements of the algorithm including its correctness and its resource consumption, implementation (commonly referred to as coding of the algorithm in a target programming language, testing, debugging, and maintaining the source code, implementation of the build system and management of derived artefacts such as machine code of computer programs. The algorithm is often only represented in human-parsable form and reasoned about using logic. Source code is written in one or more programminglanguages (suchas C, C++, C#,Java, Python, Smalltalk, JavaScript, etc.).

Programming languages

The purpose of programming is to find a sequence of instructions that will automate performing a specific task or solve a given problem. The process of programming thus often requires expertise in many different subjects, including knowledge of the application domain, specialized algorithms and formal logic.

23.3 How to Operate a PC

Now a days, a PC has become a basic need in day today life every place. To get updated and be in touch with the latest work in any field we must have the knowledge of computers. To operate a PC following are the steps to use a PC:

Step 1: Check all the connections are correctly made i.e. power cord, mouse & keyboard and monitor with CPU all are connected.

Step 2: Press the power button and the PC will start booting. A screen will be visible infront of you in the monitor known as **Desktop**. A username and

password may be requested; otherwise, the Operating System may be loaded directly to display the desktop to the user.

Step 3: Install all the software needed by you to work like browser for internet, editor for making programs, games to play etc. You may create a shortcut key of any application on desktop known as **Icons**

Step 4: To use any of the programs we may double click the icons from the left click of the mouse or To launch the software, simply click on the 'Start' Menu, choose 'All Programs' and select from the menu the program intended to be run. To create a new document, folder or file we right click the mouse and chose an option.

Step 5: To write a program we need an editor to type on, a compiles to compile the program depending upon the language we are writing program on and operating system we are using.

Step 6: The proper way to shut down or turn off the computer system is by clicking on the 'Start' button and choosing the 'Turn Off Computer' option. This will display the options to 'Standby', 'Restart', or 'Turn Off' the machine.

23.4 How to run standard programs and packages

To run a standard program and packages, we have to follow the following points:

Step 1: Identify the problem to solve. Choose the language in which you want to program and install the software of the same.

Step 2: Start writing the program in the editor and save it with appropriate name along with extension to make it executable. We import appropriate header or packages in the program to make the use of functions or methods used in the program.

Step 3: Compile the program using the compiler of the software installed to find the errors and faults in the program.

Step 4: Now run the program by giving appropriate commands.

Example 23.1: Write a program in C language to add two numbers.

Step 1: Install the Turbo C software and open it.

Step 2: By clicking on it the editor of Turbo C++ will be opened. We will import the necessary functions through header files. We save the program with name ‘sum’ and extension ‘.c’ i.e. sum.c

Step 3: Compile the program, by giving the command or by clicking on compile and see if there are any errors because of which programming is not running. The commands may change according to the operating system being used.

Step 4: Now run the file by giving appropriate commands or clicking on run to get the final output.

23.5 Execution of Linear Regression

Linear Regression

In statistics, linear regression is an approach for modeling the relationship between a scalar dependent variable *'y'* and one or more explanatory variables denoted *'x'*. The case of one explanatory variable is called *simple linear regression*. For more than one explanatory variable, it is called *multiple linear regression*.

Regression Formula

Regression Equation (Y) = a + bX

Slope (b) = $(n\Sigma xy - (\Sigma x)(\Sigma y)) / (n\Sigma x^2 - (\Sigma x)^2)$

Intercept (a) = $(\Sigma y - b(\Sigma x)) / n$

where X and Y are the variables.

b = The slope of the regression line

a = The intercept point of the regression line and the y axis.

n = Number of values or elements

x = First Score

y = Second Score

Σxy = Sum of the product of first and Second Scores

Σx = Sum of First Scores

Σy = Sum of Second Scores

Σx^2 = Sum of square First Scores

Regression Example 23.2 : To find the Simple/Linear Regression of {(-2, -1), (1, 1), (3, 2)}

To find regression equation, we first find slope, intercept and use it to form regression equation.

Step 1: Count the number of values.

n = 3

Step 2: Find xy, x^2, Σx, Σy, Σxy, Σx^2

x	y	x y	x^2
-2	-1	2	4
1	1	1	1

3	2	6	9
$\Sigma x = 2$	$\Sigma y = 2$	$\Sigma xy = 9$	$\Sigma x^2 = 14$

Step 3: Substitute in the above slope formula given.

Slope (b) = $(n\Sigma xy - (\Sigma x)(\Sigma y)) / (n\Sigma x^2 - (\Sigma x)^2) = 0.61$

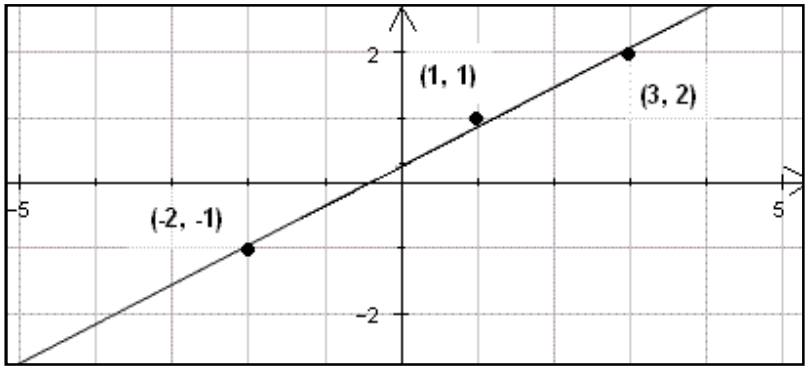
Step 4 : Substitute in the above intercept formula given.

