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Chapter 1

Biochemistry

1.1 ATOMS AND MOLECULES

1.1.1 Matter

Anything that possesses mass and occupies space (volume) is called **matter**. It constitutes the observable universe and, together with energy, forms the basis of all objective phenomena. Matter can exist in four states which are solid, liquid, gas and plasma (**Figure 1.1**). Matter is made up of elements. An **element** is a substance which can't be broken down into further simpler substances by any chemical means. An element consists of only one type of particles which can be atoms or molecules.

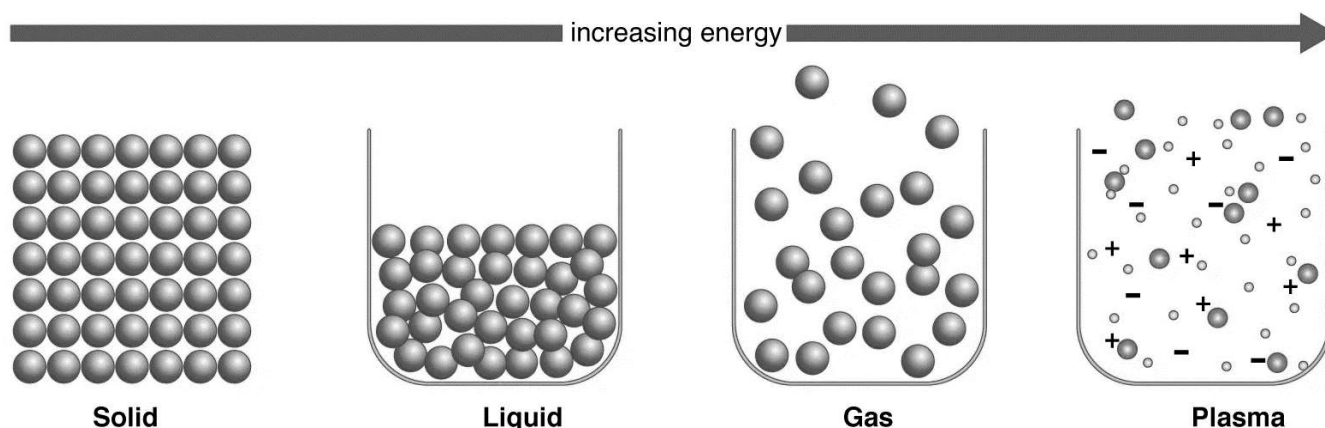


Figure 1.1: States of Matter

To date, 118 elements are known and among these, 92 are naturally occurring while rest all are produced by scientists via nuclear processes. Out of these 118 elements, approximately 25 elements are present in biological systems which are mentioned in the **Table 1.1**.

Table 1.1: Elemental Composition of Living Cell

Element by weight	Symbol	Percentage in body
Oxygen	O	65
Carbon	C	18.5
Hydrogen	H	9.5
Nitrogen	N	3.2
Calcium	Ca	1.5
Phosphorous	P	1.0
Potassium	K	0.4
Sulphur	S	0.3
Sodium	Na	0.2
Chlorine	Cl	0.2
Magnesium	Mg	0.1
Trace elements	B, Cr, Co, F, I, Fe, Mn, Mo, Se, Si, Sn, V, Zn	Less than 0.1

Among these 25 elements, six elements are most common inside the biological cell. These are called the **CHNOPS** elements (carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulphur). These six elements contribute approximately 98% of the total mass of cells.

The reason for their abundance in biological system, is that these 6 elements are small in size, thus will have large surface area to volume ratio, therefore, they form the tightest and most stable bonds. Moreover H, O, N and C atoms are capable of forming one, two, three and four electron bonds respectively which provides flexibility and versatility to biomolecules.

Carbon and silicon both lie in the same group in periodic table (group 14) but life is carbon based and not silicon based. The reason is C-C bonds are more stable in aqueous environment and oxides of carbon are not toxic like those of oxides of silicon.

1.1.2 Atom and Subatomic Particles

- An **atom** is the fundamental particle of an element that has all the chemical properties of that element. Atom of one element differs in its size and mass from the atoms of the other elements. Atoms are composed of

further smaller subatomic particles, namely electrons, protons and neutrons.

