

# **BIO202 Final term notes**

Regards By Admins:

VU Friends

## **Q.1 Write types of alcohol?**

Glycerol and Sphingosine are the two types of alcohols most commonly found in lipids.

**1..Glycerol**

**2..Sphingosine**

### **1.Glycerol:**

- ☐ It is a simple poly hydroxy alcohol (also called polyol or sugar alcohol) and part of a class of lipids: glycolipids
- ☐ It contains 3 carbons and 3 hydroxyl (OH) groups.
- ☐ Glycerol is synthesized from Dihydroxyacetone Phosphate (an intermediate of the glycolytic pathway
- ☐ Dihydroxyacetone phosphate is acted upon by two enzymes to form glycerol, namely Glycerol Phosphate Dehydrogenase and Glycerol Kinase respectively.
- ☐ Glycerol is a precursor for synthesis of triacylglycerols and of phospholipids in the liver and adipose tissue.
- ☐ When the body uses stored fat as a source of energy, glycerol and fatty acids are released into the bloodstream And enter the glycolysis pathway directly

### **2. Sphingosine:**

- ☐ Sphingosine is an amino alcohol, which is a component of the class of lipids known as sphingolipids
- ☐ Sphingosine is synthesized in the body in the form of ceramide, to which different moieties are added to form sphingolipids.

- ☐ **C** Serine and palmitoyl CoA condense to form a product (ketosphinganine) that is reduced.
- ☐ A very long-chain fatty acid forms an amide with the amino group. a double bond is generated, and ceramide is formed.
- ☐ There is no direct route of synthesis from sphinganine (dihydrosphingosine) to sphingosine; it has to be acylated first to dihydroceramide, which is then dehydrogenated to **ceramide**.
- ☐ Sphingosine is formed via degradation of sphingolipid in the lysosome. Therefore ceramide is the structural parent of all sphingolipids.
- ☐ In short, Serine + Palmitate = Sphingosine
- ☐ Sphingosine + FA = ceramide

## Q.2 write Properties of Glycerol?

- ☐ Popularly known as glycerin,
- ☐ Glycerol is widely used in pharmaceutical and cosmetic preparations.
- ☐ It has the following properties:
  - ☐ Colorless
  - ☐ Viscous oily liquid with
  - ☐ sweet taste.

### Acrolein Test:

On heating with sulfuric acid or  $\text{KHSO}_4$  (dehydration) it gives acrolein that has a bad odor. used for detection of free glycerol or any compound containing glycerol.

Potassium bisulfate is a potassium acid salt of sulfuric acid, with the molecular formula  $\text{KHSO}_4$

- In contrast to glycerol

**Sphingosine** does not show positive acrolein test.

Therefore glycerolipids and sphingolipids can be differentiated on the basis of acrolein test.

Glycerol combines with three molecules of nitric acid to form Glycerol trinitrate that is used as explosive and vasodilator

## Q.3 Explain Simple lipids?

Esters of fatty acids with various alcohols  
These contain:

- a. Fats (and Oils) and

**b. Waxes.**

**a. Fats:**

Esters of fatty acids with glycerol (**Oils** are fats in the liquid state)

**b. Waxes:**

Esters of fatty acids with higher molecular weight monohydric alcohols.  
(having one OH group)

**Q.4 What is Triacylglycerols (TAGs) and its structure?**

The simplest lipids constructed from fatty acids are the triacylglycerols, Also referred to as; triglycerides, fats, or neutral fats or storage lipids. Triacylglycerols are composed of three fatty acids in ester linkage with a single glycerol

**Structure of triacylglycerols:**

- ☐ The three fatty acids esterified to a glycerol molecule are usually **not** of the same type
- ☐ The fatty acid on **carbon 1** is typically saturated,
- ☐ Whereas that on **carbon 2** is unsaturated, and that on **carbon 3** can be either Simple triglycerides:
- ☐ Fatty acids connected to glycerol are of the same type e.g., tripalmitin.

Mixed triglycerides:

- ☐ Fatty acids are of different types, e.g., stearo-diolein and palmito-oleo-stearin.
- ☐ **Simple triglycerides:**

Fatty acids connected to glycerol are of the same type  
**e.g.,**

tripalmitin.

- ☐ **Mixed triglycerides:**
- ☐ Fatty acids are of different types, **e.g.,** stearo-diolein and palmito-oleo-stearin.
- ☐ The main difference between fats and oils is for oils being liquid at room temperature, whereas, fats are solids.
- ☐ This is mainly due to presence of larger percentage of unsaturated fatty acids in oils than fats that has mostly saturated fatty acids
- ☐ **TAGs** containing saturated fatty acids are solid at room temperature such as butter whereas

- ☐ TAGs containing unsaturated fatty acids are liquid at room temperature such as olive oil.(Oleic acid, 18:1,9)
- ☐ Because the polar hydroxyls of glycerol and the polar carboxylates of the fatty acids are bound in ester linkages
- ☐ Therefore the triacylglycerols are nonpolar, hydrophobic molecules, essentially insoluble in water
- ☐ Triacylglycerols provide
- ☐ Stored Energy and Insulation.

### Q.5 Define Adipocytes? How Triacylglycerols provides energy?

In vertebrates, specialized cells called **adipocytes**, or fat cells, store large amounts of triacylglycerols as fat droplets that nearly fill the cell

- ☐ Triacylglycerols are also stored as oils in the seeds of many types of plants.
- ☐ **Thus providing energy** and biosynthetic precursors during seed germination
- ☐ **Adipocytes** and germinating seeds contain lipases, enzymes that catalyze the hydrolysis of stored triacylglycerols.
- ☐ Therefore releasing fatty acids for export to sites where they are required

### Q.6 Write Significance of Triacylglycerols (TAGs) ?

There are two significant advantages to using triacylglycerols as stored fuels, rather than polysaccharides such as glycogen and starch.

#### **First,**

The carbon atoms of fatty acids are more reduced than those of sugars, and oxidation of triacylglycerols yields more than twice as much energy, as the oxidation of carbohydrates

#### **Second,**

- Because triacylglycerols are hydrophobic and therefore unhydrated
- ☐ The organism that carries fat as fuel does not have to carry the extra weight of water of hydration that is associated with stored polysaccharides (2 g per gram of polysaccharide)
  - ☐ Moderately obese **people with 15 to 20 kg** of triacylglycerols deposited in their adipocytes could meet their energy needs for months by drawing on their fat stores
  - ☐ In contrast, the human body can store less than a day's energy supply in the form of glycogen (the polymer of glucose)

- ☐ In some animals, triacylglycerols stored under the skin serve as insulation against low temperatures.
- ☐ Seals, penguins, bears and other warm-blooded polar animals are amply padded with triacylglycerols.

### Q.7 Write Physical properties of TAGs?

#### Properties of TAGs:

Neutral fats are

1. colourless,
2. odorless and
3. tasteless substances

#### 4. Solubility:

They are insoluble in water but soluble in organic fat solvents(e.g., ether, benzene, acetone, chloroform)

#### 5. Specific gravity:

The specific gravity of all fats is less than 1.0, consequently all fats float in water.

#### 6. Emulsification:

- ☐ Emulsions of fat may be made by shaking vigorously in water and by emulsifying agents such as gums and soaps
- ☐ These agents have both a hydrophilic and a lipophilic part in their chemical structure In Mustard variety of chemicals in the mucilage surrounding the seed hull act as emulsifiers
- ☐ The emulsification of dietary fats in intestinal canal, brought about by bile salts, is a prerequisite for digestion and absorption of fats.
- ☐ The **bile salts**, act to break apart the fat globules in the small intestines and allow them to become more "soluble" for absorption
- ☐ The **hydrophobic fat molecules** will clump together into globules in the watery mixture in the digestive system.
- ☐ The emulsifiers break them down to smaller "globules" and allow them to become more soluble.

### Q.8 Write chemical Properties of TAGs?

There are following chemical properties:

1. Hydrolysis
2. Additive reaction
3. Rancidity

#### 1.Hydrolysis :

The fats may be hydrolysed with super heated steam, by acids, or alkalies, by the specific fat splitting enzymes lipases to

- free fatty acids
- glycerol

### **Saponification:**

- ☐ Hydrolysis of a fat by an alkali is called saponification
- ☐ The resultant products are; glycerol and the alkali salts of the fatty acids, which are called **“soaps”**

The number of mg of NaOH/KOH required to saponify the free and combined FA in

one gram of a given fat is called its saponification number

- ☐ The amount of alkali needed to saponify a given quantity of fat will depend upon the number of carboxylic (-COOH) group Present.
- ☐ Thus fats containing short chain fatty acids will have more -COOH groups per gram than long- chain fatty acids and this will take up more alkali
- ☐ And hence will have higher saponification number Butter containing a larger proportion of short- chain fatty acids, such as butyric (C4) acid
- ☐ Therefore it has relatively high saponification number from 220 to 230
- ☐ In contrast, Olive Oil (which contain Oleic acid (C18), a longer chain FA), has saponification number of 195 or less.

### **Chemical Properties no 2:**

#### **Q.9 What is additive reaction?**

### **2.Additive Reactions:**

The unsaturated fatty acids present in neutral fat exhibits all the additive reactions,  
i.e.

- (i) hydrogenation,
- (ii) halogenation.

#### **(i)Hydrogenation:**

- ☐ A hydrogenation reaction involves conversion of a carbon-carbon double bond to a carbon carbon single bond through the addition of hydrogen As you continue to hydrogenate your molecule Melting point increases Fat becomes more solid at room temperature.
- ☐ Oils which are liquid at ordinary room temperature, on become solidified This is the basis of Banaspti ghee manufacturing.

- ☐ Where inedible and cheap oils like cotton seed oil are hydrogenated and converted to edible solid fats.
- ☐ The hydrogenation is done under high pressure of hydrogen and is catalyzed by finely divided nickel or copper and heat.

### **Q.10: What is halogenation?**

#### **(ii)Halogenation:**

- ☐ Similar to hydrogenation,
- ☐ Halogens such as chlorine, bromine and iodine can also be added to double bonds in unsaturated fatty acids.
- ☐ It is a very important property to determine the degree of unsaturation of the fat or oil that determines its biological value.
- ☐ The degree of unsaturation is reflected by Iodine number.
- ☐ **Iodine number is defined** as the number of grams of iodine absorbed by 100 gm of fat. The more the iodine number, the greater the degree of unsaturation.
- ☐ Fats rich in saturated fatty acids have low iodine numbers, while fats rich in unsaturated fatty acids have high iodine numbers
- ☐ The determination of iodine number is useful to the chemist in determining the quality of an oil or its freedom from adulteration
- ☐ Iodine number of cotton seed oil varies from 103 to 111.
- ☐ That of olive oil from 79 to 88, And that of linseed oil from 175 to 202
- ☐ A commercial lot of olive oil which has an iodine number higher than 88 might have been adulterated with cotton seed oil
- ☐ The higher is the iodine number, the more reactive, less stable, more susceptible to oxidation and rancidification is the oil or fat.

### **Chemical Properties no 3**

### **Q.11 Explain rancidity?**

#### **Rancidity:**

- ☐ The chemical deterioration of fats. When lipid-rich foods are exposed too long to the oxygen in air, they may spoil and become foul smelling.

#### **Rancidity Definition:**

- ☐ It is a physicochemical change in the natural properties of the fat leading to the development of unpleasant odor or taste or abnormal color

- ☐ It occurs particularly on aging after exposure to atmospheric oxygen, light, moisture, bacterial or fungal contamination and/or heat.
- ☐ Saturated fats resist rancidity more than unsaturated fats that have unsaturated double bonds.

### **Q.12 Write Causes of rancidity?**

Rancidity is due to

- I. Oxidation
- II. Hydrolysis

#### **1. Oxidative Rancidity:**

- ☐ Oxidation of the fat, molecules give rise to some short chain aldehydes, ketones and dicarboxylic acids which have objectionable taste and odor.
- ☐ The unpleasant taste and smell associated with rancidity result from the oxidative cleavage of double bonds in unsaturated fatty acids
- ☐ The oxygen of the air is necessary for this type of rancidity. This can be prevented by addition of antioxidants such as vitamin E to foods.

#### **2. Hydrolytic Rancidity:**

- It is due to the slow hydrolysis of fats, which in case of fats like butter results in the liberation of short chain fatty acids which are volatile and have rancid taste and odor.

### **Q.13 Define waxes and also write its properties ?**

#### **Waxes:**

- ☐ A second group of neutral lipids that are of physiological importance.
- ☐ Although they are a minor component of biological systems

#### **Properties of waxes:**

- ☐ Waxes are insoluble in water, but soluble in fat solvents and are negative for acrolein test.
- ☐ very resistant to rancidity.
- ☐ Waxes are not easily hydrolyzed as the fats and are indigestible by lipases (enzymes responsible for fat digestion in body). Thus they are of no nutritional value.

### **Q.14 Write types of waxes?**



Waxes are of two types:

(i) True waxes

(ii) Other Waxes or Non true waxes or Wax-like compounds

### First type:

#### **(i) True Waxes:**

☐ Waxes are solid simple lipids containing a monohydric alcohol (with a higher molecular weight than glycerol) esterified to longchain fatty acids.

#### **Triacanthanol:**

It is a fatty alcohol of the general formula  $C_{30}H_{62}O$ , also known as melissyl alcohol or myricyl alcohol.