Intercept (a) = $(\Sigma y - b(\Sigma x)) / n = 0.56$

Step 5: Then substitute these values in regression equation formula

Regression Equation(Y) = a + bX = 0.56 + 0.61X

We can substitute the value X in the above equation, and get the X-Y plot



X-Y Plot of Linear Regression Equation

Regression Program in C Language

```
#include "stdio.h"
#include "conio.h"
#include "math.h"
#include "string.h"

float mean(float *a, int n);
void deviation(float *a, float mean, int n, float *d, float *S);

void main() {
 float a[20], b[20], dx[20], dy[20];
 float sy = 0, sx = 0, mean_x = 0, mean_y = 0, sum_xy = 0;
 float corr_coff = 0, reg_coff_xy = 0, reg_coff_yx = 0;
 char type_coff[7];
 int n = 0, i = 0;
```

```
 clrscr();

 printf("Enter the value of n: ");
 scanf("%d", &n);
 printf("Enter the values of x and y:\n");
 for (i = 0; i < n; i++)
  scanf("%f%f", &a[i], &b[i]);
 mean_x = mean(a, n);
 mean_y = mean(b, n);
 deviation(a, mean_x, n, dx, &sx);
 deviation(b, mean_y, n, dy, &sy);

 for (i = 0; i < n; i++)
  sum_xy = sum_xy + dx[i] * dy[i];
 corr_coff = sum_xy / (n * sx * sy);
 printf("Enter the type of <span class="bg7ro" id="bg7ro_2">regression
coefficient</span> as 'x on y' or 'y on x': ");
 fflush(stdin);
 gets(type_coff);
  if (strcmp(type_coff, "x on y") == 1) {
  reg_coff_xy = corr_coff * (sx / sy);
  printf("\nThe value of linear regression coefficient is %f",
    reg_coff_xy);
 } else if (strcmp(type_coff, "y on x") == 1) {
  reg_coff_yx = corr_coff * (sy / sx);
  printf("\nThe value of linear regression coefficient is %f",
    reg_coff_yx);
 } else
  printf("\nEnter the correct type of regression coefficient.");
 getch();
}
 float mean(float *a, int n) {
 float sum = 0, i = 0;
 for (i = 0; i < n; i++)
  sum = sum + a[i];
```

```
 sum = sum / n;
 return (sum);
}
 void deviation(float *a, float mean, int n, float *d, float *s) {
 float sum = 0, t = 0;
 int i = 0;
 for (i = 0; i < n; i++) {
  d[i] = a[i] - mean;
  t = d[i] * d[i];
  sum = sum + t;
 }
 sum = sum / n;
 *s = sqrt(sum);
}
```

23.6 Numerical Integration and Differentiation

Differentiation is a technique which can be used for analysing the way in which functions change.In particular, it measures how rapidly a function is changing at any point. In engineering
applications the function may, for example, represent the magnetic field strength of a motor,
the voltage across a capacitor, the temperature of a chemical mix, etc., and it is often important
to know how quickly these quantities change.

The derivative of y(x) is written dy/dx

Applications of Differentiation

They are used for finding extreme values have practical applications in many areas of life.

- A businessperson wants to minimize costs and maximize profits.
- A traveler wants to minimize transportation time.
- Fermat's Principle in optics states that light follows the path that takes the least time

Example 23.3: Use the defifinitionnition of the derivative to find dy/dx (gradient function) when $f(x)=2x^2$

Solution: dy/dx = 6x

when x = 3, the gradient is 6×3=18.

when x = −2, the gradient is 6×(−2) = −12.

A gradient of 18 means that values of y are increasing at the rate of 18 units for every 1 unit increase in x. A gradient of −12 means that values of y are decreasing at a rate of 12 units for every 1 unit increase in x.

Program of Differentiation in C++

```
#include<iostream.h>
#include<conio.h>
#include<math.h>
float funct(float a);
int main()
{
   char choice='y';
   float f1,f2,x,h;
   clrscr();
   cout<<"X ? ";cin>>x;
   do{
      cout<<"Enter value of h ? ";cin>>h;
      cout<<endl<<"The derivative is: "<<endl;
      f1=(funct(x+h)-funct(x))/h;
      f2=(funct(x+h)-funct(x-h))/(2*h);
      cout<<"2 point derivative : "<<f1;
      cout<<endl<<"3 points derivative: "<<f2;
      cout<<endl<<"wanna continue (y/n) ? ";cin>>choice;
   }while(choice=='y');
   getch();
   return 0;
}
float funct(float x)
{
   return exp(x)*sin(x);
}
```

Integration is the process of finding a function, given its derivative, is called of f(x) anti-differentiation (or integration). If F'(x) = f(x), we say F(x) is an anti-derivative. Given a function f of a real variable x and an interval [a, b]of the real line, the definite integral

$$\int_a^b f(x)\,dx$$

is defined informally to be the signed area of the region in the xy-plane bounded by the graph of f, the x-axis, and the vertical linesx = a and x = b, such that area above the x-axis adds to the total, and that below the x-axis subtracts from the total.

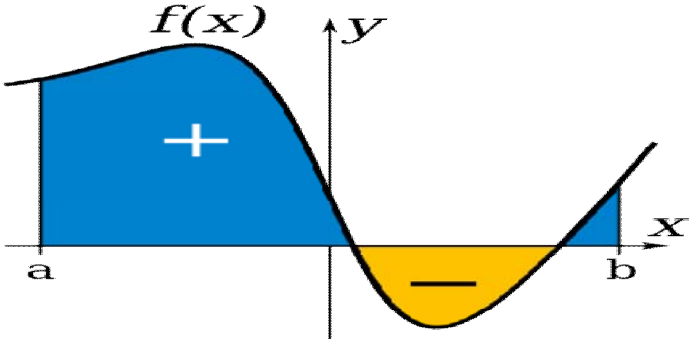
Example 23.4 : What is ∫x3 dx ?