- One **proton** possesses one unit of positive charge while one **electron** has one unit negative charge. A **neutron** does not bear any charge and is electrically neutral. Properties of subatomic particles are given in (Table 1.2).
- Neutrons and protons are tightly packed and present at the centre of atom called **atomic nucleus**. Positive charge on the nucleus is due to presence of protons inside it.
- The fast moving electrons form a negatively charged "**electron cloud**" around the nucleus. The attraction between opposite charges of electron and nucleus keep the electrons in vicinity of the nucleus.
- Neutrons and protons are similar in mass.
- Mass of subatomic particles and atoms (even molecules too) is measured in Daltons.
- Dalton is same as atomic mass unit, amu or u. One **amu** is equal to the mass of one proton. Since the mass of electron is negligible as compared to mass of proton and neutron therefore its mass is ignored while calculating mass of atom.

Table 1.2 Properties of subatomic particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	E	-1.6021×10^{-19}	-1	9.109×10^{-31}	0.00054	0
Proton	P	$+1.6021 \times 10^{-19}$	+1	1.6726×10^{-27}	1.00727	1
Neutron	N	0	0	1.6749×10^{-27}	1.00867	1

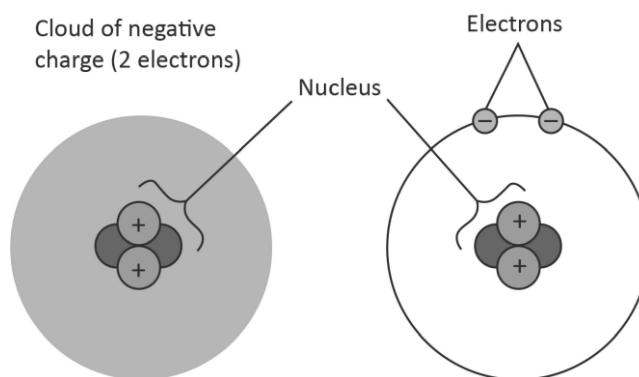


Figure 1.2: Simplified models of helium atom. The helium atom consists of 2 protons (light) and two neutrons (Dark) inside the nucleus and 2 electrons outside it. In (a), the 2 electrons are represented as electron cloud. In (b), the 2 electrons are shown as small spheres on a fixed path around nucleus.

1.1.3 Radioactivity

The phenomenon of spontaneous emission of highly active radiations by atoms having unstable nucleus is called **radioactivity**. Mostly common emission of radioactive particles are alpha (α) rays, beta (β) rays and gamma (γ) rays. Examples of radioactive elements are Uranium, Thorium, Radium, and Polonium.

- **Alpha rays** when pass through electric field show deflection towards negative plate, indicating the presence of positive charge on alpha particles. Each alpha particle consist of two protons and two neutrons bound together into a particle identical to a helium-4 nucleus.
- **Beta rays (negatron)** get deflected towards positive plate in an electric field. The constituting particles of beta rays are called β particles. Each β particle has mass and charge same as on electron.
- **Gamma rays** do not show any deflection in electric field and have no charge and carry negligible mass.
- The alpha rays have the least penetrating power while the gamma rays have the maximum magnitude.

1.1.4 Atomic Number and Mass Number

- The number of protons present inside the atomic nucleus is equal to the **atomic number (Z)**. For example, number of protons in the hydrogen nucleus is 1, in carbon it is 6, therefore their atomic numbers are 1 and 6 respectively. In order to maintain the electrical neutrality of atom, number of electrons inside an atom is equal to the number of protons (atomic number).
- The mass of the atom is due to protons and neutrons. Protons and neutrons are collectively termed as **nucleons**. **Mass number (A) or atomic mass** is the total number of nucleons inside an atom.
- Elements are identified by their atomic numbers and not by mass numbers because no two elements can have same atomic number.

1.1.5 Isobars, Isotopes, Radioisotopes & Isotones

- **Isobars** are atoms of different elements having same mass number but different atomic number. For example, carbon-14 ($Z=6$, $A=14$) and nitrogen ($Z=7$, $A=14$); another example is potassium ($Z=19$, $A=40$) and calcium ($Z=20$, $A=40$).
- **Isotopes** are atoms of same element having same atomic number but different mass number. For

example, hydrogen has three isotopes: protium (${}^1\text{H}^1$), deuterium (${}^1\text{H}^2$) and tritium (${}^1\text{H}^3$). All of them have same atomic number 1 but different mass number of 1, 2, 3 respectively. Carbon also has three isotopes ${}^{12}\text{C}$, ${}^{13}\text{C}$ and ${}^{14}\text{C}$. Difference between the isotopes is due to the presence of the different number of neutrons in the nucleus. All the isotopes of one element show same chemical behaviour.