It is found in plant cuticle waxes and in beeswax. The name cetyl derives from the whale oil (Latin: cetus) from which it was first isolated

☐ Waxes are widely distributed in nature such as the secretion of certain insects as;

(a) Bees-wax,

(b) Spermaceti of the sperm whale

☐ Waxes also form protective coatings of the skins and furs of animals and leaves and fruits of plants.

#### **True Waxes:**

##### **a. Bees-wax:**

It is secreted by the honeybees that use it to form the combs. It is a mixture of waxes chief constituent is myricyl palmitate (30C) (16C)

##### **b. Spermaceti:**

It is a wax that is most often found in the head cavities of the sperm whale.

- Fatty esters are formed essentially of cetyl palmitate and cetyl myristate.
- It was used in cosmetics, pharmacy and also in candles recent international regulation concerning whale captures, has stopped its use. It is now replaced by synthetic cetyl palmitate.

### Second type:

#### **2. Other Waxes or Non true waxes:**

I

- ☐ include esters of:
  - Cholesterol
  - Vitamin A
  - Vitamin D

### **Cholesterol esters:**

- ☐ Lanolin (or wool fat) is secreted by sheep sebaceous glands and It contains both free and esterified cholesterol, e.g., cholesterolpalmitate
- ☐ Lanolin secretion helps sheep in reducing water evaporation from the skin. It is used as industrial lubricant and in cosmetics.

### **Q.15 Write lipid and nutrition and measure different biochemical parameters?**

#### **Lipids and Nutrition:**

- Dietary fats strongly influence the incidence of coronary heart disease (CHD). In the past, dietary recommendations emphasized decreasing the total amount of fat in the diet.
- Research now indicates that the type of fat is more important than the total amount of fat consumed To gauge the effect of these dietary fats on CHD,

#### **we measure different biochemical parameters, which include:**

- ☐ LDL-Cholesterol HDL-Cholesterol
- ☐ Total Cholesterol TAG
- ☐
- ☐ **LDL and HDL** stand for Low Density Lipoprotein and High Density Lipoprotein respectively
- ☐ They are included in the class of complex lipids and serve to transport lipids in the blood.
- ☐ **Serum Cholesterol and TAGs** are a risk factor for CHD among others.
- ☐ The risk increases progressively with higher values for serum total cholesterol and that of LDL cholesterol
- ☐ Association of TAGs is weaker than that of LDL cholesterol with CHD.
- ☐ A much stronger correlation exists between the levels of blood LDL cholesterol and heart disease.
- ☐ In contrast, high levels of HDL cholesterol have been associated with a decreased risk for heart disease'
- ☐ In order to understand the influence of these parameters on CHD, we must first

Understand biochemical role of Lipoproteins:

### Q.16 What is lipoprotein?

- ☐ Lipoprotein particles are spherical aggregates with hydrophobic lipids at the core and hydrophilic protein side chains and lipid head groups at the surface.
- ☐ These proteins are **called apolipoproteins**. Lipoproteins function is to keep their

component lipids soluble as they transport them in the aqueous environment of plasma.

Due to imbalanced metabolism of these lipoproteins there can be a gradual deposition of lipid especially cholesterol in tissues, which in arteries of the heart, can lead to CHD

### **Lipoproteins include:**

The lipoprotein particles include

- (i) chylomicrons (CM),
- (ii) very-low-density lipoproteins (VLDL),
- (iii) low-density lipoproteins (LDL), and
- (iv) high-density lipoproteins (HDL).

They differ in lipid and protein composition, size, density and site of origin

### **(i)Chylomicrons:**

Chylomicrons are formed and assembled in intestinal mucosal cells after a fatty meal

And carry dietary triacylglycerol, cholesterol, and cholesteryl esters to the peripheral Tissues. As the chylomicron circulates and most of its dietary TAG are degraded and taken up by peripheral tissues in the form of fatty acids, the particle size decreases and density increases.

The remaining particle, called Chylomicron Remnant, is removed from the circulation by the liver.

### Q.17 What is very-low-density lipoproteins (VLDL)..?

#### **(ii)**

- ☐ **VLDLs** are assembled in the liver. composed predominantly of TAGs synthesized in liver and contain some cholesterol and cholesteryl esters
- ☐ As VLDL pass through the circulation, TAG is degraded and taken up by peripheral tissues in the form of fatty acids, causing the VLDL to decrease in size and become denser, called **VLDL remnant**.

### Q.18 What is low-density lipoproteins (LDL)?

#### **(iii)**

### **LDL:**

- ☐ LDL particles contain much less triacylglycerol than their VLDL predecessors, and have a high concentration of cholesterol and cholesteryl esters
- ☐ LDLs contain apoB- 100 as their major apolipoprotein they carry cholesterol to extra hepatic tissues that have specific plasma membrane receptors that recognize apoB-100.
- ☐ Oxidized LDL can also accumulate in the macrophage cells lining the arteries resulting in the formation of atherosclerosis.
- ☐ further removal of triacylglycerol from these remnants produces low-density lipoprotein (LDL)

### **Q.19 What is high-density lipoproteins (HDL)?**

**(iv)**

#### **HDL:**

- ☐ The fourth major lipoprotein type, high-density lipoprotein, originates in the liver and small intestine as small, protein-rich particles that contain little cholesterol and no cholesteryl esters
- ☐ They take up cholesterol from nonhepatic (peripheral) tissues and return it to the liver as cholesteryl esters
- ☐ When cholesterol is taken up by HDL, it is immediately esterified and becomes hydrophobic and which is sequestered in the core of the HDL,
- ☐ Mature HDL then returns to the liver, where the cholesterol is unloaded in a process called **reverse cholesterol transport pathway** This is the basis for the inverse relationship seen between plasma
- ☐ A much stronger correlation exists between the levels of blood LDL cholesterol and heart disease
- ☐ In contrast, high levels of HDL cholesterol have been associated with a decreased risk for heart disease
- ☐ Abnormal levels of plasma lipids (dyslipidemias) act in combination with smoking, obesity, sedentary lifestyle, insulin resistance, and other risk factors to increase the risk of CHD
- ☐ Clinical studies have demonstrated that dietary or drug treatment of hypercholesterolemia is effective in decreasing LDL, increasing HDL, and reducing the risk for cardiovascular events.

### **Q.20 Explain role of dietary lipids?**

### **Role of dietary Lipids:**

- (i) Unhealthy Fat contains
- (ii) Trans fat
- (iii) Saturated Fat
- (iv) Increased cholesterol content

#### **(i)Trans fat:**

- ☐ Elevate serum LDL (but not HDL), Therefore they increase the risk of CHD
- ☐ Fatty acids of *trans* configuration in our food come from two different sources:
- ☐ industrially produced partially hydrogenated fat (IPTFA) and ruminant produced Trans Fatty acid (RPTFA)

**Ruminants** include cattle, sheep, goats, buffalo, deer, giraffes and camels

#### **Industrially produced trans fatty acid (IP-TFA):**

These are made by partial hydrogenation of vegetable fat, and to a lesser extent, of fish oils by heating to about 400°C under high pressure and with the addition of different catalysts such as Nickel

#### **Ruminant produced Trans Fatty acid (RPTFA):**

☐ These are made by bacterial metabolism of polyunsaturated fatty acids in the rumen of ruminants, such as cow & sheep And are consequently present in all fats from these animals.

- ☐ The concentration of IP-TFA in partially hydrogenated fat may be as high as 60%. Whereas the maximum content of RP-TFA in ruminant fat is about 6%. In milk, RP-TFA is 4-6% of the fat.
- ☐ Recent studies suggest that with equal amounts of intake IP-TFA is more harmful than RP-TFA when compared on a gram-to-gram basis. The deleterious effects of trans fats occur at intakes of 2 to 7 g/day.
- ☐ Therefore, to reduce the harmful effects of trans fats, one should limit intake of foods prepared in IP-TFA containing oils such as baked goods and fast foods etc.

#### **(ii) Role of dietary Lipids** **Saturated fats**

### Q.21 Explain saturated fats in details?

- ☐ Saturated fats Consumption of saturated fats is associated with high levels of total plasma cholesterol and LDL cholesterol.
- ☐ **Saturated fats Found in:**
  - butter,
  - hard cheeses,
  - whole milk,
  - animal fats,
  - palm oil, and coconut oils.
- ☐ Among the SFAs, stearic acid (18:0) appears to have a neutral effect on LDL-C.

While lauric (12:0), myristic (14:0), and palmitic (16:0) acids are considered to be

Hypercholesterolemic

- ☐ Saturated Fats increase plasma LDL-C by; increasing the formation of LDL in the plasma compartment and by decreasing LDL turnover.
- ☐ The lowering of plasma LDL-C observed with PUFAs is likely due to; redistribution of cholesterol between plasma and tissue pools and up regulation of the LDL receptor

### Q.22 Write dietary cholesterol and the Mediterranean diet?

#### Dietary cholesterol:

- ☐ Cholesterol is found only in animal products.
- ☐ Dietary cholesterol has little effect on plasma cholesterol. Therefore, effect of dietary cholesterol on plasma cholesterol is less important than the amount and types of fatty acids consumed.
- ☐ A further reduction in dietary cholesterol seems to be unnecessary in those people; who have already reduced their intake of saturated fat and increased the ratio of polyunsaturated to saturated fatty acids

#### The Mediterranean Diet:

- ☐ Mediterranean cultures, show a low incidence of coronary heart disease
- ☐ The Mediterranean diet is an example of a diet rich in monounsaturated fatty acids (from olive oil) and  $\omega$ -3 fatty acids (from fish oils and some nuts), but low in saturated fat•
- ☐ The Mediterranean diet contains seasonally fresh food, with an abundance of plant material, low amounts of red meat, and olive oil as the principal source of fats.

- ☐ Mediterranean diet is associated with decreased serum total cholesterol and LDL cholesterol but little change in HDL cholesterol when compared with a diet typical of Western diet higher in saturated fats.

### Q.23 Write Structure of phospholipids?

There are two classes of phospholipids:

- i. Glycerophospholipids
- ii. Sphingophospholipids

#### Glycerophospholipids:

Those that have glycerol as a backbone: glycerophospholipids

#### Sphingophospholipids:

Those that contain sphingosine: sphingophospholipids

- ☐ **Phospholipids** are the predominant lipids of cell membranes. Membrane lipids are **amphipathic** i.e. one end of the molecule is hydrophobic, the other hydrophilic.
- ☐ Their hydrophobic interactions with each other and their hydrophilic interactions with water direct their packing into sheets called **membrane bilayers**.

The formation of membrane bilayers help in partitioning the cellular environment from extracellular environment.

- ☐ Non-membranebound phospholipids serve additional functions in the body,

**for example,**

As components of lung surfactant essential components of bile.

In contrast to triacylglycerol which is essentially synthesized only in liver, adipose tissue, lactating mammary glands, and intestinal mucosal cells. essentially all cells except mature erythrocytes can synthesize phospholipids.

### Q.24 What is Glycerophospholipids? (Phosphatidic acid)

#### Glycerophospholipids:

- ☐ It is the simplest phosphoglyceride,

- ☐ It is a diacylglycerol with a phosphate group on the third carbon of glycerol.
- ☐ **Phosphatidic acid** is the precursor of the other members of this group. Further esterification with a low-molecular weight alcohol gives a glycerophospholipid
- ☐ All glycerophospholipids are derivatives of phosphatidic acid and are named for their polar head.
- ☐ In general, glycerophospholipids contain a C16 or C18 saturated fatty acid at **C-1** and a C18 or C20 unsaturated fatty acid at **C-2** in addition to a phosphate group on **C-3**
- ☐ C16 or C18 saturated fatty acid at C-1, C18 or C20 unsaturated fatty acid at C-2
- ☐ The fatty acids in glycerophospholipids can be any of a wide variety, so a given

Phospholipid (phosphatidylcholine, for example) may consist of several molecular species, each with its unique complement of fatty acids.

The phosphate group on phosphatidic acid (PA) can be esterified to another compound containing a hydroxyl group

Serine + PA → phosphatidylserine

Ethanolamine + PA → phosphatidylethanolamine

Choline + PA → phosphatidylcholine (lecithin)

Inositol + PA → phosphatidylinositol

### Q.25 Write Phosphatidylcholines (Lecithins)?

#### Lecithins:

- ☐ The most abundant phospholipids of the cell membrane represent a large proportion of the body's store of choline- important in nervous transmission, as acetylcholine.
- ☐ Dipalmitoyl phosphatidyl choline (DPPC or dipalmitoylecithin), is also the major lipid component of lung surfactant.

#### Examples of Lecithins:

- ☐ Dipalmitoyl phosphatidyl choline and
- ☐ Palmitoyl-oleylphosphatidylcholine are two different examples of Lecithins.
- ☐ **Alveoli:**  
These are the structural and functional unit of respiratory system in which gaseous exchange takes place. A thin fluid layer lines the alveoli for efficient gas exchange.



☐ **Surface tension:**

When the water forms a surface with air, the water molecules on the surface (in contact of air) are strongly attracted to each other trying to reduce the surface area of contact. This is called "**surface tension**". surface tension might result in alveolar collapse it requires a certain inflation pressure to maintain expanded alveoli the higher the surface tension, the more pressure required to inflate the bubble, especially in small alveoli.