On Rules of Integration there is a "Power Rule" that says:

$\int x^n\,dx = x^{n+1} / (n+1) + C$

We can use that rule with n=3:

$\int x^3\,dx = x^4/4 + C$



Applications of Integration

- *Displacement from Velocity, and Velocity from Acceleration*
- *Voltage across a Capacitor*
- Area under a Curve
- *Volume of Solid of Revolution*
- *Moments of Inertia*

Program for Integration in C++

```
#include<iostream.h>
#include<conio.h>
#include<math.h>
```

```
float funct(float a);


int main()
{
   char choice='y';
   float f,x,h,a,b,sum;
   clrscr();
   cout<<"a & b ? ";cin>>a>>b;
   do{
      sum=0;
      x=a;
      cout<<"Enter value of h ? ";cin>>h;
      while(x<b)
      {
         sum+=(funct(x)+funct(x+h));
         x=x+h;
      }
      cout<<endl<<"The integration is: "<<sum*h/2<<endl;
      cout<<endl<<"wanna continue (y/n) ? ";cin>>choice;
   } while(choice=='y');
   getch();
   return 0;
}

float funct(float x)
{
   return x*exp(x)-2;   // sin takes arguments in radian.....
}
```

23.7 Differential Equation Solution Programs

A **differential equation** is a mathematical equation that relates some function of one or more variables with its derivatives. Differential equations arise whenever a

deterministic relation involving some continuously varying quantities (modeled by functions) and their rates of change in space and/or time (expressed as derivatives) is known or postulated. Because such relations are extremely common, differential equations play a prominent role in many disciplines including engineering, physics, economics, and biology.

Applications of Differential Equations to Real World Systems

- Cooling/Warming Law
- Population Growth and Decay
- Radio-Active Decay and Carbon Dating
- Mixture of Two Salt Solutions
- Series Circuits
- Survivability with AIDS
- Draining a tank
- Economics and Finance
- Mathematics Police Women
- Drug Distribution in Human Body
- A Pursuit Problem
- Harvesting of Renewable Natural Resources

Example 23.5** : **Solve the ordinary differential equation (ODE)

$$\mathrm{d}x/\mathrm{d}t=5x-3$$

for $x(t)$

Solution: Using the shortcut method outlined in the introduction to ODEs, we multiply through by dt and divide through by $5x-3$:

$$dx/5x-3=dt.$$

We integrate both sides

$$\int dx/5x-3 = \int \mathrm{dt}$$
$$1/5\ \log|5x-3| = 5\mathrm{t} + \mathrm{C1}$$
$$5x-3x = \pm\exp(5t+C1)$$
$$x = \pm 1/5\ \exp(5t+C1)+3/5.$$

Letting $C=1/5\ \exp(C1)$, we can write the solution as

$$x(t)=Ce^{5t}+3/5.$$

We check to see that $x(t)$ satisfies the ODE:

$$dx/dt = 5Ce^{5t}$$

$$5x-3 = 5Ce^{5t} + 3 - 3 = 5Ce^{5t}.$$

Both expressions are equal, verifying our solution.

Program for solving a differential equation in C

C program for Euler's method for solving a differential equation with initial conditions

to solve dy/dx = f(x,y)
y(x0) = y0
f(x,y) is being evaluated as a separate function "funct" which can be suitably adjusted

```
#include<stdio.h>
#include<conio.h>
#include<math.h>

float funct(float x,float y)
{

  float f;
  /*edit f into required function*/
  f= (x+y)/2 ;
  return (f);
}
void clearline(int i)
 {
 /*funtion for clearing "i" lines */
int j;
for(j=1; j<=i;j=j+1)

            printf("\n");
 }
main()
{
  float x,y,x0,y0,xn,yn,xcurr=0,ycurr,xnext,ynext,h;
```

```
int n=0;

 clearline(50);

printf("\nEnter the initial values:x0=");
 scanf("%f",&x0);
  printf("Enter the initial values:y0=");
 scanf("%f",&y0);

  printf("Enter the final value of x for which y is required:xn=");
 scanf("%f",&xn);
 printf("Enter the value ofh, h=");
 scanf("%f",&h);

 xcurr=x0;
 ycurr=y0;

 iterat:

                if(h>0 && xcurr>=xn)
                                goto end;

                if(h<0 && xcurr<=xn)
                                goto end;

                ynext = ycurr + h*funct(xcurr,ycurr);
                xnext = xcurr + h;

                 printf("y[%f] = %f \n ",xnext,ynext);
                 xcurr = xnext;
                 ycurr = ynext;
                   n=n+1;

                  if((n%10)==0)
                  {
```

```
                printf("press enter to continue");
                getch();
                printf("\n");
                }
        goto iterat;

end:
getch();
    }
```

23.8 Summary

Chapter deals with the Use of Programming in various fields to solve mathematical problems.

We have studied about the hardware and software used in computers, how to operate it easily.

How to execute the standard programs and packages, although various programming languages are available but the basic logics are the same. So we have tried to build basic concepts on the topics in the chapter. We also study about Linear Regression and its graphical representation in computer using programs. At the end we have discussed about differentiation, integration and the differential equations and how to solve any problem given to us using various languages through computers.

23. 9 Review Questions

1. Define Computer. What is the use of computers?
2. What are the two basic parts of the computer? How do they interact?
3. How to operate a PC?
4. How to run standard programs and packages?
5. Discuss about the Execution of Linear Regression.
6. What is Differentiation and Integration?
7. How to run program on Differentiation?
8. Explain with example the execution of Integration.
9. Explain Differential Equations with example.

10. How to solve Numerical Differential Equation problems using computer program?

23.10 References

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Unit – 24 : Use of Computer Programmes II

Structure of the Unit:

24.0 Objective

At the end of the unit learner will be able to

- Understand the Monte Carlo method
- Get the knowledge of Molecular dynamics
- Learn how to operate on MATLAB
- Understand the working of EASYPLOT
- Get the knowledge of LOTUS and FOXPRO
- Know the importance of WORDSTAR /MS WORD

24.1 Introduction

A chapter deal gives a quick introduction to the two approaches to performing molecular simulations: the stochastic and the deterministic. The stochastic approach, called Monte Carlo, is based on exploring the energy surface by randomly probing the geometry of the molecular system. The deterministic approach, called Molecular Dynamics (MD), actually simulates the time evolution

of the molecular system and provides us with the actual trajectory of the system. The information generated from simulation methods can in principle is used to fully characterize the thermodynamic state of the system.
Chapter deals with the use of EASYPLOT with which you can work directly with graphs. There is also an idea of MATLAB.