- **Radioisotopes** of some elements are the isotopes that frequently decay by emitting excess nuclear energy because their nucleus is unstable. For example, tritium (H^3), C^{14} , iodine ^{131} .
- **Isotones** are the atoms of different elements which contain same number of neutrons. However, both the atomic number and mass numbers are different for the isotones. A few examples include ${}^{14}\text{C}$, ${}^{15}\text{N}$, ${}^{16}\text{O}$ are isotones of each other.

1.1.6 The Energy Levels of Electrons

- Atoms have large empty space inside them. During a chemical reaction, only electrons of an atom participate; nuclei of two atoms never come close to each other. Electrons have **potential energy** because they are located at some distance from the nucleus. More is the distance between an electron and its atomic nucleus, more is the amount of potential energy that electron possesses. Potential energy is energy that any matter possesses because of its location.
- Electrons exist only at fixed levels of potential energy known as **electron shells or orbits**. Each electron shell has characteristic *average* distance from nucleus and energy associated with it. These shells are represented by letters **K, L, M, N** or by the number "n" such that **K= (n=1), L= (n=2), M= (n=3) & N= (n=4)** and diagrammatically shells are shown as concentric circles around the nucleus. The first electron shell, K is closest to the nucleus and electrons in this shell have the lowest potential energy.
- The maximum number of electrons that can be present in any shell is given by the formula $2n^2$, where n= shell number. For example, K shell can have 2 electrons because $n=1$ for K shell. Consider electron distribution of neon, it contains 10 protons and 10 electrons. According to $2n^2$ rule K shell can have 2 electrons therefore remaining 8 electrons will lie in L shell because L shell can accommodate maximum of 8 electrons. If more number of electrons are present than a new shell M would be required.

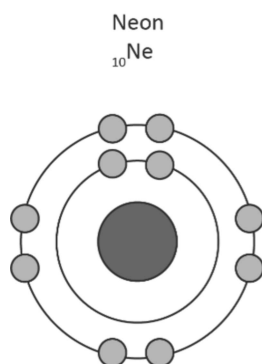


Figure 1.3: Electronic distribution in neon atom

- Electrons can jump from one shell to another by absorbing or emitting the amount of energy equal to the difference in potential energy between its position in the old shell and that in the new shell. When an electron absorbs energy, it becomes excited and move to a shell which is located away from the nucleus while when any electron loses energy, it falls back to a shell lying closer to the nucleus, and the energy which is lost is emitted as heat energy into the environment.
- Chemical behaviour of an atom depends upon the number of **valence electrons** (electrons present in the outermost shell which an atom can lose or gain) present in it. Atoms having same number of valence electrons have similar chemical properties. Atoms whose outermost shells are completely filled, they are *unreactive or stable or inert*

1.1.7 Electron Orbitals

- The shells represent an average distance between the electron in that shell and atomic nucleus; hence the concentric-circle diagrams do not provide real picture of an atom. We can never locate the exact position of an electron inside any atom but we can describe a space in which an electron spends most of its time. **Orbital** is the three-dimensional space where an electron is present 90% of the time. Orbital can be considered as part of electron shell where the probability of finding an electron is very high. Each orbital has characteristic shape and orientation.
- One orbital can accommodate only two electrons of opposite spins. The first innermost electron shell contains one spherical *s* orbital (**known as 1s**); the second shell has four orbitals: one large spherical *s* orbital (**called 2s**) and three dumbbell-shaped *p* orbitals (**called 2p** orbitals).

1.2. MOLE CONCEPT AND CONCENTRATION OF SOLUTION

1.2.1 Mole Concept

Atoms and molecules are very small in size and their numbers in even a little amount of any substance is quite large. Therefore, to count large numbers, a large unit is required.