- ☐ Are made and secreted by lung cells, surfactant serves to decrease the surface Tension of this fluid layer.
- ☐ It scatters among the fluid molecule decreasing the attraction between them.

**Q.26 Write Phosphatidyl ethanol amine and phosphatidylserine?**

- ☐ These are also found in cell membranes and differ from phosphatidylcholine only in that ethanolamine or serine, respectively, replaces choline
- ☐ **Serine** is a standard amino acid which on decarboxylation produces ethanolamine: a primary alcohol and a primary amine.
- ☐ Phosphatidylserine also plays a role in apoptosis (programmed cell death)

**Q.27 Explain cardiolipin? diphosphatidylglycerol**

**Cardiolipin:**

- ☐ Two molecules of phosphatidic acid esterified through their phosphate groups to an additional molecule of glycerol
- ☐ In eukaryotes, cardiolipin is virtually exclusive to the inner mitochondrial membrane, where it appears to be required for the maintenance of certain respiratory complexes of the electron transport chain.
- ☐ Decreased cardiolipin levels or alterations in its structure or metabolism cause mitochondrial dysfunction in aging and in pathological conditions including heart failure.
- ☐ Cardiolipin is antigenic, and is recognized by antibodies raised against *Treponema pallidum*, the bacterium that causes syphilis
- ☐ **Antigen** : usually protein, is a molecule capable of generating immune respons

### Q28 Write VDRL test?

The VDRL test measures immunoglobulin G (IgG) and IgM antibodies to lipoidal material released from damaged host cells as well as to lipoprotein like material and possibly cardiolipin released from the treponemes.

#### NOTE:

**.Syphilis** is a bacterial infection usually spread by sexual contact. Anti-cardiolipin antibodies may also be found nonspecifically in certain autoimmune diseases. Such as SLE and rheumatoid arthritis

### Q.29 What is PI (Phosphatidylinositol)?

- ☐ It consists of phosphatidic acid and Inositol in an ester linkage
- ☐ Phosphatidylinositol (PI) is an unusual phospholipid in that it often contains stearic acid on carbon 1 and arachidonic acid on carbon 2 of the glycerol
- ☐ PI, therefore, as a reservoir of arachidonic acid, serves as precursor for prostaglandin synthesis
- ☐ Specific proteins can be covalently attached via a carbohydrate bridge to membrane-bound PI.
- ☐ Phosphatidylinositol is a precursor of second messengers.

#### **PIP2:**

- ☐ The phosphorylation of membrane-bound phosphatidylinositol produces phosphatidylinositol 4,5-bisphosphate (**PIP2**). The degradation of PIP2 by phospholipase C occurs in response to the binding of a variety of neurotransmitters, hormones, and growth factors to receptors on the cell membrane.
- ☐ The products of this degradation are inositol 1,4,5 trisphosphate (IP3) and diacylglycerol (DAG)

### Glycerophospholipids

### Q.30 Explain ether lipids and write also its significance?

#### **Ether lipids:**

- ☐ They are type of Glycerophospholipids, in which one acyl chains is attached to glycerol in ether linkage, rather than ester linkage.
- ☐ Ether lipids with an unsaturated group (alkenyl) at the 1<sup>st</sup> position on the glycerol chain are called **Plasmalogens**.
- ☐ These compounds constitute as much as 10% of the phospholipids of brain and muscle.
- ☐ Vertebrate heart tissue is uniquely enriched in ether lipids
- ☐ About half of the heart phospholipids are plasmalogens.
- ☐ The membranes of halophilic bacteria, ciliated protists, and certain invertebrates also contain high proportions of ether lipids.

**NOTE:**

salt-loving. **Halophiles** are organisms that thrive in high salt concentrations.

**Significant of ether lipids:**

The functional significance of ether lipids in these membranes is unknown; perhaps their resistance to the phospholipases that cleave ester-linked fatty acids from membrane lipids is important in some roles.

**Q.31 What is Platelet-activating factor (PAF)?**

**Platelet-activating factor (PAF):**

- ☐ This is an unusual ether glycerol phospholipid, with a saturated alkyl group in an ether link to carbon 1 and an acetyl residue (rather than a fatty acid) at carbon 2 of the glycerol backbone.
- ☐ PAF is synthesized and released by a variety of cell types
- ☐ It binds to surface receptors, triggering potent thrombotic and acute inflammatory events.
- ☐ It causes platelets to aggregate and degranulate (required for clotting), and neutrophils and alveolar macrophages to generate superoxide radicals (required for microbial killing).

**Q.32 Write Sphingolipids..?**

- ☐ Sphingolipids, like other membrane lipids, are composed of a hydrophobic portion, (ceramide) and a polar head group.
- ☐ The first three carbons at the polar end of sphingosine are analogous to the three carbons of glycerol in glycerophospholipids
- ☐ The amino group at C-2 bears a fatty acid in amide linkage

- ☐ The fatty acid is usually saturated or monounsaturated, with 16, 18, 22, or 24 carbon atoms.
- ☐ Ceramide is the parent compound for this group.

### Q.33 Write Subclasses of sphingolipids?

There are two subclasses of sphingolipids.

- (i) Sphingomyelins
- (ii) Sphingoglycolipids

#### (i)Sphingomyelins:

- ☐ It contain phosphocholine or phosphoethanolamines as their polar head group and are therefore classified along with glycerophospholipids as phospholipids.
- ☐ **Sphingomyelins** are present in the plasma membranes of animal cells and are especially prominent in nerve tissue including myelin, - thus the name "sphingomyelins"
- ☐ Sphingomyelin of the myelin sheath contains predominant longerchain fatty acids such as lignoceric acid and nervonic acid (24 carbon)
- ☐ whereas gray matter of the brain has sphingomyelin that contains primarily stearic acid(18 carbon).

#### (ii)Sphingoglycolipids:

They are molecules that contain both carbohydrate and lipid (in the form of ceramide) components.

- ☐ **Glycosphingolipids** are molecules that contain both carbohydrate and lipid components
- ☐ Like the phospholipid sphingomyelin, they are derivatives of ceramide They are also an important component of membrane bilayers.
- ☐ They occur largely in the outer face of plasma membranes have polar head groups with
- ☐ one or more sugars connected directly to the -OH at C-1 of the ceramide moiety by an O-glycosidic bond.

When the alcohol group at carbon 1 of sphingosine is esterified to phosphorylcholine, sphingomyelin, the only significant sphingophospholipid in humans, is produced.

### Q.34 What is cerebrosides and globosides?

#### Cerebrosides:

- ☐ **Cerebrosides** have a single sugar linked to ceramide; galactocerebrosides are found in the plasma membranes of neural cells, glucocerebrosides in the plasma membranes of non neural cells.
- ☐ A glycosphingolipid that has only one sugar as the side chain is called a cerebroside
- ☐ Cerebrosides have a single sugar linked to ceramide.

#### Globosides:

- ☐ **Globosides** are glycosphingolipids with two or more sugars, usually D -glucose, D- galactose, or N-acetyl-Dgalactosamine
- ☐ Globosides are highly abundant in RBCs. ~AS Globosides are also found in human serum, spleen and liver.
- ☐ **Galactosylceramide** is a major glycosphingolipid of brain and other nervous tissue,
- ☐ It contains a number of characteristic C24 fatty acids, eg, cerebronic acid

### Q.35 Explain Gangliosides?

#### Gangliosides:

- ☐ They have oligosaccharides as their polar head groups and one or more residues of N-acetylneuraminic acid (a sialic acid), at the termini.
- ☐ Sialic acids are acidic sugars with a nine carbon backbone, of which the most common is N-acetylneuraminic acid
- ☐ Sialic acid gives gangliosides the negative charge at Ph 7.

- ☐ Gangliosides with one sialic acid residue are in the GM (M for mono-) series,  
those with two are in the GD (D for di-) series, and so on (GT three sialic acid residues; GQ, four)
- ☐ About 6% of brain lipids are gangliosides and were first isolated from the ganglion of brain cells
- ☐ They act as specific receptors for glycoprotein hormones in the cells.
- ☐ Some gangliosides also serve as receptors for some bacterial protein toxins e.g.
- ☐ Cholera toxin binds to the GM1 gangliosides on the surface of target cells
- ☐ Gangliosides also help in cell-cell recognition and thus have a significant role in growth and differentiation of tissues and also in carcinogenesis.

### **Q.36 What is sulfatides ?**

#### **Sulfatides:**

- ☐ Sulfoglycosphingolipids (sulfatides) are cerebroside that contain sulfated galactosyl residues, and are therefore negatively charged at physiologic pH
- ☐ Sulfatides are found predominantly in nerve tissue and kidney.

### **Q.37 What is Glyceroglycolipids and galactolipids?**

#### **Glyceroglycolipids:**

- ☐ These are the predominant membrane lipids of the plants, such as those of chloroplast.
- ☐ They include
  - (i) Galactolipids and
  - (ii) Sulfolipids
- ☐ As the name indicates these glycolipids contain glycerol instead of sphingosine as their backbone.

#### **Galactolipids:**

- ☐ In galactolipids, the C3 of the glycerol moiety is connected to one or more galactose residues by glycosidic linkages.
- ☐ The head groups of these galactolipids are uncharged but polar.
- ☐ Galactolipids are localized in the internal membranes of chloroplast

- ☐ They constitute about 70% to 80 % of plant membrane lipids and thus are the most abundant lipids in the biosphere.

### Q.38 What is sulfolipids?

#### Sulfolipids:

- ☐ They are membrane glycolipids with sulfur containing functional groups
- ☐ Sulfonated glucose is joined to the **C3** of diacylglycerol in glycosidic linkage

### Q.39 What is steroids?

#### Steroids:

- ☐ A **steroid** is a lipid whose structure is based on the tetracyclic (four-ring) structure consists of :  
3 cyclohexane rings.  
1 cyclopentane ring.
- ☐ Steroids with eight to ten carbon atoms in the side chain at C- 17 and a hydroxyl group at C-3 are classified as sterols.

### Q.40 Explain cholesterol?

#### Cholesterol:

- ☐ Cholesterol is the major sterol in animal tissues.
- ☐ Cholesterol has an eight carbon branched hydrocarbon chain attached to **C-17** of the D ring.
- ☐ Ring A has a hydroxyl group at C- 3, and ring B has a double bond between C-5 and C-6.
- ☐ Cholesterol is an amphipathic lipid.
- ☐ Cholesterol is a structural component of all cell membranes, modulating their Fluidity.
- ☐ Cholesterol is a precursor of bile acids steroid hormones vitamin D.
- ☐ All tissues containing nucleated cells are capable of cholesterol synthesis, which occurs in the endoplasmic reticulum and the cytosol.

- ☐ Cholesterol is present in tissues and in plasma either as free cholesterol or combined with a long-chain fatty acid as cholesteryl ester
- ☐ In plasma, both forms are transported in lipoproteins.
- ☐ In esterified form, with a FA attached at C-3, the structure becomes more hydrophobic than free cholesterol.
- ☐ Cholesterol is excreted from the body via the bile either in the unesterified form or after conversion into bile acids in the liver.

### **Cholesteryl esters:**

Cholesterol esters are not found in membranes, and are normally present only in low levels in most cells.

### **Q.41 Write bile acids and bile salts?**

- ☐ Bile is a fluid that is made and released by the liver and stored in the gallbladder
- ☐ Bile helps with lipid Digestion.
- ☐ Bile can either pass directly from the liver into the duodenum, or be stored in the gallbladder when not immediately needed for digestion.
- ☐ Bile consists of a watery mixture of organic and inorganic compounds.

### **Bile acid:**

- ☐ Phosphatidylcholine (lecithin) and bile salts (conjugated bile acids) are quantitatively the most important organic components of bile.

### **Bile acids:**

- ☐ The primary bile acids are synthesized in the liver from cholesterol
- ☐ These are cholic acid and chenodeoxycholic acid.
- ☐ The bile acids contain 24 carbons, with two or three hydroxyl groups and a side chain that terminates in a carboxyl group
- ☐ The carboxyl group has a pKa of about 6 and, is not fully ionized at physiologic pH- hence the term "**bile acid**"
- ☐ The bile acids are amphipathic molecules They therefore can act as emulsifying agents in the intestine

### **Q.42 What is eicosanoic acid ?**



- ☐ Eicosanoids are a large group of lipid messengers with potent effects on every tissue in the body.
- ☐ Eicosanoids are derived from metabolism of 20-carbon, polyunsaturated fatty acids (eicosanoic acids).
- ☐ **Eicosanoids include (but not limited to):**
  - ☐ **Prostanoids** consisting of Prostaglandins, Prostacyclins, Thromboxanes
  - ☐ **Leukotrienes**
  - ☐ **Lipoxins**
  - ☐ **Epoxides**
- ☐ These extremely potent compounds acting through their specific receptors elicit a wide range of physiologic and pathologic responses.
- ☐ particularly important in eliciting inflammatory response that occurs after infection or injury and produce **symptoms** such as pain, swelling, and fever. they also control bleeding through forming blood clots.
- ☐ Eicosanoids are derived from either omega-3 ( $\omega$ -3) or omega-6 ( $\omega$ -6) fatty acids.
- ☐ **Arachidonic acid** is the most common precursor of the eicosanoids.

#### Q.43 Write pathway for the metabolism of arachidonic?

Three major pathways for the metabolism of arachidonic have been discovered so far.

