Unit 3:

Buffers and Colligative properties

Acids, bases, Arrhenius concept, proton transfer theory, Lewis concept, Lowry and Bronsted concepts. Buffers, composition, pH, pH scale, Henderson- Hassel Balch equation, titration curve of H_3PO_4, pK value, isoelectric pH, ionization of HCl, HNO_3, H_2SO_4. Colligative properties and anomalous colligative properties of solutions, structure of water, phase diagram of pure water, ionic product of water, special properties of water, buffers in animal system. Solutions and types, ionizable solutes, non-ionizable solutes, vapor pressure and its application in distillation, Vant Hoff law, Roult`s law, boiling point, freezing point, de-icing, osmosis and osmotic pressure determination, reverse osmosis, surface tension.

Acids

Most of the acids taste sour, the word "acid" has been derived from a latin word "acidus" meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste.

Bases

Bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes.

When acids and bases are mixed in the right proportion they react with each other to give salts. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate.

Arrhenius Concept of Acids and Bases

According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+_{(aq)}$ and bases are substances that produce hydroxyl ions $OH^-_{(aq)}$. The ionization of an acid $HX_{(aq)}$ can be represented by the following equations:

$$HX_{(aq)} \rightarrow H^+_{(aq)} + X^-_{(aq)}$$

or

$$HX_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + X^-_{(aq)}$$
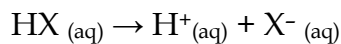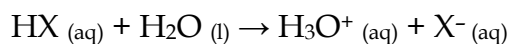
A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give trigonal pyramidal hydronium ion (H_3O^+).

Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH_{(aq)} \rightarrow M^+_{(aq)} + OH^-_{(aq)}$$

The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

## Bronsted-Lowry Acids and Bases

According to Bronsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+. In short, acids are proton donors and bases are proton acceptors.
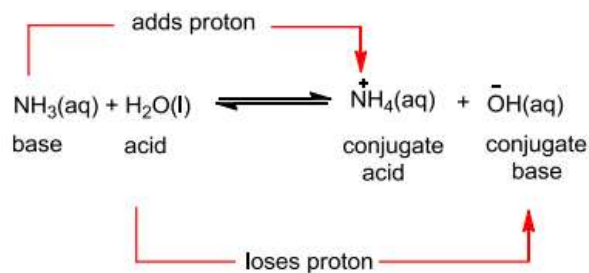
The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Bronsted acid and base, respectively. In the reverse reaction, H+ is transferred from NH_4^+ to OH^-. In this case, NH_4^+ acts as a Bronsted acid while OH^- acted as a Bronsted base. The acid-base pair that differs only by one proton is called a conjugate acid-base pair. Therefore, OH^- is called the conjugate base of an acid H_2O and

NH_4^+ is called conjugate acid of the base NH_3. If Bronsted acid is a strong acid then its conjugate base is a weak base and viceversa. It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. $HCl_{(aq)}$ acts as an acid by donating a proton to H_2O molecule which acts as a base.
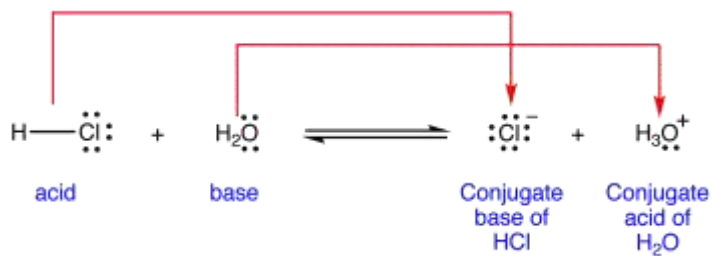

It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Proton transfer theory

Bronsted-Lowry theory, also called proton transfer theory of acids and bases, introduced independently in 1923 by the Danish chemist Johannes Nicolaus Bronsted and the English chemist Thomas Martin Lowry, stating that any compound that can transfer a proton to any other compound is an acid, and the compound that accepts the proton is a base. A proton is a nuclear particle with a unit positive electrical charge; it is represented by the symbol H^+ because it constitutes the nucleus of a hydrogen atom.