Chapter also deals in Lotus software which is used mainly by companies for employees use. It functions as spreadsheets, calendar, email, and office suite.

The learner will also be able to get the knowledge and importance of FoxPro which is a programming Language. There is also knowledge of MSWORD which is used widely.

24.2 Monte Carlo

The true picture of a molecular system is far from the static, idealized image provided by molecular mechanics. The atoms and groups in molecules are in constant motion, and, especially in the case of biological macromolecules, these movements are concerted (correlated) and may be essential for biological function. In molecular mechanics, the information is derived from a single geometry of the molecule. Simulation methods require thousands to millions of geometries to produce meaningful results.
Molecular simulations are a recent addition to molecular modeling systems. They are also more complex conceptually than molecular mechanics. There are essentially two approaches to performing molecular simulations: the stochastic and the deterministic.
The stochastic approach, called Monte Carlo(MC method), is based on exploring the energy surface by randomly probing the geometry of the molecular system.
It is essentially composed of the following steps:

1. Specify the initial coordinates of atoms.
2. Generate new coordinates by changing the initial coordinates at random.
3. Compute the transition probability $W(0, a)$.
4. Generate a uniform random number R in the range [0, 1].
5. If $W(0, a) < R$, then take the old coordinates as the new coordinates and go to step 2.
6. Otherwise accept the new coordinates and go to step 2.

The most popular realization of the Monte Carlo method for molecular systems is the Metropolis method which is described below.

1. Specify the initial atom coordinates (e.g., from molecular mechanics geometry optimization).
2. Select some atom *i* randomly and move it by random displacement.
3. Calculate the change of potential energy corresponding to this displacement.
4. If the change of potential energy is less than zero, then accept the new coordinates and go to step 2.
5. Otherwise, select a random number *R* in the range [0, 1]

Note that in the MC methodology, only the energy of the system is computed at any given point. The Monte Carlo method is accepted more by physicists than by chemists, probably because MC is not a deterministic method and does not offer time evolution of the system in a form suitable for viewing. The stronghold of MC in chemistry is in the area of simulations of liquids and solvation processes.

Monte Carlo methods are most frequently used in computational statistical mechanics. Especially useful is simulation of liquids.

Monte Carlo methods are probabilistic, rather than deterministic, procedures; atoms are moved more or less randomly during the course of the simulation.

Thermodynamic and other properties of the system can be computer as ensemble averages during the simulation. Depending on the property of interest, several hundred thousand to several million steps may be necessary to compute the property accurately (some properties ' converge' more rapidly than others). For example, average internal energy may converge relatively quickly, but heat capacity may require a much larger ensemble sample to compute reliability.

It is desirable to use a large random step size and attain high step acceptance ratio so as to sample a large number of energetically accessible (and distinctly different) states in a limited number of steps. Usually, the step size is adjusted so that approximately 50% of the attempted steps are accepted. Use of a large random step size in biomolecule simulations generally yields poor step acceptance ratios. Use of small step sizes

Can improve the acceptance ratio to efficient levels (~50%), but severely restricts the sampling of configuration space, leading to slow convergence of calculated properties.

24.3 Molecular Dynamics

Molecular Dynamics methods are nearly as old as the Metropolis MC method. The first applications of MD techniques for molecular simulation were made for simple fluids. Molecular dynamics consists of examining the time dependent behavior of a molecule, such as vibration motion or Brownian motion. This is most often done within a classical mechanical description similar to a molecular mechanics calculation.

The application of molecular dynamics to solvent/solute systems allows the computation of properties such as diffusion coefficients or radial distribution functions for use in statistical mechanical treatments. Usually the scheme of a solvent/solute calculation is that a number of molecules are given some initial position and velocity. New positions are calculated a small time later based on this movement and this process is iterated for thousands of steps in order to bring the system to equilibrium and give a good statistical description of the radial distribution function.

The deterministic approach, called Molecular Dynamics (MD), actually simulates the time evolution of the molecular system and provides us with the actual trajectory of the system. The information generated from simulation methods can in principle is used to fully characterize the thermodynamic state of the system. In practice, the simulations are interrupted long before there is enough information to derive absolute values of thermodynamic functions; however the differences between thermodynamic functions corresponding to different states of the system are usually computed quite reliably.

In molecular dynamics, the evolution of the molecular system is studied as a series of snapshots taken at close time intervals .For large molecular systems the computational complexity is enormous and supercomputers or special attached processors have to be used to perform simulations spanning long enough periods of time to be meaningful.

MD is a deterministic procedure. Atoms move according to the laws of Newtonian mechanics. A MD simulation is performed by integrating Newton's equations of motion over time for the molecular system.

In a Molecular Dynamics simulation, first, we prepare a sample: we select a model system consisting of N particles and we solve Newton's equations of motion for this system until the properties of the system no longer change with time (we equilibrate the system). After equilibration, we perform the actual measurement.

1.3.1. Molecular Dynamics: A Program

The best introduction to Molecular Dynamics simulations is to consider a simple program. The program we consider is kept as simple as possible to illustrate a number of important features of Molecular Dynamics simulations.

The program is constructed as follows:

1. Read in the parameters that specify the conditions of the run (e.g.,initial temperature, number of particles, density, time step).
2. Initialize the system (i.e., we select initial positions and velocities).
3. Compute the forces on all particles.
4. Integrate Newton's equations of motion. This step and the previous one make up the core of the simulation. They are repeated until the time evolution of the system for the desired length of time is computed.
5. After completion of the central loop, compute and print the averages Of measured quantities, and stop.