These are :

- (i) **Cyclooxygenase pathway:**  
prostaglandins and thromboxanes.
- (ii) **lipoyxygenase pathway:**  
leukotrienes, HETEs, and lipoxins.
- (iii) **cytochrome P450 pathway:**  
Epoxides and HETEs

#### Q.44 Write different series of eicosanoids which depends upon?

- ☐ Depending on the precursor 20 C FA. derived from the essential fatty acids  
**linoleic acid** and **linolenic**, OR

- ☐ Directly from dietary **arachidonic acid** and **eicosapentaenoic acid**.
- ☐ Depending on the precursor different numbers of double bonds are present in these eicosanoids reflecting the parent 20C FA.

#### **Q.45 Explain Cyclooxygenase pathway and write its nomenclature?**

Cyclooxygenase pathway include :

- (i) Prostaglandins and
- (ii) Thromboxanes.

##### **(i) Prostaglandins:**

- ☐ Prostaglandins are fatty acids containing 20 carbon atoms, including an internal 5-carbon ring.
- ☐ Prostaglandins have a hydroxyl group at C 15, a double bond between C 13 and C 14, and various substituents on 5 membered ring at C9 and C11
- ☐ Double bonds also may be present between carbons 5 and 6 and between carbons 17 and 18 in case of series 2 and 3.

##### **Nomenclature of prostaglandins (PGs) involves:**

- ☐ The assignment of a capital letter ( PGE), a numeral subscript PGE**1**), and for the PGF family, a Greek letter subscript (PGF**2 $\alpha$** ).
- ☐ The capital letter refers to the ring substituents at positions X and Y.
- ☐ R4 contains four carbons. R7 and R8 contain seven and eight carbons, respectively. prostacyclins (PGI) contain two rings.
- ☐ The numeral subscript that follows the capital letter(e.g. PGE**1**) refers to the PG series 1, 2, or 3, determined by the number of unsaturated bonds present in the linear portion of the hydrocarbon chain.
- ☐ It does not include double bonds in the internal ring.
- ☐ The double bonds between carbons 13 and 14 are trans; the others are cis
- ☐ The Greek letter subscript, found only in the F series, refers to the position of the hydroxyl group at carbon 9.

##### **Cyclooxygenase pathway:**

##### **(ii) Thromboxanes (TX):**

Thromboxanes also formed via the cyclooxygenase pathway, differ from PGs in that they contain a 6- membered ring that includes an oxygen atom. Thromboxanes have a six membered ring containing an oxygen atom. Substituents are attached to the ring at carbons 9 and 11. In the case of TXA<sub>2</sub>(shown above), an oxygen atom connects carbons 9 and 11.

#### Q.46 Write Biosynthesis of the PGS and TX..?

- ☐ Those derived from arachidonic acid, the 2-series, (such as PGE<sub>2</sub>,TXA<sub>2</sub>), are described here because the 1-series and the 3-series are present in very small amounts in humans.
- ☐ **The initial step**, which is catalyzed by a cyclooxygenase (COX), forms the five-membered ring and adds four atoms of oxygen (two between C 9 and C11, and two at C 15) to form the unstable PGG<sub>2</sub>.
- ☐ The hydro-peroxy group at carbon 15 is quickly reduced to a hydroxyl group by a peroxidase to form PGH<sub>2</sub>
- ☐ PGH<sub>2</sub> is the precursor of all other PGs and TXAs.
- ☐ **The next step is** tissue specific For example, PGH<sub>2</sub> may be reduced to PGE<sub>2</sub> or PGD<sub>2</sub> by specific isomerases (PGE synthase or PGD synthase respectively).
- ☐ For example, TXA Synthase is present in high concentration in platelets and forms TXA<sub>2</sub>.
- ☐ In the vascular endothelium, however, PGH<sub>2</sub> is converted to the PGI<sub>2</sub> by action of Prostacyclin Synthase.
- ☐ The beneficial effect of cold water fish (e.g., salmon), with a high content of eicosapentaenoic( TX<sub>3</sub>) acid (EPA), and docosahexaenoic acid (DHA) comes from the fact that they lead to formation of more TXA<sub>3</sub> relative to TXA<sub>2</sub>.
- ☐ TXA<sub>3</sub> is less effective in stimulating platelet aggregation than its counterpart in the 2- series, TXA<sub>2</sub>.

#### Q.47 Explain Lipxygenase Pathway?

Synthesis of the

- (i) Leukotrienes,
- (ii) HETEs, and
- (iii) Lipoxins

- ☐ In addition to serving as a substrate for the cyclooxygenase pathway, arachidonic acid and other 20 C FAs also act as substrate for the lipoxygenase pathway.
- ☐ In contrast to products of the cyclooxygenase pathway which are cyclical.

Products of lipoxygenase pathway are linear.

- ☐ **Similar nomenclature** rules are followed for Leukotrienes and Lipoxins, except that there are no series of 1 and 2. The series starts from 3.
- ☐ Eicosa-tri-enoic acid (ETA) have 3 double bonds from; Arachidonic acid have 4 double bonds From; Eicosapentaenoic acid (EPA) have 5 double bonds .
- ☐ The double bonds at which oxygen is added are between C5 & C6, between C11 and C12 and between C14 and C15.
- ☐ As a result of this isomerization, double bond between C5 & C6 moves to C6 & C7, between C11 & C12 moves to C10 & C11 between C14 & C15 moves to C13 & C14

#### (i) **HETEs:**

- ☐ The hydro-peroxy group is unstable and can be converted to the more stable hydroxy group to form HETEs.
- ☐ HETEs themselves act as messenger molecules.

#### (ii) **leukotrienes(LTs):**

- ☐ The other alternate is the conversion of HPETEs to leukotrienes(LTs) and Lipoxins(LXs),
- ☐ Which are more potent and have more defined physiological roles.
- ☐ The leukotrienes(LTs) and Lipoxins(LXs), Have 3 to 5 double bonds as described earlier, in comparison to prostaglandins which have 1 to 3 double bonds.
- ☐ The major leukotrienes are produced by 5- lipoxygenase 5-HPETE is converted to leukotriene **A<sub>4</sub>** (LTA<sub>4</sub>).
- ☐ Other functional leukotrienes are formed from LTA<sub>4</sub> for example, LTA<sub>4</sub> is converted to LTB<sub>4</sub>, as a 5,12- dihydroxy derivative. the addition of reduced glutathione to carbon 6 forms LTC<sub>4</sub>
- ☐ Removal of glutamate residue from LTC<sub>4</sub> forms LTD<sub>4</sub>. LTD<sub>4</sub> on removal of glycine becomes LTE<sub>4</sub>
- ☐ Leukotrienes were so named because they were first discovered in leukocytes(white blood cells).

#### (iii) **Lipoxins:**

- ☐ The lipoxins are formed through the action of 15- lipoxygenase followed by the action of 5- lipoxygenase on arachidonic acid.
- ☐ A series of reductions of the resultant hydro-per-oxy groups leads to the formation of tri-hydroxy derivatives of arachidonic acid known as the lipoxins.
- ☐ Lipoxins induce chemotaxis and stimulate superoxide radicals for killing of microorganisms. Chemotaxis is migration of WBCs to the tissue site of injury or inflammation.
- ☐ Prostaglandins, thromboxanes, leukotrienes and lipoxins have very short half lives and rapidly degraded in the body.
- ☐ In summary, Eicosanoids are derived from C20 (eicosanoic) fatty acids synthesized from the essential fatty acids and make up important groups of physiologically active compounds.

#### **Q.48 Write Biomedical importance of nucleotides in details?**

##### **(i) Precursors of nucleic acids:**

Nucleotides are the building blocks of nucleic acids. Without them, DNA or RNA can not be produced.

##### **(ii) Transmission of genetic information:**

This gives them the ability to store and transmit genetic information from; one generation to the next which is a fundamental condition for life.

##### **(iii) Protein synthesis:**

The ultimate expression of this information, is therefore dependent on nucleotides.

##### **(iv) Energy currency:**

- ☐ Nucleotides play an important role as "energy currency" in the cell.
- ☐ Nucleoside tri- and diphosphates such as **ATP and ADP** are the principal donors and acceptors of phosphoryl group in metabolism. By doing this, they play a key role in the energy transduction.
- ☐ This energy is used in almost every energy requiring process in the body, such as; Muscle contraction, Transmission of nerve impulse,

##### **(v) Carriers of intermediates:**

- ☐ Nucleotides also serve as carriers of activated intermediates in the synthesis of some carbohydrates, lipids, and proteins.

- ☐ The sugar derivatives UDP-glucose and UDP-galactose participate in sugar inter conversions

**(vi) Co-enzymes:**

When linked to vitamins nucleotides are structural components of several essential coenzymes, for example, coenzyme A, FAD, (Flavin Adenine Dinucleotide)

NAD<sup>+</sup> (Nicotinamide adenine Dinucleotide) and NADP<sup>+</sup> (Nicotinamide adenine Dinucleotide Phosphate)

**(vii) Regulatory compounds:**

- ☐ Nucleotides are important regulatory compounds for many of the pathways of intermediary metabolism, inhibiting or activating key enzymes.
- ☐ Roles that nucleotides perform in metabolic regulation include: ATP-dependent enzyme phosphorylation in key metabolic reactions.

**(viii) Sulfate group donor:**

Adenosine 3'-phosphate- 5'-phosphosulfate is the sulfate donor for sulfated proteoglycans sulfate conjugates of drugs.

**(ix) Methyl group donor:**

S-adenosylmethionine is a methyl group donor e.g Nor-adrenaline → Adrenaline by methylation. **N** These are neurotransmitter of the sympathetic nerves in the cardiovascular system.

**(x) Second messengers:**

Nucleotides, such as cyclic AMP (cAMP) and cyclic GMP (cGMP), serve as second messengers in signal transduction pathways.

**(xi) Signal Transduction:**

GTP and GDP play key roles in activating or inhibiting proteins in various cellular signaling cascades.

**(xii) Medical applications:**

- ☐ Specifically medical applications include the use of synthetic purine and pyrimidine analogs that contain halogens, thiols, or additional nitrogen atoms;
- ☐ Their use includes chemotherapy for cancer as suppressors of the immune response during organ transplantation. as anti-viral drugs such as in the treatment of AIDS.

#### **Q.49 Write Composition of Nucleotides and explain each composition?**

Nucleotides are composed of:

- (i) A nitrogenous base (purine or pyrimidine)
- (ii) A pentose monosaccharide
- (iii) One, two, or three phosphate groups

#### **Q.50 Explain Nitrogenous base?**

##### **(i) Nitrogenous Bases: (First composition of Nucleotides)**

The nitrogen-containing bases belong to two families of compounds:

- (a) Purines**
- (b) Pyrimidines**
- ☐ The suffix “ine” in these bases denotes the presence of nitrogen (amine) in the ring. However, there are some exceptions such as naming of uracil
- ☐ The utility of these nitrogen-containing ring structures lies in the ability of the nitrogen to form hydrogen bonds and to accept and donate electrons while still part of the ring.

##### **(a) Purines:**

Both DNA and RNA contain the same purine bases:

Adenine (A)  
Guanine (G)

**Adenine** when combined with pentose the structure is known as Adenosine or deoxyadenosine. Adenine is 6-aminopurine

**Guanine** when combined with pentose the structure is known as Guanosine or Deoxyguanosine. Guanine is 2-amino,6-hydroxypurine.

**Minor Purine Bases:** Inosine (I) & methyl guanine (7mG)

**Unnatural:** Mercaptopurine, Allopurinol & 8- Azaguanine Other purines include: hypoxanthine and xanthine.

(b) **Pyrimidines:**

Pyrimidines include:

Cytosine (C)—in both DNA and RNA

Thymine (T)—only in DNA

Uracil (U) —only in RNA

**Cytosine** when combines with pentose it becomes deoxycytidine and Cytidine. Cytosine is 2-oxy-4-amino-pyrimidine

**Thymine** becomes thymidine and deoxythymidine .Thymine is 2,4-dioxy-5-methyl-pyrimidine.

**Uracil (U)** becomes uridine and deoxyuridine depending on the type of sugar.

Uracil is 2,4-dioxypyrimidine

T and U differ by only one methyl group, which is present on T but absent on U

**Minor Pyrimidine Bases:** Dihydrouridine (DHU) , 5-Methyl Cytadine & 5-Hydroxy-Methyl Cytadine

**Unnatural PyrimidineBases:** Fluorouracil (5FU) & 6-Aza Cytosine (AZC)

**Q51: Write Pentose Sugar...? Nucleotides)**

**(second composition of**

ii. **Pentose Sugar:**

D-ribose and 2-deoxy D-ribose are the only sugars so far found in the nucleic acids.

These also pentoses belong to D-family

They are present as Furanose (ring) in the form of  $\beta$ -Anomer .

If the sugar is **Dribose**, a ribonucleoside is produced.

If the sugar is **2- deoxy D- ribose**, a deoxyribonucleoside is produced.

**Phosphate group:**

There may be one, two, or three phosphate groups present in nucleotides.

**Nucleotides** are monophosphate, diphosphate, or triphosphate esters of nucleosides.



These phosphate groups give an over all negative charge to the nucleotides.

### **Q.52 Write different Properties of Nitrogenous Bases?**

#### **(i) Aromatic:**

The Nitrogen containing bases are aromatic i.e. they have alternate double bonds.