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$
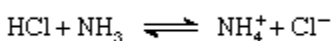
Lewis concept

G.N. Lewis defined an acid as a species which accepts electron pair and base which donates an electron pair. As far as bases are concerned, there is not much difference between Bronsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3. BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

$BF_3 + :NH_3 \rightarrow BF_3:NH_3$
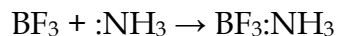
Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

Buffers and composition

Buffers are aqueous systems that tend to resist changes in pH when small amounts of acid (H^+) or base (OH^-) are added. A buffer system consists of a weak acid (the proton donor) and its conjugate base (the proton acceptor).

Types of buffer solutions are:

Acidic buffers

A weak acid together with a salt of the same acid with a strong base. These are called Acidic buffers.

Example, $CH_3COOH + CH_3COONa$.

Basic buffers

A weak base and its salt with a strong acid. These are called Basic buffers.

Example, $NH_4OH + NH_4Cl$.

pH

The pH of a solution is the negative logarithm of the hydrogen-ion concentration.

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

pH, quantitative measure of the acidity or basicity of aqueous or other liquid solutions. The pH is usually measured with a pH meter, which translates into pH readings the difference in electromotive force between suitable electrodes placed in the solution to be tested.

pH scale

It ranges between about 1 and 10^{-14} gram-equivalents per litre—into numbers between 0 and 14. In pure water, which is neutral (neither acidic nor alkaline), the concentration of the hydrogen ion is 10^{-7} gram-equivalents per litre, which corresponds to a pH of 7. A solution with a pH less than 7 is considered acidic; a solution with a pH greater than 7 is considered basic, or alkaline.
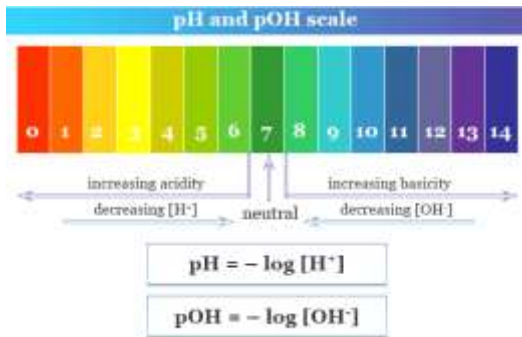
Henderson- Hasselbalch equation

Henderson - Hasselbalch equation, which is important for understanding buffer action and acid-base balance in the blood and tissues of vertebrates. This equation is simply a useful way of restating the expression for the dissociation constant of an acid. For the dissociation of a weak acid HA into H^+ and A^- , the Henderson- Hasselbalch equation can be derived as follows:

$$Ka = \frac{[H^+] [A^-]}{[HA]}$$

First solve for $[H^+]$:

$$[H^+] = Ka \frac{[HA]}{[A^-]}$$

Then take the negative logarithm of both sides,

$$-\log[H^+] = -\log Ka -\log \frac{[HA]}{[A^-]}$$

Substitute pH for -log [H⁺] and pKa for -log Ka,

$$pH = pKa -\log \frac{[HA]}{[A^-]}$$

Now invert log [HA] / [A⁻], which involve changing its sign, to obtain the Henderson-Hasselbalch equation:

$$pH = pKa + \log \frac{[A^-]}{[HA]}$$

Stated more generally,

$$pH = pKa + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

pK value

pKa is the negative logarithm of the acid dissociation constant (Ka) of a solution.

$$pKa = -\log Ka$$

pK values are often used to compare the strengths of different acids. The lower the pKa value, the stronger the acid. For example, the pKa of acetic acid is 4.8, while the pKa of lactic acid is 3.8. Using the pKa values, one can see lactic acid is a stronger acid than acetic acid.

Titration Curve of H₃PO₄

Titration is used to determine the amount of an acid in a given solution. A plot of pH against the amount of NaOH added (a titration curve) reveals the pKa of the acid. Consider the titration of a 0.1 M solution of phosphoric acid with 0.1 M NaOH at 25^0C.