Algorithm 1 is a short pseudo-algorithm that carries out a Molecular Dynamics simulation for a simple atomic system.

1.3.2. Algorithm 1 (A Simple Molecular Dynamics Program)

```
program md                  simple MD program
call init                   initialization
t=0
do while (t.lt.tmax)        MD loop
call force(f,en)            determine the forces
call integrate(f,en)        integrate equations of motion
t=t+delt
call sample                 sample averages
enddo
stop
end
```

Comment to this algorithm:

1. Subroutines init*,* force*,* integrate*, and* sample *will be described in*

Algorithms 2, 3, and 4, respectively. Subroutine sample *is used to calculate averages like pressure or temperature.*

1.3.2.1. Initialization

To start the simulation, we should assign initial positions and velocities to all particles in the system. The particle positions should be chosen compatible with the structure that we are aiming to simulate. Often this is achieved by initially placing the particles on a cubic lattice.

1.3.3. Algorithm 2 (Initialization of a Molecular Dynamics Program)

```
subroutine init                initialization of MD program
sumv=0
sumv2=0
do i=1,npart
x(i)=lattice pos(i)            place the particles on a lattice
v(i)=(ranf()-0.5)              give random velocities
sumv=sumv+v(i)                  velocity center of mass
sumv2=sumv2+v(i)**2             kinetic energy
enddo
sumv=sumv/npart                velocity center of mass
sumv2=sumv2/npart              mean squared velocity
fs=sqrt(3*temp/sumv2)          scale factor of the velocities
do i=1,npart                   set desired kinetic energy and set
v(i)=(v(i)-sumv)*fs            velocity center of mass to zero
xm(i)=x(i)-v(i)*dt             position previous time step
enddo
return
end
```

1.3.4 Algorithm 3 (Calculation of the Forces)

```
subroutine force(f,en)              determine the force
en=0                               and energy
do i=1,npart
f(i)=0                             set forces to zero
enddo
do i=1,npart-1
do j=i+1,npart                      loop over all pairs
```

```
xr=x(i)-x(j)
xr=xr-box*nint(xr/box)        periodic boundary conditions
r2=xr**2
if (r2.lt.rc2) then           test cut-off
r2i=1/r2
r6i=r2i**3
ff=48*r2i*r6i*(r6i-0.5)       Lennard-Jones potential
f(i)=f(i)+ff*xr                    update force
f(j)=f(j)-ff*xr
en=en+4*r6i*(r6i-1)-ecut      update energy
endif
enddo
enddo
return
end
```

1.3.5. Integrating the Equations of Motion

Now that we have computed all forces between the particles, we can integrate Newton's equations of motion.

Algorithm 4 (Integrating the Equations of Motion)

```
subroutine integrate(f,en)          integrate equations of motion
sumv=0
sumv2=0
do i=1,npart                        MD loop
xx=2*x(i)-xm(i)+delt**2*f(i)        Verlet algorithm (1.5)
vi=(xx-xm(i))/(2*delt)              velocity (1.6)
sumv=sumv+vi                        velocity center of mass
sumv2=sumv2+vi**2                        total kinetic energy
xm(i)=x(i)                          update positions previous time
x(i)=xx                              update positions current time
enddo
temp=sumv2/(3*npart)                instantaneous temperature
etot=(en+sumv2)/(2*npart)           total energy per particle
return
end
```

To start the MD simulation we need an initial set of atom positions (i.e., geometry) and atom velocities. In practice, the acceptable starting state of the system is achieved by ``equilibration'' and ``heating'' runs prior to the ``production'' run. The initial positions of atoms are most often accepted from the prior geometry optimization with molecular mechanics. Formally, such positions correspond to the absolute zero temperature. The velocities are assigned randomly to each atom from the Maxwell distribution for some low temperature (say 20 K). The random assignment does not allocate correct velocities and the system is not at thermodynamic equilibrium. To approach the equilibrium the ``equilibration'' run is performed and the total kinetic energy (or temperature) of the system is monitored until it is constant. The velocities are then rescaled to correspond to some higher temperature, i.e., the heating is performed. Then the next equilibration run follows. The absolute temperature, T, and atom velocities are related through the mean kinetic energy of the system.

Molecular dynamics for larger molecules or systems in which solvent molecules are explicitly taken into account, is a computationally intensive task even for the most powerful supercomputers, and approximations are frequently made.

Even supercomputers have their limitations and there is always some practical limit on the size (i.e., number of atoms) of the simulated system. For situations involving solvent, the small volume of the box in which the macromolecule and solvent are contained introduces undesirable boundary effects.

In fact, the results may depend sometimes more on the size and shape of the box than on the molecules involved. To circumvent this limited box size difficulty, *periodic boundary conditions* are used. Like the original box containing a solute and solvent molecules is surrounded with identical images of itself, i.e., the positions and velocities of corresponding particles in all of the boxes are identical. The common approach is to use a cubic or rectangular parallelepiped box, but other shapes are also possible (e.g., truncated octahedron).

24.4 MATLAB

MATLAB is widely used in all areas of applied mathematics, in education and research at universities, and in the industry. MATLAB stands for MATrix LABoratory and the software is built up around vectors and matrices. This makes the software particularly useful for linear algebra but MATLAB is also a great tool

for solving algebraic and differential equations and for numerical integration. MATLAB has powerful graphic tools and can produce nice pictures in both 2D and 3D. It is also a programming language, and is one of the easiest programming languages for writing mathematical programs. MATLAB also has some tool boxes useful for signal processing, image processing, optimization, etc.

How to start MATLAB

Choose the submenu "Programs" from the "Start" menu. From the "Programs" menu, open the "MATLAB" submenu. From the "MATLAB" submenu, choose "MATLAB".

You can quit MATLAB by typing exit in the command window.