#### **(ii) Heterocyclic:**

They are heterocyclic i.e. structures that contain other atoms in addition to carbon, such as nitrogen in the ring structure. The six-atom rings of purines and pyrimidines are numbered in opposite directions.

#### **(iii) Weak Bases:**

Purines or pyrimidines with an – NH<sub>2</sub> group are weak Bases.

#### **(iv) Functional Groups:**

The most important functional groups of pyrimidines and purines are ring nitrogens carbonyl groups exocyclic amino groups

#### **(v) Hydrophobicity:**

The purine and pyrimidine bases are hydrophobic and relatively insoluble in water at the nearneutral cell pH.

#### **(vi) Stacking Interaction:**

- ☐ Hydrophobic stacking interactions in which two or more bases are positioned with the planes of their rings parallel (like a stack of coins) are one of two important modes of interaction between bases in nucleic acids.
- ☐ Base stacking helps to minimize contact of the bases with water, and these interactions are\ very important is stabilizing the three dimensional structure of nucleic acids.

#### **(vii) UV light absorbance:**

- ☐ The conjugated double bonds of purine and pyrimidine derivatives absorb ultraviolet light.
- ☐ Nucleic acids are characterized by a strong absorption at wavelengths near 260 nm.
- ☐ The mutagenic effect of ultraviolet light is due to its absorption by nucleotides that results in chemical modifications in DNA.
- ☐ This property is also utilized in quantitative and qualitative analysis of nucleotides and nucleic acids.

**(viii) Tautomerism:**

- ☐ All these bases can exist in keto-enol or amine-imine form. at physiologic pH keto and amine form is predominant.
- ☐ Note that the smaller pyrimidine molecule has the *longer* name and the larger purine molecule the *shorter* name.

**(ix) N-glycosidic bond:**

- ☐ Sugars are linked to the heterocycle by a  $\beta$  -N-glycosidic bond, almost always to the N-1 of a pyrimidine N-9 of a purine.
- ☐ The N-glycosyl bond is formed by removal of the elements of water a hydroxyl group from the pentose and hydrogen from the base.

**(x) Numbering of Carbon and Nitrogen Atoms:**

- ☐ The carbon and nitrogen atoms in the rings of the base and the sugar are  
Numbered separately.
- ☐ The atoms in the rings of the bases are numbered. 1 to 6 in pyrimidines &  
1 to 9 in purines.
- ☐ The carbons in the pentose are numbered 1' to 5 '.
- ☐ Numerals with a prime (e.g., 2' or 3') distinguish atoms of the sugar from those  
of the heterocycle.

**(xi) Phosphodiester Bond:**

- ☐ When two or more nucleotides combine together a phosphodiester bond is formed.
- ☐ This bond is formed mainly between the 3'OH group of sugar of one Nucleotide and 5'PO<sub>4</sub> group of sugar of another nucleotide creating a phosphodiester linkage.

- ☐ By definition, the 5' end lacks a nucleotide at the 5' position and the 3' end lacks a nucleotide at the 3' position.
- ☐ The sugar and phosphate group is called the **backbone** of the nucleic acid.

The backbones of both DNA and RNA are hydrophilic.

- ☐ The hydroxyl groups of the sugar residues form hydrogen bonds with water.
- ☐ The phosphate groups, are completely ionized and negatively charged at pH 7.
- ☐ Depending on the number of nucleotides mono- di-, tri-, oligo and polynucleotides are formed as a result of phosphodiester bond formation.

### Q.53 Write Cyclic Nucleotides?

There are two important cyclic nucleotides:

- (i) Cyclic AMP cAMP
- (ii) Cyclic GMP cGMP

#### (i) Cyclic AMP:

Cyclic AMP is a cyclic nucleotide cAMP is synthesized in tissues from ATP chemically it is 3'-5' adenosine monophosphate.

#### Functions of c-AMP:

- ☐ Acts as second messenger in the cell. It has role in glycogen metabolism It decreases cholesterol synthesis.
- ☐ It causes activation of protein kinases which in turn; activate or deactivate other enzymes.
- ☐ Moreover, it regulates insulin secretion, catecholamine biosynthesis & Melatonin synthesis.

#### (ii) Cyclic GMP:

Cyclic GMP is synthesized from GTP. It serves as a second messenger in response to nitric oxide during relaxation of smooth muscle (especially blood vessels) so it has role in smooth muscle relaxation and vasodilatation.

### It also has role in:

- Protein phosphorylation
- Neurotransmission
- Insulin action
- Regulation of sodium channels.

### Q.54 Explain DNA....?

- ☐ It stands for Deoxyribonucleic acid.
- ☐ DNA is present in nuclear chromosomes of eukaryotes, mitochondria, chloroplasts and plasmids of Prokaryotes.
- ☐ DNA is a polymer of deoxyribonucleoside monophosphates covalently linked by 3' 5'- phosphodiester bonds.
- ☐ DNA is a repository of genetic information
- ☐ In eukaryotic cells, DNA is present in the chromosomes in the nucleus.
- ☐ It is found associated with basic proteins HISTONES and also various other proteins present in nucleus (nucleoproteins).
- ☐ Prokaryotic cells lack nuclei, and have a single chromosome.
- ☐ The protein-DNA complex is present in a non membrane bound region known as **nucleoid**.
- ☐ It also contain nonchromosomal DNA in the form of plasmids. Nucleic acid structure can be described in terms of hierarchical levels of complexity (primary, secondary, tertiary)  
A hierarchy ( Greek ) is an arrangement of items.
- ☐ The **primary structure** of a nucleic acid is its covalent structure and nucleotide sequence.
- ☐ Any regular, stable structure taken up by some or all of the nucleotides in a nucleic acid can be referred to as **secondary structure** In DNA double helix, the two strands of DNA are held together by hydrogen bonds.
- ☐ The secondary structure is responsible for the shape that the nucleic acid assumes.
- ☐ The complex folding of large chromosomes within eukaryotic chromatin and bacterial nucleoids is generally considered **tertiary structure**.

### Q. 55 Explain DNA Interactions?

- ☐ The purine and pyrimidine bases are hydrophobic and relatively insoluble in water at the near neutral pH of the cell.
- ☐ Hydrophobic stacking interactions in which bases are positioned with the planes of their rings parallel.
- ☐ Hydrophobic stacking are an important interaction between bases in nucleic acids.
- ☐ The stacking also involves a combination of van der Waals and dipole-dipole interactions between the bases.
- ☐ Base stacking helps to minimize contact of the bases with water.
- ☐ Therefore basestacking interactions are very important in stabilizing the three dimensional structure of nucleic acids.
- ☐ The most important functional groups of pyrimidines and purines are ring nitrogens, carbonyl groups, and exocyclic amino groups.
- ☐ Hydrogen bonds involving the amino and carbonyl groups are the second important mode of interaction between bases in nucleic acid molecules.
- ☐ The most important hydrogen-bonding patterns are those defined by James D. Watson and Francis Crick, in which A bonds specifically to T (or U) and G bonds to C.

### **Q.56 Explain DNA primary, secondary and tertiary structure?**

#### **DNA Primary Structure:**

- ☐ The primary structure of a nucleic acid is its covalent structure and nucleotide sequence.
- ☐ The back bone of the primary structure is the linear strand made by sugar phosphate residues, linked together, while the bases project laterally.
- ☐ This way a long, unbranched chain is formed. The resulting long, unbranched chain has polarity. Both 5'-end and 3'-end are free. at 5'-end there is a free phosphate. at 3'-end there is a free OH that are not attached to other nucleotides.
- ☐ Purines and pyrimidines project laterally from the backbone and forms a variable part.
- ☐ The variable part is concerned with the expression of genetic information.
- ☐ By convention, the structure of a single strand of nucleic acid is always written with the 5' end at the left and the 3' end at the right that is, in the 5' to 3' direction.

### **DNA Secondary Structure:**

- ☐ Any regular, stable structure taken up by some or all of the nucleotides in a nucleic acid can be referred to as secondary structure.
- ☐ This model was presented by Watson and Crick in 1953.
- ☐ The two polydeoxyribonucleotide strands are coiled around a common axis called **axis of symmetry**.
- ☐ The overall structure resembles a twisted ladder.
- ☐ **Grooves:** The spatial relationship between the two strands in the helix creates a major (wide) groove a minor (narrow) groove.
- ☐ These grooves provide access for the binding of regulatory proteins to their specific recognition sequences along the DNA.

### **DNA tertiary Structure:**

- ☐ The complex folding of large chromosomes within eukaryotic chromatin and bacterial nucleoids is generally considered tertiary structure.
- ☐ Eukaryotic DNA is associated with tightly bound basic proteins, called **histones**.
- ☐ These serve to order the DNA into fundamental structural units, called **nucleosomes**.
- ☐ There are five classes of histones, designated H1, H2A, H2B, H3, and H4.
- ☐ Two molecules each of H2A, H2B, H3, and H4 form the structural core of the nucleosome.
- ☐ Around this core, a segment of the DNA double helix is wound nearly twice approximately 140bp.
- ☐ The linker DNA this 50 bp DNA is complexed with the fifth type of histone, H1.
- ☐ Nucleosomes can be packed more tightly to form a polynucleosome also called a nucleofilament or a 30-nm fiber.

### **Q.57 Write properties of DNA?**

#### **(i)Template and Nontemplate Strands:**

**Template strand:**

The term template strand refers to the sequence of DNA that is copied during the synthesis of mRNA.

The 3'-5' strand is called Template strand

**Non Template:**

The opposite strand is called the Non Template or coding strand or the mRNA like

strand it has base sequence directly corresponding to the mRNA sequence the sequence corresponds to the codons that are translated into protein.

5'-3' strand is called Non Template (coding strand).

**Base Pairing:**

The bases of one strand of DNA are paired with the bases of the opposite strand,

so that Adenine is always paired with thymine Cytosine is always paired with guanine.

**(ii)Chargaff's Rules:**

- ☐ Due to specific base pairing of DNA i.e A to T and G to C In any sample of double-stranded DNA the amount of adenine equals the amount of thymine.
- ☐ The amount of guanine equals the amount of cytosine the total amount of purines equals the total amount of pyrimidines ;  
i.e.  $A + G = T + C$ .
- ☐ The base pairs are held together by hydrogen bonds  
Two between A and T  
Three between G and C
- ☐ The base composition does not change with age, nutritional status and environment.

**Q.58 Write DNA denaturation and DNA renaturation?**

- ☐ **DNA Denaturation:**
- ☐ Separation of the two strands of the double helix when hydrogen bonds between the paired bases are disrupted.
- ☐ Disruption can occur in the laboratory if the pH or the salt concentration of the DNA solution is altered if the solution is heated above 80°C RNA duplexes are more stable than DNA duplexes.

**Melting temperature:**

- ☐ **T<sub>m</sub>**= When DNA is heated, the temperature at which one half of the helical structure is lost is defined as the melting temperature.

- ☐ The absorbance of double-stranded DNA (dsDNA) at 260 nm is less than that of either single-stranded DNA (ssDNA) or the free bases. This is called “**hyperchromism.**”
- ☐ So single-stranded DNA has a higher relative absorbance at this wavelength than does double-stranded DNA.
- ☐ Denaturation can be monitored by measuring its absorbance at 260 nm.

### **Factors affecting T<sub>m</sub>:**

- The T<sub>m</sub> is influenced by
  - the base composition of the DNA
  - the salt concentration of the solution
- The higher the content of GC base pairs, the higher the melting point of the DNA.
- This is because GC base pairs, with three hydrogen bonds, require more heat energy to dissociate than AT base pairs.
- An *increase* in salt concentration *increases* and a decrease in salt concentration decreases the T<sub>m</sub>'

### ☐ **DNA Renaturation:**

- Under appropriate conditions (*temp. & salt concentration*), separated strands of DNA will renature or reassociate and form the double helix by the process called renaturation (or reannealing).
- This reannealing process is also referred to as hybridization.
- Renaturation of a DNA molecule is a rapid one-step process.
- Under appropriate conditions DNA will form a hybrid with a complementary DNA or with a complementary RNA
- Hybridization is combined with gel electrophoresis techniques that separate nucleic acids by size,
- coupled with radioactive or fluorescent probe labeling to provide a detection of a nucleotide sequence.

### **Q.59 Explain RNA..?**

- The genetic master plan is contained in the nucleotide sequence of DNA.
- It is through the ribonucleic acid (RNA)—the "working copies" of the (DNA) — that the master plan is expressed
- RNA is a polymer of ribonucleotides of Adenine, Uracil, Guanine and Cytosine, joined together by 3'-5' phosphodiester bonds.
- RNA does not contain thymine except in rare cases.



- The pentose sugar of RNA is D-ribose.
- **Location:** RNA is found in the nucleolus, ribosomes, mitochondria, and cytoplasm.
- The genetic material for some animal and plant viruses is RNA rather than DNA.
- There is a wide variety of RNAs.
- **Messenger RNAs** (mRNAs)- transfer genetic information from DNA to the protein-synthesizing machinery.
- **Ribosomal RNAs** (rRNAs)- contribute to the formation and function of ribosomes
- **Transfer RNAs** (tRNAs)- adapter molecules that carry specific amino acids for protein synthesis .
- **Small nuclear RNA** (snRNA)- play pivotal roles in RNA processing, particularly mRNA processing.
- **Ribozymes** some RNA molecules have intrinsic catalytic activity these RNA enzymes, are called ribozymes.