- Mole is used to count items which are microscopic in size like atoms and molecules. 1 mole of any substance = 6.022×10^{23} number of particles of that substance. 6.022×10^{23} is known as **Avogadro constant or Avogadro number**. Therefore, 1 mole of hydrogen atoms = 6.022×10^{23} atoms or 1 mole of water molecules = 6.022×10^{23} water molecules.
- Mass of one mole of a substance in grams is called its **molar mass**. Molar mass is numerically equal to atomic or molecular or formula mass in amu. For example, molar mass of water is 18g.
- To conclude: **1 mole of atoms = 6.022×10^{23} number of atoms = gram molar mass of atom** or **1 mole of molecules = 6.022×10^{23} number of molecules = gram molar mass of molecule**. This is called **mole concept**.
- Number of moles of any substance can be calculated by the formula: given weight of substance/molar mass of that substance.
- Number of moles of any substance can also be calculated by the formula: given number of particles of substance/ Avogadro number.

1.2.2 Concentration of Solution

When a solute is added to a solvent, a solution is formed. Concentration of a solution can be defined as the amount of solute present in given amount of solvent. There are various methods in which concentration of a solution can be expressed such as mass percent, volume percent, mass/volume percent, parts per million, mole fraction, molarity, molality, normality and strength. Mass percent and volume percent do not have any units.

- Mass percent (w/w)**

Mass percent of a solution is defined as mass of solute (in g) per 100 g of solution.

$$\text{mass percent} = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100$$

- **Volume percent (v/v)**

Volume percent of a solution is defined as volume of solute (in ml) per 100 ml of solution.

$$\text{volume percent} = \frac{\text{volume of solute (ml)}}{\text{volume of solution (ml)}} \times 100$$

- **Mass/volume percent (w/v)**

It is defined as grams of solute present in total volume of solution.

$$\begin{aligned} \text{mass/volume percent} \\ = \frac{\text{mass of solute (g)}}{\text{volume of solution (ml)}} \times 100 \end{aligned}$$

- **Parts per million (ppm)**

It is used for dilute solutions. ppm can be defined as parts of solute present in 1 million parts of solution.

$$\text{ppm} = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 10^6$$

or

$$\text{ppm} = \frac{\text{volume of solute (ml)}}{\text{volume of solution (ml)}} \times 10^6$$

or

$$\text{ppm} = \frac{\text{mass of solute (g)}}{\text{volume of solution (ml)}} \times 10^6$$

If we add 'x' mg of solute in 1000 ml of solution, concentration of solution will be 'x' ppm.

For very dilute solutions there is another concentration term known as **parts per billion (ppb)**. When 'x' µg of solute is dissolved in 1000 ml solution, the concentration of solution will be 'x' ppb. Both ppm and ppb are used for very dilute solutions where % solution is not convenient as it will be very low.

- **Mole fraction (χ)**

Mole fraction is the ratio of number of moles of one component to the total number of moles of all the components present in the solution. If a solution is made up of two components A and B and their number of moles are n_A and n_B respectively; then,

$$\begin{aligned} \text{mole fraction of A } (x_A) \\ = \frac{\text{number of moles of A } (n_A)}{\text{number of moles of solution } (n_A + n_B)} \end{aligned}$$

$$\begin{aligned} \text{mole fraction of B } (x_B) \\ = \frac{\text{number of moles of B } (n_B)}{\text{number of moles of solution } (n_A + n_B)} \end{aligned}$$

Mole fraction being a ratio do not have any units. Sum of mole fractions of different components in a solution is always equal to 1 that means ($x_A + x_B = 1$). If we know mole fraction of A then mole fraction of B can be calculated as 1- mole fraction of A.

- **Molarity (M)**

Molarity is number of gram moles of solute present in 1 litre of solution. It is expressed in moles/litre.

$$\text{Molarity (M)} = \frac{\text{gram moles of solute}}{\text{volume of solution in litres}}$$

$$\begin{aligned} & \frac{\text{Mass of solute in grams}}{\text{molar mass}} \\ & = \frac{\text{volume of solution in ml}}{1000} \end{aligned}$$

$$= \frac{\text{Mass of solute in grams} \times 1000}{\text{molar mass} \times \text{volume of solution in ml}}$$

1M NaCl means 1 mole of NaCl is dissolved in 1 litre of solution. When V_1 volume of solution of molarity M_1 is mixed with V_2 volume of another solution of molarity M_2 , then molarity M_3 of the resulting solution is calculated as:

$$M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$$

- **Molality (m)**

Molality of a solution is defined as the number of gram moles of solute dissolved in 1 kg of solvent.

$$\text{Molality (m)} = \frac{\text{gram moles of solute}}{\text{mass of solvent in kg}}$$

$$\begin{aligned} & \frac{\text{Mass of solute in grams}}{\text{molar mass}} \\ & = \frac{\text{mass of solvent in grams}}{1000} \end{aligned}$$

Molality is better than molarity for expressing the concentration of solution because molality does not depend upon volume and does not change with change in temperature. But disadvantage of using molality is that density of the solution must be known.