The MATLAB environment

The MATLAB environment consists of menus, buttons and a writing area similar to an ordinary word processor. The writing area that you will see when you start MATLAB, is called the *command window*. In this window you give the commands to MATLAB. For example, when you want to run a program you have written for MATLAB you start the program in the command window by typing its name at the prompt. The command window is also useful if you just want to use MATLAB as a scientific calculator or as a graphing tool. If you write longer programs, you will find it more convenient to write the program code in a separate window, and then run it in the command window.

In the command window you will see a prompt that looks like >>. You type your commands immediately after this prompt. Once you have typed the command you wish MATLAB to perform, press <enter>. If you want to *interrupt a command* that MATLAB is running, type <ctrl> + <c>.The commands you type in the command window are stored by MATLAB and can be viewed in the *Command History* window. To repeat a Command you have already used, you can simply double-click on the command in the history window, or use the <up arrow> at the command prompt to iterate through the commands you have used until you reach the command you desire to repeat.

Useful functions and operations in MATLAB

Using MATLAB as a calculator is easy.

Example: Compute 5 sin(2.53-pi)+1/75. In MATLAB this is done by simply typing 5*sin(2.5^(3-pi))+1/75 at the prompt. Care should be taken for parentheses and type * whenever you multiply.

Note that MATLAB is case sensitive.

Operation,	function or constant	MATLAB command
+	(addition)	+
-	(subtraction)	-
×	(multiplication)	*
/	(division)	/
|x|	(absolute value of x)	abs(x)
	square root of x	sqrt(x)
	ex	exp(x)
ln x	(natural log)	log(x)
log10 x	base 10 log)	log10(x)
sin x		sin(x)
cos x		cos(x)
tan x		tan(x)
cot x		cot(x)
arcsin x		asin(x)
arccos x		acos(x)
arctan x		atan(x)
arccot x		acot(x)
□□	(3.14159265...)	pi
i	(imaginary unit, sqrt(-1))	i

Obtaining Help on MATLAB commands

To obtain help on any of the MATLAB commands, type help <command> at the command prompt. For example, to obtain help on the gamma function, type at the command prompt:

help gamma.

Variables in MATLAB

Variables in MATLAB can be easily defined. Instead of typing 3.5*sin(2.9)over and over again, denote this variable as x by typing the following: x=3.5*sin(2.9)

Vectors and matrices in MATLAB

Vector in MATLAB is created by putting the elements within [ ] brackets.

Example: x=[1 2 3 4 5 6 7 8 9 10]

We can also create this vector by typing x=1:10. The vector (1 1.1 1.2 1.3 1.4 1.5) can be created by typing x=[1 1.1 1.2 1.3 1.4 1.5] or by typing x=1:0.1:1.5.
Matrices can be created according to the following example.
The matrix A={ } is created by typing A=[1 2 3 ; 4 5 6; 7 8 9], i.e., rows are separated with semi-colons. If we want to use a specific element in a vector or a matrix, then

Example:

```
x=[10 20 30]
A=[ 1 2 3 ; 4 5 6 ; 7 8 9]
x(2)
A(3,1)
```

Here we extracted the second element of the vector by typing the variable and the position within parentheses. The same principle holds for matrices; the first number specifies the row of the matrix, and the second number specifies the column of the matrix. Note that in MATLAB the first index of a vector or matrix starts at 1, not 0 as is common with other programming languages. If the matrices (or vectors which are special cases of a matrices) are of the same dimensions then matrix addition, matrix subtraction and scalar multiplication works just like we are used to.

Plotting in MATLAB

There are different ways of plotting in MATLAB. The following two techniques, illustrated by examples, are probably the most useful ones.

Example 1: Plot sin(x2) on the interval [-5,5]. To do this, type the following:

```
x=-5:0.01:5;
y=sin(x.^2);
plot(x,y)
```

The following commands are useful when plotting:

Graphing functions	MATLAB command
Label the horizontal axis.	xlabel('text')
Label the vertical axis.	ylabel('text')
Attach a title to the plot.	title('text')

Change the limits on the x and y axis. axis([xmin xmax ymin ymax])

Note that all text must be put within ' '.

24.5 EASYPLOT

Easyplot allows us to do 2-D, 3-D, polar and multiple graphs and contour plots. You can also fit curves to your data or plot mathematical expressions. It is fast and easy to use, and generates publication-quality graphs.

Launching Easyplot

Click on the Easyplot icon (blue square with lines on it). It comes up with a menu giving you a choice of plotting data or an equation. Assuming you want to plot data, then either type in the name of a file containing the data or choose *enter data* and enter your data (in columns) in the data table. Click 'plot' when you have finished.

Changing the symbols

To change the size, colour or type of a marker or tic mark, go to STYLE then RESTYLE DATA.

Tic marks scaling the axes and choosing log Axes

To change where you want tic marks and labels on the axes, or to change the scale on the axes, or select log axes, select STYLE, then AXIS SETUP (you can also click on the axes). Note that the tic marks point OUT on the screen but IN when you print - see print preview. To change the size of annotations, use the FILE, PRINT OPTIONS menu. Click on the little squares next to the axes to enter axis titles.

Error bars

To get error bars you must first enter a column of error bars in your data, and tell Easyplot what it is .A column of errors must be placed immediately after the relevant data column. To show error bars, switch them on using STYLE, ERROR BARS then STYLE, RESTYLE DATA to see them. Note that Easyplot should be set up to display error bars in the normal way, i.e. 5_1 means an error bar of 1 either side of 5. However, the program can interpret error bars in other ways, so always check that it is working correctly for your application. You can do this either by looking at the graph or by checking FILE, PREFERENCES, ERROR BARS. If the buttons 'error value' and 'half of entire bar' are on then the errors will be displayed in the normal way.