Titration of the phosphoric acid H_3PO_4 is an interesting case. Although often listed together with strong mineral acids (hydrochloric, nitric and sulfuric) phosphoric acid is relatively weak, with pKa1=2.15, pKa2=7.20 and pKa3=12.35. That means titration curve contains only two inflection points and phosphoric acid can be titrated either as a monoprotic acid or as a diprotic acid. In the first case, acid has to be titrated against indicator changing color around pH 4.7 (for example methyl orange), in the second case - against indicator changing color around pH 9.6 (for example thymolphthalein).
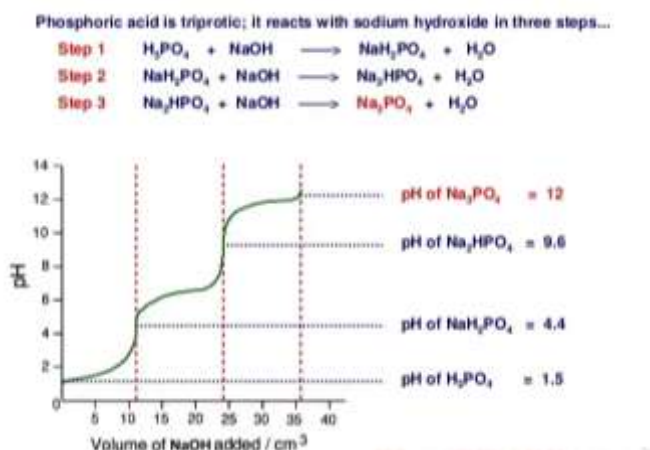
Titration curve of H₃PO₄.

Isoelectric pH (pI)

The isoelectric point (pI) is the point at which the net charge on a molecule is zero. pI is most commonly examined for proteins. Each of the amino acids in a protein carries a distinct charge, and the overall charge of a protein is the summation of the individual charges on each amino acid. This charge is also dependent on the pH of the surrounding solution. The pI can be calculated from the mean of the pKas of this molecule.

$$pI = \frac{pKa_1 + pKa_2}{2}$$

Ionization of HCl, HNO$_3$, and H$_2$SO$_4$.

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like hydrochloric acid (HCl), nitric acid (HNO$_3$) and sulphuric acid (H$_2$SO$_4$) are termed strong because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H$^+$) donors.

A strong acid dissociates completely in water, the resulting base formed would be very weak i.e., strong acids have very weak conjugate bases. Strong acids like hydrochloric acid (HCl), nitric acid (HNO$_3$) and sulphuric acid (H$_2$SO$_4$) will give conjugate base ions Cl$^-$, NO$_3^-$ and HSO$_4^-$, which are much weaker bases than H$_2$O.

HCl (Monoprotic acid)

HCl is a strong acid because it dissociates almost completely.

$$HCl_{(aq)} + H_2O(l) \rightleftharpoons H_3O^+{}_{(aq)} + Cl^-{}_{(aq)}$$
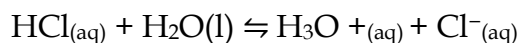
H₂SO₄ (Diprotic acid)

Sulfuric acid is a very strong acid; in aqueous solutions it ionizes completely to form hydronium ions (H_3O^+) and hydrogen sulfate ions ($HSO4^-$). In dilute solutions the hydrogen sulfate ions also dissociate, forming more hydronium ions and sulfate ions (SO_4^{2-}).

$H_2SO_4 \rightarrow H^+ + HSO_4^-$ (bisulphate ion)
$HSO_4^- \rightarrow H^+ + SO_4^{2-}$ (sulphate ion).
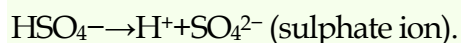
HNO₃ (Monoprotic acid)

Nitric acid is a strong acid, completely ionized into hydronium (H_3O^+) and nitrate (NO_3^-) ions in an aqueous solution, and a powerful oxidizing agent.