Relation between molarity and molality

$$\frac{\text{Molarity}}{\text{Molality}} = \frac{\text{Density of solution} \times \text{volume of solution} - \text{moles of solute} \times \text{molar mass of solute}}{\text{volume of solution in litres}}$$

- **Normality (N)**

Normality is defined as the number of gram equivalents of the solute dissolved per litre of solution.

$$\text{Normality (N)} = \frac{\text{gram equivalents of solute}}{\text{volume of solution in litres}}$$

$$\begin{aligned} &= \frac{\frac{\text{Mass of solute in grams}}{\text{equivalent mass}}}{\frac{\text{volume of solution in ml}}{1000}} \\ &= \frac{\text{Mass of solute in grams} \times 1000}{\text{equivalent mass} \times \text{volume of solution in ml}} \end{aligned}$$

Now, equivalent mass can be calculated as:

$$\text{Equivalent mass of acid} = \frac{\text{molar mass of acid}}{\text{number of } H^+ \text{ acid can donate}}$$

$$\text{Equivalent mass of base} = \frac{\text{molar mass of base}}{\text{number of } OH^- \text{ base can donate}}$$

$$\text{Equivalent mass of salt} = \frac{\text{molar mass of salt}}{\text{total positive charge on cation}}$$

$$\text{Equivalent mass of ion} = \frac{\text{formula mass of ion}}{\text{charge on ion}}$$

- **Dilution of Solution**

Preparing a less concentrated solution (working solution) from a highly concentration solution (stock solution) is called dilution. For dilution $C_1V_1 = C_2V_2$ formula is used where C_1V_1 represents concentration and volume of stock solution respectively while C_2V_2 is the concentration of and volume of working solution, respectively. Units of concentration and volume should be same on both sides of the equation while solving the questions.

1. 3. WATER

Water is the most abundant compound of living beings and act as the solvent inside the cell. All features of cell structure and functions are adapted to the physical and chemical properties of water. It accounts for approximately 70% of a cell's weight. Water is tasteless, colorless and odourless compound. Solvent properties of water influence non-covalent interactions among biomolecules for example arrangement and interaction of membrane lipids with each other is dictated by the polar properties of water.

1.3.1 Physical Properties of Water

Physical properties of water are mentioned in (Table 1.3).

Table 1.3: Physical properties of water

Physical properties	Values
Melting Point, °C	0
Boiling Point, °C	100
Heat of vaporisation, cal/g	540
Heat capacity, cal/g	1,000
Heat of fusion, cal/g	79.7
Surface tension	72.8
Dielectric constant	78.5

- Water has higher melting point, boiling point and heat of vaporisation as compared to H_2S and NH_3 and other common liquids because of strong attractions (Hydrogen bonds) between adjacent water molecules.
- Water is liquid at room temperature because of hydrogen bonding between water molecules that provide cohesive forces.
- The density of liquid water is more than the density of frozen water, thus ice floats on water.
- Due to high surface tension, water rises to unusually high levels in capillary tubes.
- Water act as temperature buffer because of high value of Heat capacity. Water resists change in temperature when given amount of heat is applied and therefore help in keeping body temperature constant.
- Water act as universal solvent because it has very high dielectric constant. Consequently, water facilitates variety of chemical reactions both outside of and within biological systems. Polar biomolecules dissolve easily in water because they form solute- water interactions which are more energetically favourable than water-water interactions.

1.3.2 Structure of Water Molecule

- In water molecule (Figure 1.4), two hydrogen atoms are covalently bonded to central oxygen atom. Atomic mass of water is 18 Daltons. Geometry of the molecule is rough tetrahedron or bent.
- The H-O-H bond angle is 104.5° and it is slightly less than 109.5° (perfect tetrahedron). The reason is due the presence of lone pairs of electrons on oxygen atom. Lone pair-lone pair repulsions are higher than bond pair-bond pair repulsion thus the angle is reduced to 104.5° .