Multiple curves and graphs

ADD then CURVE allows you to plot a new data set on an existing graph which means you can have several data lines on one graph. ADD then GRAPH allows you to define a new graph with new axes, title etc. You can change the size of a graph with the mouse (move one of the corners while holding the left-hand button down). Thus, you can have several graphs on the screen at once (these will also print at the same time if you wish to do so).

Modifying data

You may want to re-scale a curve, or mathematically transform it. Use TOOLS, TRANSFORM, CURVE, then supply an equation (e.g. y=y*10 or y=log(y)). Under EDIT, DATA you can edit your data set - either numerically or by moving points around on the graph. You can also transform the whole graph, but if you do this you will find that Easyplot retains both the original and modified graph (the original will be hidden behind the modified one: make it smaller to see both). Then any style changes you may have made will be found only on the original.

Printing

FILE PRINT - modify plot using OPTIONS if required, and uses to see what the graph will look like (or use print preview). Then type P to send to printer. If you need to prepare lots of high quality graphs, printing to a Postscript printer is very much faster. To get colour plots, select an appropriate printer and if necessary choose the colour output print option. NOTE: If you would like to include an Easyplot graph for putting into a word processing package, just copy the whole graph to the clipboard (EDIT, COPY) and paste into the document.

Entering text, lines and arrows

Easyplot allows you to type text directly on the screen. Use the ADD ANNOTATION menu for text. Once the text is written you can move it by 'dragging' with the mouse. Note that you change the size of lettering on the graph using the print options.

Use ADD LINE for lines. For lines, the cursor will change to a pencil shape. To return to the normal cursor press **Esc**. Lines can be adjusted by clicking and 'dragging' one end of a line with the mouse while the cursor is in its normal (+) mode. Hold the ALT key down as you draw the line to put an arrow at the end where you release the mouse button.

Save a plot using FILE SAVE. To call it up again use ADD GRAPH.

Highlighting curves

Use the right mouse button. You will see a little box in the lower left hand corner of the screen with a sample of curve in it. Keep hitting the right hand mouse button until you see the curve you want. If you keep the button down, the curve glimmers. To delete a curve, highlight and hit delete.

Zoom

You may zoom in (and zoom **in** only) on any part of a graph by clicking and 'dragging' with the mouse while the cursor is in normal (+) mode. The position of the cursor when you press the left mouse button and its position when you leave go define opposite corners of a rectangle for zooming in. In order to zoom out you must choose OPTIONS RANGE/AUTORANGE.

Histogram

You can enter all your data points as an x-y graph and convert that to a histogram using TOOLS, STATS, HISTOGRAM. See the help item histogram for more information - you set up the classes for the histogram by modifying the tick marks on the axes. Note that Easyplot keeps the x-y plot behind the newly-created histogram - use Window to switch between them.

Fitting curves: TOOLS menu

You may fit any curve of your choice by selecting TOOLS CURVEFIT. You may then choose to fit your curve to a few types of theoretical curves (including straight line) by making the appropriate choice. You can also fit splines etc or smooth your data using filters. Explot also calculates a Fourier Transform.

24.6 LOTUS and FOXPRO

1.6.1. FOXPRO

Visual FoxPro is a Relational Database Management System (RDBMS), which allows you to work with several logically related tables of data simultaneously. A Table in a database contains a number of Rows and Columns. One row in the table is equivalent to one record and one column is equivalent to one field.

Data is anything e.g., a number, name of a person or place, address, etc. When a data is meaningful, it is called *Information* and a *Database* is an organized collection of related information.

In FoxPro, first four characters of any command is enough to execute

For e.g.:- crea ==> create

SOME FOXPRO COMMANDS

To open a database:

Syntax:

use <dbname>

Ex:

use book

To close the database:

Syntax: Use

To close the current opened database.

Example: Close all

To close the all opened database

To create new database:

Syntax:

crea <dbname>

create <dbname>

Ex:

crea book

To Modify Structure of the Database

Syntax: Modify structure

(Or)

Modi stru

To add new records in database

Append is used to add the new record.

Syn: append

To display the records in the current database

Used to display the particular record.

Syn: Display [All]

To Display the structure of the database:

Display Structure

To display the status of the set commands:

Display Status

To edit records

EDIT

- It list all the records one by one for editing.

Any one of the record can be edited using 'FOR' as below

EDIT FOR empname = "RAM"

EDIT FOR rollno = 103

To delete records

DELETE

- To delete current record

DELETE NEXT 4

- To delete next 4 records

After using the delete command the records marked with * (asterisk) mark, i.e., marked for deletion.

RECALL

- It is used to recover the deleted records.

e.g. RECALL

RECALL NEXT 4

PACK

- To delete the records permanently. It is used after the delete command.

BLANK

- It can be used to empty the record instead of deleting.

To delete all the records in the current database

ZAP

Program: A Program is a set of instructions used to achieve the desired output.

To create new program or to edit the existing one

MODI COMM
OR MODIFY COMMAND <PRGRAM_NAME>

Comment Line

To add comments to the right of the Programming code , use &&

Clear All Command

This command is used to closes all databases files and releases all active memory variables, arrays menus or popup.

Writing Programs

FoxPro has powerful built-in editor for writing and editing.
It can be invoked from the command window by using the MODIFY COMMAND.

Syntax:

MODIFY COMMAND <prgnames>

Executing Program

Programs can be executed by DO command.

Syntax:

DO <prgname>

INPUT command

It is used to accept Numeric input from the user and store it into a memory variable.

Syntax:

INPUT [<char exp>] TO <memvar>

ACCEPT command

It is used to accept character input from the user and store it into a memory variable.

Syntax:

ACCEPT [<char exp>] TO <memvar>

Control Structures

IF statement

If Condition is True Executed and then False Not Executed.

Syntax

If (condition) then

Statement-1

End if

If….else….endif:-

The commands between if…..end if will be executed only if condition is satisfied, otherwise the next statement is executed. For every if there must be an end if.