### Q.60 Differences between DNA and RNA?

Although sharing many features with DNA, RNA possesses several specific differences.

#### **Size:**

They are considerably smaller than DNA

#### **Sugar:**

In RNA, the sugar moiety to which the phosphates and purine and pyrimidine bases are attached is ribose rather than the 2'-deoxyribose of DNA

#### **Pyrimidine:**

The pyrimidine components of RNA differ from those of DNA. Instead of thymine, RNA contains the ribonucleotide of uracil. Thymine is present in the rare case of tRNA.

#### **Single Strand:**

RNA typically exists as a single strand whereas DNA exists as a double-stranded helical molecule.

#### **Chargaff's Rules Do Not Apply:**

Since the RNA molecule is a single strand complementary to only one of the two strands of a gene,

- $G \neq C$
- $A \neq U$
- Purines  $\neq$  Pyrimidines

#### **Hydrolysis:**

RNA can be hydrolyzed by alkali to 2',3' cyclic diesters of the mononucleotides, compounds that cannot be formed from alkali-treated DNA because of the absence of a 2'-hydroxyl group.

#### **Location:**

In addition to nucleus, RNA is found in cytoplasm.

Reverse Transcription: DNA forms RNA by transcription whereas the process by which RNA form DNA is called reverse transcription.

### **RNA Structural Hierarchy:**

RNA has no simple, structural hierarchy that serves as a reference point, as does the double helix for DNA.

## **Q.61 Explain primary, secondary and tertiary structure of RNA?**

### **Primary Structure of RNA:**

- ☐ It is defined as the number and sequence of ribonucleotides in the RNA chain.
- The sequence is complementary to the template strand of the gene from which it was transcribed.
- The ribonucleotides are held together by 3' - 5' phosphodiester bonds.
- 3'-OH group of one nucleotide is bound to 5'-PO<sub>4</sub> of the other nucleotide and form a linear strand.

### **Secondary Structure of RNA:**

- Secondary structure involves coil formation of the polyribonucleotide chain.
- The coiled structures are stabilized by
- Hydrophobic interactions between purine and pyrimidine bases.
- Intra-chain hydrogen bonds between G-C and A-U

#### Common RNA secondary structures

- Internal loops: a short series of unpaired bases in a longer paired helix and
- bulges: regions in which one strand of a helix has "extra" inserted bases with no counterparts in the opposite strand.

### **Tertiary Structure of RNA:**

- It is the folding of the molecule into three dimensional structure.
- cross-linking at various sites stabilized by hydrophobic and hydrogen bonds produces a compactly coiled globular structure.
- The stacking of helices, together with specific helix-helix contacts or helix-loop interactions, lead to compact tertiary structure of the RNA assemblies, generally in the presence of divalent ions or polyamines.

## Q.62 Explain messenger RNA and also its function?

### Messenger RNA (mRNA):

- ☐ This class is the most heterogeneous in Abundance, Size (500-6000 nucleotides)  
base sequence and Stability
- ☐ mRNA comprise about 2-5% of total cellular RNA
  - mRNA molecules are formed with the help of DNA template strand (3'-5') during the process called **transcription**.
  - there are untranslated regions at its 5' and 3' ends Moreover, there is a 5' cap and a poly A tail at 3' end.

### Function of mRNA:

- The members of this class function as messengers to convey the information in a gene to the protein synthesizing machinery.
- The mRNA carries genetic information from the nuclear DNA to the cytosol, where it is used as a template for protein synthesis.

## Q.63 Explain transfer RNA in details?

### Transfer RNA (tRNA):

- t RNA is the smallest of the three major species of RNA (4S).
- They are single stranded globular molecules.
- They remain largely in cytoplasm.
- They are generated by nuclear processing of a precursor molecule.
- tRNAs compose roughly 20% of total cellular RNA
- There are at slightest 20 species of tRNA molecules in every cell.

### **Primary structure**

- ☐ t RNA molecules consist of 74-95 nucleotides in a particular sequence.
- ☐ The t RNA molecules contain not only the usual bases like adenine, guanine, cytosine, uracil but also contain unusual bases

### **Secondary Structure Pseudouridine**

- ☐ Each single stranded t RNA is folded extensively.
- ☐ Extensive intra chain base pairing which leads to a characteristic CLOVER-LEAF structure.

### Arms or loops of tRNA:

All tRNA molecules contain 4 main arms or loops.

**1-Acceptor arm:** This is made up of unpaired sequences of cytosine-cytosine-adenine (CCA) at the 3' end.

**2-Anticodon arm:** It is in the form of a loop and carries specific sequences of three bases which constitute the anticodon. The bases of anticodon are bonded with three complementary bases of codon on mRNA.

**3-D arm:** It contains the base dihydrouridine.

**4-TΨC arm:** It contains thymine, pseudouridine and cytosine. The extra arm and the TΨC arms help to define a specific tRNA.

### **Function of tRNA:**

- The tRNA molecules serve as ADAPTERS for the translation of information in the sequence of nucleotides of the mRNA into specific amino acids.

### **Q.64 Explain ribosomal RNA?**

#### **Ribosomal RNA (rRNA)**

- found in association with several proteins as a component of ribosomes--- a cytoplasmic nucleoprotein structure that acts as the machinery for the synthesis of proteins from the mRNA template.
- RNAs make up 80% of the total RNA in the cell.
- The ribosomal subunits are defined according to their sedimentation velocity in **Svedberg units**.
- Svedberg unit is related to the molecular weight and shape of the compound.
- The bases in rRNA are mainly adenine, guanine, cytosine and uracil and a few pseudouridine

#### **Eukaryotic Ribosome:**

- The mammalian ribosome contains two major nucleoprotein subunits: a larger one with 60S  
a smaller one with 40S.

#### **The 60S subunit contains:**

- a 5S rRNA
- a 5.8S rRNA
- a 28S rRNA more than 50 specific polypeptide

#### **The 40S subunit is smaller and contains:**

- a single 18S rRNA
- Approx. 30 distinct polypeptide chains.

- ☐ The rRNA are necessary for ribosomal assembly and play a key role in the binding of mRNA to ribosomes and its translation.

### **Q.65 Write Other types of RNA Small nuclear RNA (snRNA)?**

**Small nuclear RNA (snRNA)** are large number of small stable RNA species found in eukaryotic cells.

- ☐ Most of them are complexed with proteins to form ribonucleoproteins.
- They are distributed in the nucleus, in the cytoplasm or in both.

- They are significantly involved in rRNA and mRNA processing and gene regulation.

### **Large & Small Non coding Regulatory RNAs:**

- One of the most exciting discoveries in the last decade of eukaryotic regulatory biology has been the identification and characterization of regulatory nonprotein coding RNAs (ncRNAs).
- ncRNAs exist in two general size classes:
- **small** consisting of microRNA (miRNAs) and silencing (siRNAs) and
- **Large** consisting of long noncoding RNAs (lncRNAs)
- The small ncRNAs termed microRNA (miRNAs) and silencing (siRNAs)

### **long noncoding RNAs (lncRNAs):**

- ☐ lncRNAs, which as their name implies, do not code for protein (ie, the mRNA encoding genes).
- ☐ ncRNAs make up a significant portion of eukaryotic transcription
- ncRNAs play many roles ranging from contributing to structural aspects of chromatin to regulation of mRNA gene transcription by RNA polymerase II.

### **Q.66 Explain enzyme?**

- ☐ Reaction catalysts of biological systems: the enzymes, the most remarkable and highly specialized proteins.
- ☐ Enzymes have extraordinary catalytic power, often far greater than that of synthetic or inorganic catalysts.
- ☐ With the exception of some catalytic RNA molecules all enzymes are proteins. Thus the primary, secondary, tertiary, and quaternary structures of protein enzymes are essential to their catalytic activity.
- ☐ Enzyme-catalyzed reactions have three basic steps:  
binding of substrate:  $E + S \leftrightarrow ES$   
conversion of bound substrate to bound product:  $ES \leftrightarrow EP$   
release of product :  $EP \leftrightarrow E + P$
- ☐ Enzymes do not invent new reactions; they simply make reactions occur faster.
- ☐ In addition to increasing the speed of reactions, enzymes provide means for regulating the rate of metabolic pathways in the body.
- ☐ The commonly used names for most enzymes describe the type of reaction catalyzed, followed by the suffix -ase e.g. dehydrogenases remove hydrogen atoms proteases hydrolyze proteins.

### **Q.67 Write IUB Classification of Enzymes?**

- ☐ International Union of Biochemists (IUB) developed an unambiguous system of enzyme nomenclature in which each enzyme has a unique name and code number.
- ☐ Its Enzyme Commission (E.C.) number is 2.7.1.1.  
 (2) denotes the class name (transferase)  
 (7) the subclass phosphotransferase  
 (1) denotes a hydroxyl group as acceptor  
 (1) D-glucose as the phosphoryl group acceptor.
- ☐ In the systematic naming system, enzymes are divided into six major classes each with numerous subgroups.

### **Classification of enzymes:**

<b>Group of Enzyme</b>	<b>Reaction Catalysed</b>	<b>Examples</b>
<b>1. Oxidoreductases</b>	Transfer of hydrogen and oxygen atoms or electrons from one substrate to another.	Dehydrogenases Oxidases
<b>2. Transferases</b>	Transfer of specific group (a phosphate or methyl etc.) from one substrate to another.	Transaminase Kinases
<b>3. Hydrolases</b>	Hydrolysis of a substrate.	Estrases Digestive enzymes
<b>4. Isomerases</b>	Change of the molecular form of the substrate.	Phospho hexo Isomerase, Fumarase
<b>5. Lyases</b>	Nonhydrolytic removal of a group or addition of a group to a substrate.	Decarboxylases Aldolases
<b>6. Ligases (Synthetases)</b>	Joining of two molecules by the formation of new bonds.	Citric acid Synthetase

### **Q.68 Explain each IUB classification of enzymes?**

#### **1) Oxidoreductases:**

catalyze oxidation reduction reactions further divided into four subgroups;

- (i) Oxidase,
- (ii) Dehydrogenases,
- (iii) Hydroperoxidases

**(iv) Oxygenases.**

Two reactions both catalyzed by Xanthine oxidase are given

**(i)** Hypoxanthine → xanthine

**(ii)** Xanthine → Uric acid

**2) Transferases:**

These bring about a transfer of functional groups such as phosphate and amino group

from one molecule to another molecule called donor and acceptor molecules respectively.

The common **examples** of this group are

Transaminases

Phosphotransferases (Kinases)

Hexokinase is a phosphotransferase which catalyze the transfer of phosphate groups.



**3) Hydrolases:**

These enzymes catalyze hydrolysis, i.e. add water molecule to the substrate which is simultaneously decomposed; the functional group of substrate is transferred to water.

Common **example** of hydrolases are:

Protein hydrolyzing Enzymes (peptidases).

Carbohydrases

Lipid hydrolyzing enzymes e.g. Lipases and

Phospholipases.

**4) Lyases:**

These enzymes catalyze the addition of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  or  $\text{CO}_2$  to double bonds or the removal of these groups leaving behind double bonds.

Lyases are included in a separate class because they catalyze these reactions by means other than hydrolysis or oxidation.

**5) Isomerases:**

These enzymes catalyze the structural change within a single molecule by the transfer of groups within it, resulting in the formation of an isomeric form of substrate.

**6) Ligases:**

These enzymes catalyze condensation reactions joining two molecules by forming

C- C-S, C-N and C-C bonds.

The energy for condensation is provided by cleavage of high energy phosphates, e.g. ATP, GTP etc.

### Q.69 Explain Ligand in details?

In biochemistry and pharmacology, a **ligand** (from the Latin *ligandum*, *binding*) is a substance (usually a small molecule),

that forms a complex with a biomolecule to serve a biological purpose.

A molecule bound reversibly by a protein is called a **ligand**.

Ligands include substrates, inhibitors, activators, and neurotransmitters

A ligand may be any kind of molecule, including another protein.

A ligand binds at a site on the protein called the **binding site**,

binding site is complementary to the ligand size, shape, charge, and hydrophobic or

hydrophilic character.

The binding of a protein and ligand is often coupled to a conformational change in the protein that makes the binding site more complementary to the ligand, permitting tighter binding called **induced fit**.

### Q.70 Write mechanism of enzyme action and write its three steps?

#### **Mechanism of Enzyme Action:**

Enzymes bind and chemically transform other molecules— they catalyze reactions.

The molecules acted upon by enzymes are called reaction **substrates** rather than ligands.

Enzymes are highly effective catalysts, commonly enhancing reaction rates by a factor of  $10^5$  to  $10^{17}$ .

The distinguishing feature of an enzyme-catalyzed reaction is that it takes place within the confines of a pocket on the enzyme called the **active site**.

#### **Enzyme-catalyzed reactions have three basic steps:**

(i) binding of substrate:  **$E + S \leftrightarrow ES$**

(ii) conversion of bound substrate to bound product:  **$ES \leftrightarrow EP$**

(iii) release of product :  **$EP \leftrightarrow E + P$**

To understand catalysis, we must first appreciate the important distinction between

reaction equilibria and reaction rates.