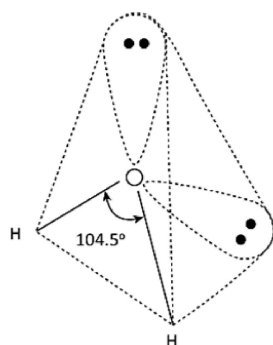


Figure 1.4: Bent geometry of water molecule

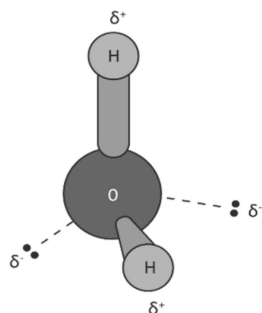


Figure 1.5: Dipolar nature of water molecule

- The oxygen is more electronegative than hydrogen and therefore pulls shared pair of electrons between H-O towards itself. The net result is formation of two electric dipoles in the water molecules, one along each O-H bond. Subsequently, each hydrogen bears δ^+ and oxygen bears $2\delta^-$ (**Figure 1.5**).
- Water is a polar molecule because its atoms share electrons unequally. Polarity of a molecule is measured with the help of dipole moment (μ). Net dipole moment of water is 1.84 Debye (D).
- Electrostatic attraction between oxygen atom of one water molecule and hydrogen atom of another water molecule result in the formation of Hydrogen bond.
- One water molecule can form maximum 4 hydrogen bonds with neighbouring water molecules. However, at room temperature water only form 3.4 hydrogen bonds with other water molecules because its molecules are disordered and are in continuous motion. In ice, water molecules are properly organised and form 4 hydrogen bonds with each other.
- Any biomolecule that forms hydrogen bond with water will be soluble in water.
- Hydrogen bonds are strongest when the three atoms that forms it are in straight line (180°)

1.3.3 Interaction of Water with Different Types of Solutes

- Compounds that dissolve readily in water are called **Hydrophilic** (Water-loving) while non-polar substances that poorly dissolve in water are known as **Hydrophobic**.
- Biomolecules having $-\text{COO}^-$, $-\text{NH}_3^+$ and phosphate esters or anhydrides are soluble in water. Water shields the **electrostatic interactions** between dissolved ions because of its high dielectric constant (a physical property of solvent). The force of interaction between charged solute in a solution is directly proportional to the amount of charge on solute but inversely proportional to the dielectric constant of solvent. Consequently, more is the value of dielectric constant of water, more it will decrease the force of interaction between charged solute particles and more it will be soluble in water.
- When a salt as NaCl, dissolves in water; NaCl dissociate into Na^+ and Cl^- leaving its organised structure and therefore entropy (randomness) of system increases. This is in accordance with the second law of thermodynamics. Also formation of solution results in negative change in free energy ($\Delta G = -ve$).
- The **non-polar** gases like N_2 , O_2 and CO_2 are poorly soluble in water and they tend to decrease the entropy of the solution therefore this is thermodynamically unfavourable condition. As a result, biological systems have water-soluble carrier proteins like haemoglobin and myoglobin to facilitate the transport of O_2 in blood.
- Compounds that contain both hydrophilic and hydrophobic regions are called **Amphipathic** molecules. For example proteins, sterols, phospholipids, pigments and some vitamins. Hydrophilic regions interact with water but hydrophobic regions of amphipathic molecule tend to escape from water. As a result, non-polar regions accumulate together to avoid contact with water and the forces responsible for holding non-polar regions together are called **Hydrophobic interactions**. Amphipathic molecules can form micelles, liposomes or bilayer sheet in which polar surface of amphipathic molecules interact with water while non-polar region is arranged to minimise the interaction with aqueous environment. (**Figure 1.6**)