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$
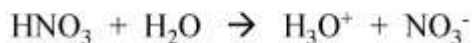
Structure of water

A water molecule consists of two hydrogen atoms and one oxygen atom. The three atoms make an angle; the H-O-H angle is approximately 104.5 degrees. The structure of a single water molecule is shown below:
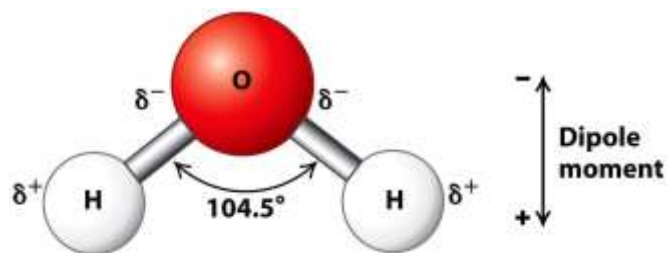
Oxygen is more electronegative than hydrogen. The hydrogen atoms end up with a partial positive charge and the oxygen atom with a partial negative charge. This separation of charge produces a net dipole moment on the molecule.

This molecular structure leads to hydrogen bonding, which is a stabilized structure in which a hydrogen atom is in a line between the oxygen atom on its own molecule and the oxygen on another molecule.

Phase diagram of pure water

Phase Diagram for Water
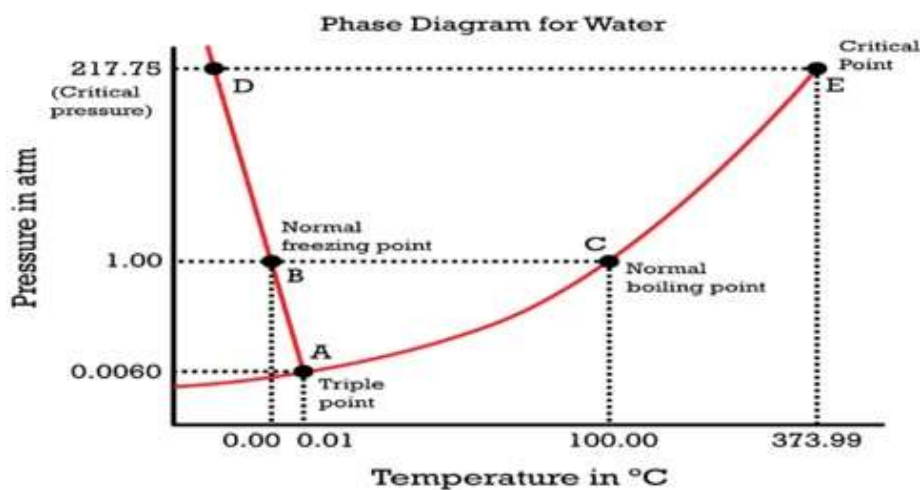
In phase diagram of water, the slope of the line between the solid and liquid states is negative rather than positive. The reason is that water is an unusual substance in that its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

The critical temperature (Tc) of a substance is the highest temperature at which the substance can possibly exist as a liquid. The point E, labeled the critical point at 373.99°C, particles of water in the gas phase are moving very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas. The critical pressure (Pc) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid. For water, the critical pressure is very high, 217.75 atm. The critical point is the intersection point of the critical temperature and the critical pressure.

Ionic product of water

Pure water is a very weak electrolyte and ionises according to the equation
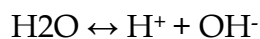
$H2O \leftrightarrow H^+ + OH^-$

Applying law of mass action at equilibrium, the value of dissociation constant,

$$K = \frac{[H^+]\,[OH^-]}{[H2O]}$$

$[H^+]\,[OH^-] = K\,[H_2 0]$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_2 0]$, may be regarded as constant. Thus, the product of water gives another constant which is designated as Kw. So,

$[H^+]\,[OH^-] = Kw$

The constant, Kw, is termed as ionic product of water.

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. The value of Kw increases with the increase of

temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

The value of Kw at 25°C is 1×10^{-14}. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH- ion concentration.