#### **Mechanism of Enzyme Action by reaction equilibria:**



### **Reaction Equilibria:**

The function of a catalyst is to increase the rate of a reaction. Catalysts *do not affect reaction equilibria*. Any reaction, such as  $S \leftrightarrow P$ , can be described by a reaction coordinate diagram

### **Activation energies, $G^\ddagger$ :**

The activation energies,  $G^\ddagger$ , for the  **$S \rightarrow P$  and  $P \rightarrow S$**  reactions are indicated.  $G'^{\circ}$  is the overall standard free-energy change in the direction  **$S \rightarrow P$**

### **Free-energy change $\Delta G$ :**

When a reacting system is not at equilibrium, the tendency to move toward equilibrium represents a driving force the magnitude of which can be expressed as the free-energy change for the reaction,  $\Delta G$

### **Standard free-energy change, $\Delta G'^{\circ}$ :**

Under standard conditions (298 K = 25 °C) when reactants and products are initially present at 1 M concentrations or for gases, at partial pressures of 101.3 (kPa), or 1 atm

## **Mechanism of Enzyme Action by ground and transition states:**

### **Q.71 What is ground and transition states?**

#### **Ground State: & Transition State**

The starting point for either the forward or the reverse reaction is called the **ground state**

The equilibrium between S and P reflects the difference in the free energies of their ground states.

The free energy of the ground state of P is **lower** than that of S. So  $G'^{\circ}$  for the reaction is negative and the equilibrium favors P.

But there is an **energy barrier** between S and P:

The energy required for

- alignment of reacting groups
- formation of transient unstable charges
- bond rearrangements
- and other transformations

#### **Transition State:**

To undergo reaction, the molecules must overcome this barrier and therefore must be raised to a higher energy level. This is called the **transition state**.

It is simply a fleeting molecular moment in which events such as bond breakage, bond formation, and charge development

The difference between the energy levels of the ground state and the transition state is the activation energy,  $G^\ddagger$ .

**Catalyst:**

A substance that modifies the transition state to lower the activation energy is termed a **catalyst**; a biological catalyst is termed an **enzyme**.

**Mechanism of Enzyme Action by activation energy:**

**Q.72 Write Activation energy  $\Delta G^\ddagger$  ?**

The difference between the energy levels of the ground state and the transition state is the **activation energy  $\Delta G^\ddagger$** .

The rate of a reaction reflects this activation energy: a higher activation energy corresponds to a slower reaction.

Alternatively, the activation energy can be lowered by adding a catalyst.

Catalysts enhance reaction rates by lowering activation energies. Enzymes lower the energy of activation,  $\Delta G^\ddagger$  of a reaction.

**Q.73 Explain The Induced Fit Hypothesis ?**

Some proteins can change their shape (conformation) When a substrate combines with an enzyme, it induces a change in the enzyme's conformation. This change in conformation when the substrate binds is induced by multiple weak interactions with the substrate.

This conformational change is referred to as induced fit.

Induced fit serves to bring specific functional groups on the enzyme into the proper position to catalyze the reaction.

The active site is also moulded into a precise conformation Making the chemical environment suitable for the reaction.

**Q.74 Explain the terms Cofactors, Coenzymes ,Prosthetic groups?**

**Cofactors:**

If the non-protein moiety is a metal ion such as  $Zn^{2+}$  or  $Fe^{2+}$ , it is called a cofactor.

**Coenzymes:**

If it is a complex organic molecule or metallo-organic compound it is termed a coenzyme.

Coenzymes serve as recyclable shuttles that transport many substrates from one point within the cell to another.

The function of these shuttles is twofold.

First, they stabilize species.

Second, they serve as an adaptor or handle.

### **Prosthetic groups:**

A coenzyme or metal ion that is very tightly or even covalently bound to the enzyme protein is called a prosthetic group.

### **Holoenzyme:**

The term holoenzyme refers to the active enzyme with its non-protein component.

### **Apoenzyme (apoprotein):**

The enzyme without its non-protein moiety is termed an apoenzyme (apoprotein) and is

inactive.

## **Q.75 Write Reaction Rates and Order of Reactions?**

### **Reaction Velocity (v) :**

The rate or velocity of a reaction (v) is the number of substrate molecules converted to product per unit time; Velocity is usually expressed as  $\mu\text{mol}$  of product formed per minute.

In this reaction, the rate depends only on the concentration of S. This is called a **first-order reaction**. The factor k is a proportionality constant. If a reaction rate depends on the concentration of two different compounds, or if the reaction is between two molecules of the same compound, the reaction is **second order**.

The rate equation then becomes

$$V = k[S_1][S_2]$$

## **Q.76 Write Factors Affecting Enzymatic Activity?**

Enzymes can be isolated from cells, and their properties studied in a test tube (that is, in vitro).

### **Factors Affecting Enzymatic Activity**

Different enzymes show different responses to changes in;

- (i) substrate concentration
- (ii) temperature, and
- (iii) pH.

### **(i)Substrate concentration:**

The rate of an enzyme-catalyzed reaction increases with substrate concentration until maximal velocity ( $V_{max}$ ) is reached.

**(ii)Temperature:**

The reaction velocity increases with temperature until a peak velocity is reached

This increase is the result of the increased number of molecules having sufficient energy to pass over the energy barrier and form the products.

**(iii)Effect of pH:**

**The pH optimum varies for different enzymes:**

The pH at which maximal enzyme activity is achieved is different for different enzymes, and often reflects the  $[H^+]$  at which the enzyme functions in the body.

For example, pepsin, a digestive enzyme in the stomach, is maximally active at pH 2.

Whereas other enzymes, designed to work at neutral pH, are denatured by such an acidic environment

Another examples is that there are two types of phosphatases in the body.

The one that acts in the alkaline pH is called **alkaline phosphatase** and the other which acts at acidic pH is known as **acid phosphatase**.

**Enzyme Kinetics**

**Q.77 Define Maximal Velocity  $V_{max}$**

$V_{max}$  is the theoretical maximal rate of the reaction - but it is never achieved in reality

This finite limit of  $V_{max}$  is called saturation kinetics.

Saturation kinetics is a characteristic property of all rate processes dependent on the binding of a ligand to a protein e.g. membrane transporter proteins.

This finite limit of  $V_{max}$  is called **saturation kinetics**.

Saturation kinetics is a characteristic property of all rate processes dependent on the binding of a ligand to a protein e.g. membrane transporter proteins.

**Enzyme Kinetics (Contd.)**

**Q.78 What is Michaelis constant  $K_m$**

The substrate concentration at which  $V_o$  is half maximal is  $K_m$ , the Michaelis constant.

$K_m$  reflects the affinity of the enzyme for the substrate.

**Small  $K_m$**  reflects a high affinity of the enzyme for substrate, because a low concentration of substrate is needed to half-saturate the enzyme i.e. to reach a velocity that is  $1/2 V_{max}$ .

A numerically **large (high)  $K_m$**  reflects a low affinity of enzyme for substrate because

a high concentration of substrate is needed to half-saturate the enzyme.

Small  $K_m$ : A numerically small (low)  $K_m$  reflects a high affinity of the enzyme for substrate, because a low concentration of substrate is needed to half-saturate the enzyme—that is, to reach a velocity that is  $1/2 V_{max}$ .

Hexokinase catalyses the first step in glucose metabolism in most cells, the transfer of a phosphate from ATP to glucose to form glucose 6-phosphate.

Hexokinase I, the isozyme in red blood cells has a low  $K_m$  for glucose of

approximately 0.05

mM- helpful in utilizing blood glucose even when the blood glucose concentration is very low.

- The isozyme of hexokinase, called **glucokinase**, which is found in the liver has a much higher  $K_m$  of approximately 5 to 6 mM- helpful in storing large amounts of “excess” glucose as glycogen or converting it to fat after a carbohydrate meal.

### Q.79 Write Michaelis-Menten equation, the rate equation?

Leonor Michaelis and Maud Menten in 1913, proposed a simple model that accounts for most of the features of enzyme-catalyzed reactions.

- ☐ They postulated that the enzyme first combines reversibly with its substrate to form an enzyme-substrate complex in a relatively fast reversible step:  $k_1$



$K-1$

- ☐ The ES complex then breaks down in a slower second step to yield the free enzyme (E) and the reaction product (P):  $K_2$



$K-2$

- ☐ The overall reaction then reduces to  $k_1$   $K_2$



$K-1$

**E** = Enzyme **S** = Substrate **P** = Product

**ES** = Enzyme-Substrate complex

$k_1$  rate constant for the forward reaction

$k_{-1}$  = rate constant for the breakdown of the ES to substrate

$k_2$  = rate constant for the formation of the products

### Q.80 Write the Michaelis-Menton Equation at low [S]?

Interpreting  $V_{max}$  and  $K_m$  shows a simple graphical method for obtaining an approximate value for  $K_m$ .

This graph shows the kinetic parameters that define the limits of the curve at high and low [S].

low [S];  $K_m \gg [S]$

- $$V_0 = \frac{V_{max} [S]}{K_m + [S]}$$

Since  $V_{max}$  and  $K_m$  are both constants, their ratio is a constant. In other words, when [S] is considerably below  $K_m$ ,  $V_0$  is proportionate to  $k[S]$ . The initial reaction velocity,  $V_0$ , therefore is directly proportionate to [S].  $V_0$  exhibits a linear dependence on [S], as observed here. (First order Reaction). Therefore at concentrations below  $K_m$  reaction rate is first order i.e. it is directly proportional to the concentration of the substrate.

### Q.81 Write the Michaelis-Menton Equation at high [S]?

At high [S]  $[S] \gg K_m$

The term  $K_m + [S]$  is essentially equal to [S].

The  $K_m$  term in the denominator of the Michaelis-Menten equation becomes insignificant

Replacing  $K_m + [S]$  with [S] reduces equation

high [S]  $[S] \gg K_m$

- $$V_0 = \frac{V_{max} [S]}{[S]}$$

$$K_m + [S]$$

Ignoring  $K_m$

$$\bullet V_0 = \frac{V_{\max} [S]}{[S]} \quad V_0 = V_{\max}.$$

This is consistent with the plateau observed at high [S]. (Zero Order Reaction)

The rate of reaction is then independent of substrate concentration **[S]**, and is said to be **zero order** with respect to substrate concentration.

The Michaelis-Menten equation is therefore consistent with the observed dependence of  $V_0$  on [S], and the shape of the curve is defined by the terms;

$V_{\max}/K_m$  at low [S] and  
 $V_{\max}$  at high [S].

### Q. 82 Write first and zero Order of Reaction?

#### First order of reaction:

When **[S]** is much less, then the velocity of the reaction is approximately proportional to the substrate concentration. The rate of reaction is then said to be first order with respect to substrate.

#### Zero order of reaction:

When **[S]** is much greater than  $K_m$  the velocity is constant and equal to  $V_{\max}$ .

The rate of reaction is then independent of substrate concentration, and is said to be zero order with respect to substrate concentration.

### Q 83 Reaction Orders with Respect to Substrate Concentration:

Order	Reaction equilibrium	Comment
Zero	Rate = k	Rate is independent of substrate concentration
First	First rate = $k[S]$	Rate is proportional to the first power of substrate concentration

Second	Rate = $k[S_1][S_2]$	Rate is proportional to the first power of each of two reactants
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#### Q.84 Write relationship of velocity to enzyme concentration?

The rate of the reaction is directly proportional to the enzyme concentration. There is a linear relationship between reaction rate and enzyme concentration (at constant substrate concentration)

**For example,** if the enzyme concentration is halved, the initial rate of the reaction ( $V_0$ ) as well as that of  $V_{max}$  are reduced to one half that of the original.

#### Q.85 Explain Lineweaver-Burke plot?

This form of the Michaelis-Menten equation is called the **Lineweaver-Burk equation** describing the Lineweaver-Burke plot.

The Michaelis-Menten equation can be algebraically transformed into **Lineweaver-Burke plot**, a Double Reciprocal Plot, that is useful in the practical determination of  $K_m$  and  $V_{max}$ .

$$V_0 = \frac{V_{max} [S]}{K_m + [S]}$$

Lineweaver-Burke transformation is derived simply by taking the reciprocal of both sides of the Michaelis-Menten equation:

$$\frac{1}{V_0} = \frac{K_m + [S]}{V_{max} [S]}$$

$$\frac{1}{V_0} = \frac{K_m}{V_{max} [S]} + \frac{1}{V_{max}}$$

$$\frac{1}{V_0} = \frac{K_m}{V_{max} [S]} + \frac{1}{V_{max}}$$

$$\bullet \frac{1}{V_0} = \frac{K_m}{V_{max} [S]} + \frac{1}{V_{max}}$$



$$V_o = \frac{V_{max}[S]}{K_m + [S]}$$

Lineweaver-Burk plot, has the great advantage of allowing a more accurate determination of  $V_{max}$ ,

Which can only be approximated from a simple plot of  $V_o$  versus  $[S]$ .

### Q.86 Write Inhibition of enzyme activity?

Enzyme inhibitors are molecular agents that interfere with catalysis, slowing or halting enzymatic reactions.

Any substance that can diminish the velocity of an enzyme-catalyzed reaction is called an **inhibitor**

Two broad classes of enzyme inhibitors:

1. Reversible
2. Irreversible

#### **1. Reversible:**

Reversible inhibitors typically bind to enzymes through noncovalent bonds,

#### **3. Irreversible:**

In general, irreversible inhibitors bind to enzymes through covalent bonds.

The two most commonly encountered types of reversible inhibition are;

- (a) Competitive and
- (b) Noncompetitive.