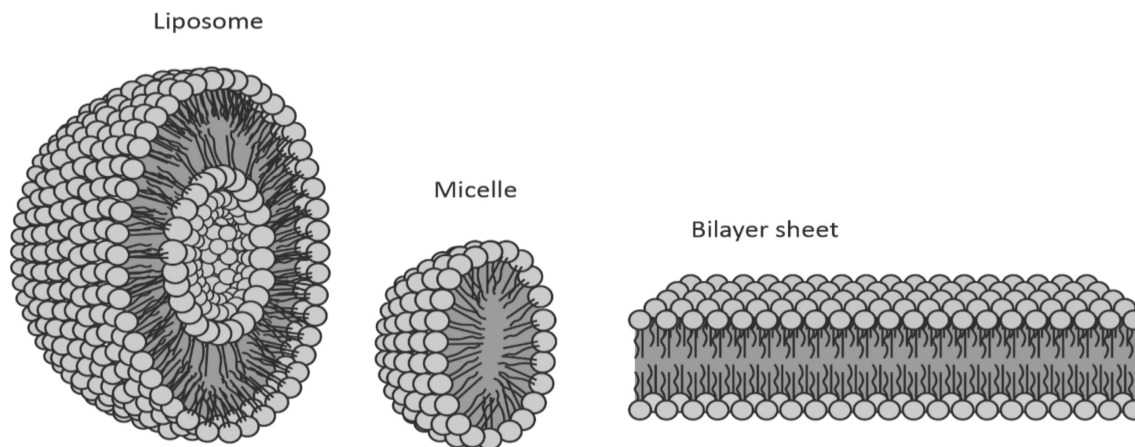


Figure 1.6: Amphipathic molecules can form liposomes, Micelle or bilayer sheet when placed in aqueous environment.

1.4 IONISATION OF WATER AND WEAK ACIDS

1.4.1 Ionisation of Pure Water

- Pure water is slightly ionised. Ionisation of water means dissociation of water molecule into its constituent hydrogen ions (H^+) and hydroxide ions (OH^-). Water is therefore an **amphoteric** molecule (It can act as acid as well as base as it can donate H^+ as well as OH^-). Water molecules undergo reverse ionisation but H^+ formed in water immediately form hydronium ions (H_3O^+) due to hydrogen bonding between H^+ and H_2O ; thus water is **amphiprotic** (it can either donate or accept a proton).
- Extent of ionisation of water can be measured quantitatively by equilibrium constant, K_{eq} .

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} \quad (1-1)$$

At $25^\circ C$, concentration of pure water is 55.5 M therefore putting this value in K_{eq} expression (Equation 1-1), we get:

$$K_{eq} = \frac{[H^+][OH^-]}{55.5M}$$

which on rearrangement becomes,

$$K_{eq}(55.5M) = [H^+][OH^-] = K_w \quad (1-2)$$

where K_w is called **ion product of water** at $25^\circ C$.

K_{eq} of pure water is calculated experimentally which is equal to $1.8 \times 10^{-16}M$ at $25^\circ C$. Substituting this value of K_{eq} in (equation 1-2) to get K_w :

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

$$= 1.0 \times 10^{-14}M^2$$

Hence at $25^\circ C$, the product $[H^+][OH^-]$ in pure water is always equals to $1.0 \times 10^{-14}M^2$ which is called ion product of water, K_w .

Significance of K_w

- From ion product of water, concentration of H^+ can be calculated provided concentration of OH^- is known.
- At neutral pH (when concentration of H^+ is equal to the concentration of OH^-), K_w can be used to find out the concentration of H^+ and OH^- as follows:

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

Solving for $[H^+]$ gives

$$[H^+] = \sqrt{K_w} = \sqrt{1 \times 10^{-14}M^2}$$

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

1.4.2 The pH Scale

In 1909, Soren Sørensen used a logarithmic scale for expressing the concentration of H^+ . This scale was designated as pH, where p stands for power and H for hydrogen ion concentration. The pH of a solution is defined as negative logarithm of concentration (in Molarity) of Hydrogen ions.

$$pH = \log \frac{1}{[H^+]} = -\log[H^+]$$

The symbol p denotes "negative logarithm of". For neutral solution at $25^\circ C$, the $[H^+]$ is $1 \times 10^{-7}M$, therefore pH can be calculated as :