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

or $[H^+] [OH^-] = x^2 = 1 \times 10^{-14}$

or $x = 1 \times 10^{-7}$ M

or $[H^+] = [OH^-] = 1 \times 10^{-7}$ mol litre^{-1}

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

Special properties of water

➢ **Water is polar**. Water molecules are polar, with partial positive charges on the hydrogens, a partial negative charge on the oxygen, and a bent overall structure. This is because oxygen is more electronegative, meaning that it is better than hydrogen at attracting electrons.

➢ **Water is an excellent solvent.** Water has the unique ability to dissolve many polar and ionic substances. This is important to all living things because, as water travels through the water cycle, it takes many valuable nutrients along with it.

➢ **Water has high heat capacity.** It takes a lot of energy to raise the temperature of a certain amount of water by a degree, so water helps with regulating temperature in the environment. For example, this property allows the temperature of water in a pond to stay relatively constant from day to night, regardless of the changing atmospheric temperature.

➢ **Water has high heat of vaporization.** Humans (and other animals that sweat) use water's high heat of vaporization to cool off. Water is converted from its liquid form to steam when the heat of vaporization is reached. Since sweat is made mostly of water, the evaporating water absorbs excess body heat, which is released into the atmosphere. This is known as evaporative cooling.

➢ **Water has cohesive and adhesive properties.** Water molecules have strong cohesive forces due to their ability to form hydrogen bonds with one another. Cohesive forces are responsible for surface tension, the tendency of a liquid's surface to resist rupture when placed under tension or stress. Water also has adhesive properties that allow it to stick to substances other than itself.

➢ **Water is less dense as a solid than as a liquid.** As water freezes, the molecules form a crystalline structure that spaces the molecules further apart than in liquid water. This means that ice is less dense than liquid water, which is why it floats.

Buffers in Animal system

A buffer is a chemical substance that helps maintain a relatively constant pH in a solution on addition of acids or bases. Buffering is important in living systems as a means of maintaining a fairly constant internal environment, also known as homeostasis. Small molecules such as bicarbonate and phosphate provide buffering capacity as do other substances, such as hemoglobin and other proteins.

Bicarbonate Buffer

The maintenance of blood pH is regulated via the bicarbonate buffer. This system consists of carbonic acid and bicarbonate ions. When the blood pH drops into the acidic range, this buffer acts to form carbon dioxide gas. The lungs expel this gas out of the body during the process of respiration. During alkaline conditions, this buffer brings pH back to neutral by causing excretion of the bicarbonate ions through the urine.

Phosphate Buffer

The phosphate buffer system acts in a manner similar to the bicarbonate buffer, but has much stronger action. The internal environment of all cells contains this buffer comprising hydrogen phosphate ions and dihydrogen phosphate ions. Under conditions when excess hydrogen enters the cell, it reacts with the hydrogen phosphate ions, which accepts them. Under alkaline conditions, the dihydrogen phosphate ions accept the excess hydroxide ions that enter the cell.

Protein Buffer

Proteins consist of amino acids held together by peptide bonds. The amino acids possess an amino group and a carboxylic acid group. At physiological pH, the carboxylic acid exists as the carboxylate ion (COO-) with a negative charge and the amino group exists as the NH3+ ion. When the pH becomes acidic, the carboxyl group takes up excess hydrogen ions to return back to the carboxylic acid form. If the blood pH becomes alkaline, there is a release of a proton from the NH3+ ion, which takes the NH2 form.

Hemoglobin Buffer

The respiratory pigment present in blood, hemoglobin, also has buffering action within tissues. It has an ability to bind with either protons or oxygen at a given point of time. Binding of one releases the other. In hemoglobin, the binding of protons occurs in the globin portion whereas oxygen binding occurs at the iron of the heme portion. Hemoglobin helps in the buffering action by binding these protons, and simultaneously releasing molecular oxygen.

Solutions and types

Solutions are homogeneous mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes.

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

Ionizable solute

Ionizable solutes are molecules when dissolved in solution, will give that solution the ability to conduct electricity. This is because when a salt dissolves, its dissociated ions can move freely in solution, allowing a charge to flow.