Syntax:-

If<condition>

<Command sequence-1>

Else

<Command sequence-2>

End if

DO CASE

Case Commands are used to check for a specified condition.

Syntax:

DO Case
Case <variable> = <value>
Statement -1
Case <variable> = <value>
Statement -2
Otheriwse
Statement -3
End Case

FOR LOOP

To repeatedly execute a series of lines in a Program. The lines of code b/w FOR and ENDOFR will be executed until the memory variable is equal to the final condition specified.efault STEP value is 1.

Syntax

FOR <memvar> = <initial value> TO <final value> STEP <no>
.....
.....
ENDFOR

1.6.2. LOTUS

Lotus software is used mainly by companies for employees use. It function as spreadsheets, calendar, email, and office suite. Lotus software was recently purchase by IBM. Lotus' solution was marketed as a three-in-one solution, handing spreadsheet calculations, charting and databasefunctionality - thus the name "1-2-3".

24.7 MS WORD

Microsoft WORD is a powerful word processing program that gives a professional result.

To Open MS Word

On the Desktop - Click on START, PROGRAMS, and select Microsoft WORD in the side menu To Start a NEW Document - look at the gray toolbar below the dark blue border - click on FILE, SELECT NEW. A panel may or may not open on the right side, Select BLANK DOCUMENT from the menu by clicking on it.

To Create a New Document

There are at least two ways to do this. You can also do the following: 1. Click on START, 2. PROGRAMS, and select 3.MICROSOFT WORD on the side menu.Another was is by clicking the gray Toolbar below the dark blue line border. Click on FILE, Select NEW. A clean page will open.

To Open an Existing Document

To open a document you have already saved to a disk, place the diskette into the appropriate a:/drive (found in the middle of the computer tower). Go to the Tool bar and click either on File, Open OR Click on the yellow folder on the menu toolbar.

To Set Margins

To set of change page margins, go the File, click on PAGE SETUP and then click the MARGINS tab. You can keep the default margins or change margins by clicking on the up or down arrows next to the margin indicator. You can also choose portrait or landscape paper orientations here as well.

To Insert Page Numbers/Date/Time

Click INSERT on the menu tool bar and Select PAGE NUMBERS. Select where you would like the page numbers to appear.

Insert a Picture

Graphics can be added to your document by going to the menu toolbar and select INSERT, then PICTURE. You can select images from Clip Art or a saved File. Click once where you want the image to go in your document. To insert an image from a saved file from a diskette - use the same procedure as opening an existing WORD document. To insert Clip Art, click on INSERT, PICTURE, CLIP ART. On the side you should see a long dialogue box where you can choose the clip art

you want. Type in the category you want (i.e., Books) and click the SEARCH button. RIGHT CLICK your selection and click on INSERT.

The following is a ***list of commonly used keys*** that have special functions in MS Word (key functions can change depending on which program you are using):

1. *Backspace*: This key deletes letters backward.
2. *Delete:* This key deletes letters forward.
3. *Shift:* This key, when pressed WITH another key, will perform a secondary function.
4. *Spacebar*: This key enters a space between words or letters.
5. *Tab*: This key will indent what you type, or move the text to the right. The default indent distance is usually ½ inch.
6. *Caps Lock*: Pressing this key will make every letter you type capitalized.
7. *Control (Ctrl):* This key, when pressed WITH another key, performs a shortcut.
8. *Enter*: This key either gives you a new line, or executes a command (pressed in MS Word, it begins a new line).
9. *Number Keypad*: These are exactly the same as the numbers at the top of the keyboard; some people just find them easier to use in this position.
10. *Arrow Keys*: Like the mouse, these keys are used to navigate through a document or page.

Cutting, Copying, and Pasting Text

In MS Word, you can CUT or COPY text from one area of the document and save that text to be PASTED elsewhere (these commands are found on the Home Tab). When you CUT text, you actually delete it from where you took it, as opposed to COPYING it, which makes a copy of your selection. When you CUT or COPY text, it is stored on the CLIPBOARD. The Clipboard is a tool in MS Word that stores cuts and copies of your work, to be pasted in other places in the document. Once your selection is on the CLIPBOARD, you can PASTE it as many times as you want. CUTTING a selection will place it on the clipboard, just in case you want to PASTE it elsewhere.

To CUT a selection, first highlight it. Then, click on the CUT icon from the Home Tab. The highlighted text will disappear, as you have just cut it out, but a copy is now on your clipboard, and MS Word is waiting for you to paste it somewhere else.

To PASTE this cut selection, place your cursor where you want the selection to go. Click on the PASTE icon from the Home Tab toolbar, and it will pop the text into place, right w here you have your cursor.

To COPY, simply follow those same steps, replacing the CUT command with COPY.

The COPY command will not alter your original selection at all, as it simply makes a copy of the selection without changing or deleting it in any way.

Creating Bulleted and Numbered Lists

Word allows you to create lists within your document that can be organized with bullets or numbers.

24.8 Summary

Monte Carlo (MC method), is based on exploring the energy surface by randomly probing the geometry of the molecular system. Molecular dynamics consists of examining the time dependent behavior of a molecule, such as vibration motion or Brownian motion.

MATLAB is widely used in all areas of applied mathematics, in education and research at universities, and in the industry. MATLAB stands for MATrix LABoratory and the software is built up around vectors and matrices.

Easyplot allows us to do 2-D, 3-D, polar and multiple graphs and contour plots. FoxPro is a Relational Database Management System (RDBMS), which allows you to work with several logically related tables of data simultaneously. Lotus software is used mainly by companies for employees use. It functions as spreadsheets, calendar, email, and office suite. Microsoft WORD is a powerful word processing program that gives a professional result.

24.9 Review Questions

1. Describe Molecular dynamics.
2. Describe the Monte Carlo method.
3. What is the use of LOTUS.
4. Explain the use of MATLAB.
5. Describe the use EASYPLOT.
6. Explain various commands of FOXPRO.

24.10 References

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