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

$$= -[(\log 1) + (-7)\log 10]$$

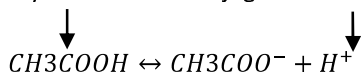
$$= -[0 + (-7)(1)]$$

$$= 7$$

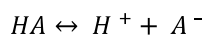
- Solutions having $\text{pH} > 7$ are alkaline or basic while the solutions whose $\text{pH} < 7$ are considered acidic. Greater is the acidity of a solution, the lower is its pH.
- pH scale is logarithmic scale that means when two solutions differ in pH by 2 pH unit it means that one solution has hundred times the concentration of the other. For example when pH of solution decreases 2 units from 7 to 5, the H^+ concentration has increased hundred times from 10^{-7} M to 10^{-5} M .
- Various dyes, like litmus, phenolphthalein, and phenol red can be used to approximately measure the pH of aqueous solutions. These dyes give characteristic change in color in the presence of acids or bases.
- pH affects the structure and activity of biomolecules; For example active site of an enzyme contains certain amino acid residues whose side chains undergo protonation or deprotonation depending upon the pH of surrounding aqueous solution and thus affect the catalytic activity of enzymes.

1.4.3 Ionisation of Weak Acids

Acid is a substance which donate a proton; conversely a substance that can accept a proton is called **base**. A proton donor (an acid) and its corresponding proton acceptor (a base) make up a **conjugate acid base pair**. For example acetic acid (CH_3COOH) is proton donor and acetate ion (CH_3COO^-) is the corresponding proton acceptor and together they constitute a conjugate acid-base pair.



- A strong acid ionizes almost completely in water and has high tendency to lose its proton. A weak acid ionises partially in aqueous solution. The tendency of an acid (HA) to give up a proton and form its conjugate base is defined by equilibrium constant (K_{eq}) for reversible reaction as:



$$K_{eq} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a$$

Equilibrium means the rate of forward reaction has become equal to the rate of backward reaction. It appears as if the reaction has stopped but reaction do not stop when it reaches equilibrium. Equilibrium is the state at which there is no net change in the concentration of reactants or products.

- Equilibrium constants for ionisation reaction are called **ionisation constant or dissociation constant, K_a** . Strong acids (phosphoric acid, carbonic acids) have large dissociation constants whereas weaker acids (HPO_4^{2-}) have smaller dissociation constants.
- **pKa** is defined is negative logarithm of K_a . It is a measure of relative strength of a weak acid or base.

$$\text{pKa} = \log \frac{1}{K_a} = -\log K_a$$

Stronger is the acid, more is its tendency to lose its proton, higher will be its K_a value and lower will be its pKa. Conversely, the stronger is the base, the higher is its pKa.

1.4.4 Titration Curve Reveal pKa of Weak Acids

- **Titration** is a method which is used to determine the amount of an acid in a given solution. During titration, a measured volume of weak acid is titrated with a solution of strong base (example NaOH) of known concentration. The base is added in small increments until the acid is consumed, which is determined with the help of pH meter. A plot of pH of solution against the amount of NaOH added is called titration curve. Titration curve reveals the pKa of weak acids.
- Consider the titration of 0.1 M solution of acetic acid with 0.1 M NaOH at 25°C

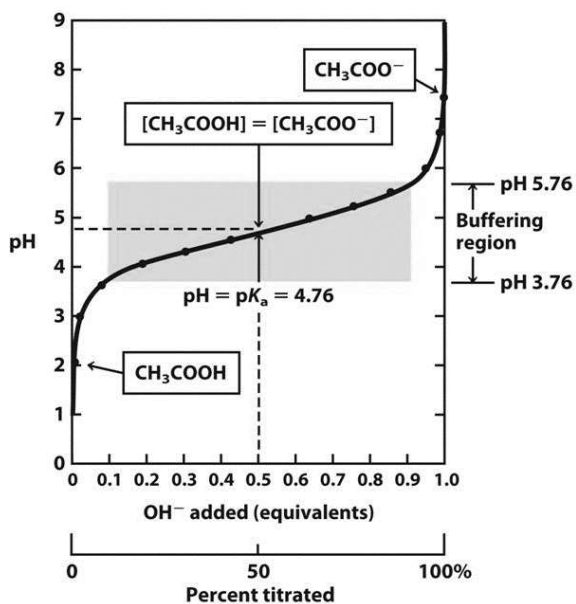


Figure 1.7: The titration curve of acetic acid. At lower pH protonated acidic form i.e. CH_3COOH predominates while at higher pH deprotonated conjugate base i.e. CH_3COO^- predominates.