(a) **Competitive inhibitors** resemble the substrate and compete for binding to the active site of the enzyme.

(b) **Noncompetitive inhibitors** do not bind at the active site. They bind either free enzyme at a site other than active site or the ES complex.

### Q.87 Write Competitive Inhibition and write its effects?

This type of inhibition occurs when the inhibitor binds reversibly to the same site that the substrate would normally occupy i.e. active site and, therefore, competes with the substrate for that site.

### **1. Effect on Vmax:**

The effect of a competitive inhibitor is reversed by increasing [S]. At a sufficiently high substrate concentration, the reaction velocity reaches the  $V_{max}$  as observed in the absence of inhibitor. When [S] far exceeds [I], the probability that an inhibitor molecule will bind to the enzyme is minimized and the reaction exhibits a normal  $V_{max}$ . Therefore, a competitive inhibitor does not decrease  $V_{max}$ .

### **2. Effect on Km:**

The [S] at which  $V_0 = 1/2 V_{max}$ , the apparent  $K_m$ , increases in the presence of inhibitor. A competitive inhibitor increases the apparent  $K_m$  ( $\alpha K_m$ ) for a given substrate.

### **3. Effect on Lineweaver-Burk plot:**

Competitive inhibition shows a characteristic Lineweaver-Burke plot the plots of the inhibited and uninhibited reactions intersect at a single point on the y-axis at  $1/V_{max}$ .

$V_{max}$  is unchanged We know that  $V_{max}$  is unchanged by the presence of a competitive inhibitor. This is because more substrate means more formation of ES complex vs EI complex.

### **Q.88 Explain Noncompetitive Inhibition?**

Inhibitors bind enzymes at sites distinct from the substrate-binding site and generally bear little or no structural resemblance to the substrate.

#### **1. Effect on $V_{max}$ :**

The apparent  $V_{max}$  changes, because the inhibitor is capable of preventing catalysis regardless of whether the substrate is bound to the enzyme. Noncompetitive inhibition cannot be overcome by increasing the concentration of substrate. Thus, noncompetitive inhibitors decrease the  $V_{max}$  of the reaction.

#### **2. Effect on Km:**

Noncompetitive inhibitors do not interfere with the binding of substrate to enzyme. Thus, the enzyme shows the same  $K_m$  in the presence or absence of the noncompetitive inhibitor.

#### **3. Effect on Lineweaver-Burk plot:**

Noncompetitive inhibition shows a characteristic Lineweaver-Burke plot the plots of the inhibited and uninhibited reactions intersect at a single point on the x-axis at  $K_m$ .  $K_m$  is unchanged.

### **Q.89 Explain Water and write its properties?**

Water is the most abundant substance in living systems, making up 70% or more of the weight of most organisms'

The hydrogen bonding between water molecules and the slight tendency of water to ionize are of crucial importance to the structure and function of biomolecules

### **Hydrogen Bonding gives Water its Unusual Properties:**

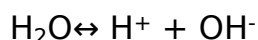
- Water has a higher
- melting point,
- boiling point, and
- heat of vaporization than most other common solvents
- Each hydrogen atom of a water molecule shares an electron pair with the central oxygen atom
- The geometry of the molecule is dictated by the shapes of the outer electron orbitals of the oxygen atom
- The result of this unequal electron sharing is two electric dipoles in the water molecule
- Each hydrogen bears a partial positive charge ( $\delta^+$ ), and the oxygen atom bears a partial negative charge equal to the sum of the two partial positives ( $2\delta^-$ ).

### **Q.90 Write Ionization of Water ?**

#### **Ionization of Water:**

Although many of the solvent properties of water can be explained in terms of the uncharged  $H_2O$  molecule, the small degree of ionization of water into

hydrogen ions ( $H^+$ ) and hydroxide ions ( $OH^-$ ) must also be taken into account Pure Water Is Slightly Ionized Water molecules have a slight tendency to undergo reversible ionization to yield a hydrogen ion (a proton) and a hydroxide ion, giving the equilibrium reaction



Hydrogen ions formed in water are immediately hydrated to hydronium ions ( $H_3O^+$ ), The ionization of water can be measured by its electrical conductivity

### Q.91 Explain the Ionization Of Water Is Expressed By an Equilibrium Constant?

The degree of ionization of water at equilibrium is small

At 25<sup>0</sup> C only about two out of every 10<sup>9</sup> molecules in pure water are ionized at any instant.

According to the **law of mass action** the rate of a chemical reaction is proportional to the product of the masses of the reactants. Necessarily, this implies that for a chemical reaction mixture that is in equilibrium, the ratio between the concentration of reactants and products is constant.

The equilibrium constant for the reversible ionization of water is

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

Since 1 mole (mol) of water weighs 18 g,

- 1 liter (L) (1000 g) of water contains  $1000 \div 18 = 55.56$  mol Pure water thus is 55.56 molar(M)
- 2 Accordingly, we can substitute 55.5 M in the equilibrium constant expression to yield

$$K_{eq} = [H^+][OH^-]/55.5$$

$$K_{eq} = [H^+][OH^-]/55.5$$

On rearranging, this becomes

$$(K_{eq})(55.5) = [H^+][OH^-] = K_w$$

3. Where  $K_w$  designates the product (55.5M)( $K_{eq}$ ), the ion product of water at 25<sup>0</sup> C

The value for  $K_{eq}$ , determined by electrical conductivity measurements of pure water, is

$$1.8 \times 10^{-16} \text{ M at } 25^\circ \text{ C}$$

$$K_w = (K_{eq})(55.5) = [H^+][OH^-]$$

$$K_w = (1.8 \times 10^{-16} \text{ M})(55.5 \text{ M}) = [H^+][OH^-]$$

$$K_w = 1.0 \times 10^{-14} \text{ M}^2 = [H^+][OH^-]$$

$$K_w = [H^+][OH^-] = [H^+]^2 = [OH^-]^2$$

Solving for  $[H^+]$  gives:

$$[H^+] = \sqrt{K_w} = \sqrt{10^{-14} \text{ M}^2}$$

$$[H^+] = 10^{-7} \text{ M}$$

4. Thus the product  $[H^+][OH^-]$  in aqueous solutions at 25<sup>0</sup> C always equals  $1 \times 10^{-14} \text{ M}^2$

When there are exactly equal concentrations of  $H^+$  and  $OH^-$ , as in pure water, the solution is said to be at neutral pH. As the ion product of water is constant, whenever  $[H^+]$  is greater than  $1 \times 10^{-7} M$ ,  $[OH^-]$  must be less than  $1 \times 10^{-7} M$ , and vice versa.

**Q.92 What is the concentration of  $H^+$  in a solution of 0.1 M NaOH?**

**Solution:**

$$K_w = [H^+][OH^-]$$

- With  $[OH^-] = 0.1 M$ , solving for  $[H^+]$  gives
- $[H^+] = K_w / [OH^-]$

$$= 1 \times 10^{-14} M^2 / 0.1 M$$

$$= 10^{-14} M^2 / 0.1 M$$

$$= 10^{-13} M$$

**Q.93 What is the concentration of  $OH^-$  in a solution with an  $H^+$  concentration of  $1.3 \times 10^{-4} M$ ?**

**Solution:**

- $K_w = [H^+][OH^-]$
- With  $[H^+] = 1.3 \times 10^{-4} M$ , solving for  $[OH^-]$  gives
- $[OH^-] = K_w / [H^+]$
- $= 1 \times 10^{-14} M^2 / 1.3 \times 10^{-4} M$
- $= 7.7 \times 10^{-11} M$

**Q.94 Define pH Scale?**

Designates the  $H^+$  and  $OH^-$  Concentrations. The pH of a solution is defined as the logarithm to the base 10 of the reciprocal of the  $[H^+]$ , i. e the negative logarithm of the  $[H^+]$

$$pH = \log 1/[H^+]$$

$$= -\log[H^+]$$

The pH of water at 25°C, in which H<sup>+</sup> and OH<sup>-</sup> ions are present in equal numbers, is 7.0

$$\text{pH} = -\log[1 \times 10^{-7}] = 7$$

The symbol p denotes "negative logarithm of" For each pH unit less than 7.0, the [H<sup>+</sup>] is increased tenfold; for each pH unit above 7.0, it is decreased tenfold

### Q.95 What will be the pH of 0.1 M HCl ?

Assuming that being a strong acid HCl is completely dissociated, it's 0.1 M solution will contain 0.1 or 10<sup>-1</sup> grams H<sup>+</sup> per litre

$$\begin{aligned}\text{pH} &= -\log [\text{H}^+] \\ \text{pH} &= -\log [10^{-1}] \\ &= -[-1] \\ &= 1\end{aligned}$$

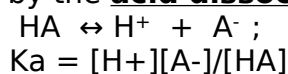
### Q.96 Explain Weak Acids and Bases ?

- Each acid has a characteristic tendency to ionize in an aqueous solution
- The stronger the acid, the greater its tendency ionize i.e. to lose its proton
- This tendency is measured by an acid dissociation constant
- Weak Acids and Bases have Characteristic Acid Dissociation Constants
- HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>, commonly called strong acids, are fully ionized in aqueous solutions
- The strong bases NaOH and KOH are also completely ionized
- **Acids** may be defined as proton donors and **bases** as proton acceptors
- A proton donor and its corresponding proton acceptor make up a **conjugate acid-base pair**.

- **Acetic acid** (CH<sub>3</sub>COOH), a proton donor, and the acetate anion (CH<sub>3</sub>COO<sup>-</sup>), the corresponding proton acceptor, constitute a conjugate acid-base pair, related by the reversible reaction:



The tendency of any acid (HA) to lose a proton and form its conjugate base (A<sup>-</sup>) is defined by the **acid dissociation constant (K<sub>a</sub>)** for the reversible reaction.



**Stronger acids**, have larger dissociation constants ( $K_a$ ) i.e they ionize completely

**Weaker acids**, have smaller dissociation constants ( $K_a$ ) i.e. they ionize only partially.

### Q.97 write $pK_a$ and working with $pK_a$ ?

**$pK_a$ :**

analogous to pH,  $pK_a$  is defined by the equation

$$pK_a = \log 1/K_a$$

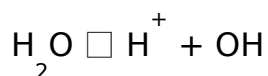
$$= -\log K_a$$

The stronger the tendency to dissociate a proton, the stronger is the acid and the lower its  $pK_a$ .

### **Working with $pK_a$ :**

Titration is used to determine the amount of an acid in a given solution  
Consider the titration of a 0.1M solution of acetic acid with 0.1M NaOH at 25 °C

Two reversible equilibria are involved in the process (here, for simplicity, acetic acid is denoted HAc)



The equilibria must simultaneously conform to their characteristic equilibrium constants, which are, respectively,

$$K_w = [H^+][OH^-]$$

$$= 1 \times 10^{-14} \text{ M}^2$$

$$K_a = [H^+][Ac^-]/[HAc]$$

$$= 1.74 \times 10^{-5} \text{ M}$$

### Q.98 Write The Henderson-Hasselbalch (HH) Equation?

The HH equation relates pH,  $pK_a$ , and buffer concentration

This equation is simply a useful way of restating the expression for the ionization constant of an acid

For the ionization of a weak acid HA, the HH equation can be derived as follows:

$$K_a = [H^+][A^-]/[HA]$$

First solve for  $[H^+]$ :

$$[H^+] = K_a[HA]/[A^-]$$

Then take the negative logarithm of both sides:

$$-\log[H^+] = -\log K_a - \log[HA]/[A^-]$$

Substitute pH for  $-\log [H^+]$  and pKa for  $-\log K_a$

$$pH = pKa - \log[HA]/[A^-]$$

- Now invert  $-\log [HA]/[A^-]$ ,

$$pH = pKa + \log[A^-]/[HA]$$

This equation shows why the pKa of a weak acid is equal to the pH of the solution at the midpoint of its titration

At that point,  $[HA] = [A^-]$

- $pH = pKa + \log[A^-]/[HA]$
- $pH = pKa + \log 1$
- $pH = pKa + 0$
- $pH = pKa$

**Q.99 Calculate the pKa of lactic acid, given that when the concentration of lactic acid is 0.01M and the concentration of lactate is 0.087 M, the pH is 4.80**

$$pH = pKa + \log [\text{lactate}]/[\text{lactic acid}]$$

$$pKa = pH - \log [\text{lactate}]/[\text{lactic acid}]$$

$$= 4.80 - \log 0.087/0.01$$

$$= 4.80 - \log 8.7$$

$$= 4.80 - 0.94$$

$$= 3.9$$

**In summary,**

- when  $[HA] = [A^-]$  ;  $pH = pKa$
- when  $[HA] > [A^-]$  ;  $pH < pKa$
- when  $[HA] < [A^-]$  ;  $pH > pKa$

**Q.100 Explain Buffer Solutions?**



Buffers are aqueous systems that tend to resist changes in pH when small amounts of acid ( $\text{H}^+$ ) or base ( $\text{OH}^-$ ) are added

A buffer system consists of a weak acid (the proton donor) and its conjugate base (the proton acceptor) As an example, a mixture of ; acetic acid and acetate ion, is a buffer system,

Each conjugate acid-base pair has a characteristic pH zone in which it is an effective buffer

For example, the  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  pair has a pKa of 6.86 and thus can serve as an effective buffer system between approximately pH 5.9 and pH 7.9

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