Ionizable solutions are normally formed when a salt is placed into a solvent such as water. For example, when table salt, NaCl, is placed in water, the salt (a solid) dissolves into its component ions, according to the dissociation reaction:

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
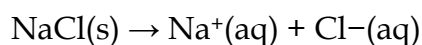
Non-ionizable solutes

Non-ionizable solutes are compounds that do not ionize at all in solution. As a result, solutions containing nonelectrolytes will not conduct electricity. Typically, nonelectrolytes are primarily held together by covalent rather than ionic bonds. A common example of a nonelectrolyte is glucose, or $C_6H_{12}O_6$. Glucose (sugar) readily dissolves in water, but because it does not dissociate into ions in solution, it is considered a nonelectrolyte; solutions containing glucose do not, therefore, conduct electricity.

Colligative properties of solutions

A colligative property is a property of a solution that is dependent on the ratio between the total number of solute particles (in the solution) to the total number of solvent particles. Colligative properties are not dependent on the chemical nature of the solution's components. The four colligative properties that can be exhibited by a solution are:

- Boiling point elevation
- Freezing point depression
- Relative lowering of vapour pressure
- Osmotic pressure

Boiling point elevation

The boiling point of a liquid is the temperature at which the vapour pressure is equal to atmospheric pressure. We know that on the addition of a non-volatile liquid to a pure solvent, the vapour pressure of a solution decrease. Therefore to make vapour pressure equal to atmospheric pressure we have to increase the temperature of the solution. The

difference in the boiling point of the solution and the boiling point of the pure solvent is termed as elevation in boiling point.

If T^0b is the boiling point of the pure solvent and Tb is the boiling point of the solution then elevation in boiling point is given as

$\Delta Tb = T^0b - Tb$

Experimental results show that there is a relation between elevation in boiling point and molality 'm' of the solute present in solution

$\Delta Tb \propto m$

$\Delta Tb = kb\ m$

Where,

kb = molal elevation constant

Substituting the value of 'm' in the above relation we get

$\Delta Tb = 1000 \times kb \times m2 / M2 \times m1$

Where,

m2 = mass of solvent in g

M1 = mass of solvent in kg

M2 = molar mass of solute

Freezing point depression

The freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour of the corresponding solid. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at a lower temperature. The difference between the freezing point of the pure solvent and its solution is called depression in freezing point.

If T^0f is the boiling point of the pure solvent and Tf is the boiling point of the solution then depression in freezing point is given as

$\Delta Tf = T^0f - Tf$

Just like elevation in boiling point, depression in freezing point is also directly related to molality 'm'.

$\Delta Tf = 1000 \times kf \times m2 / M2 \times m1$

Where,

kf = molal depression constant

m2 = mass of solvent in g

M1 = mass of solvent in kg

M2 = molar mass of solute

Relative lowering of vapour pressure

In a pure solvent, the entire surface is occupied by the molecules of the solvent. If a non-volatile solute is added to the solvent, the surface now has both solute and solvent molecules; thereby fraction of surface covered by solvent molecules gets reduced. Since the vapour pressure of the solution is solely due to solvent alone, at the same temperature the vapour pressure of the solution is found to be lower than that of the pure solvent.
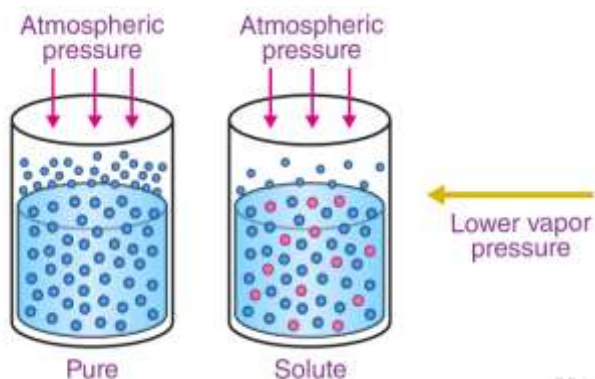
If P_0 is the vapour pressure of pure solvent and Ps is the vapour pressure of the solution. The difference Po – Ps is termed as lowering in vapour pressure. The ratio   of Po – Ps / Po is known as the relative lowering of vapour pressure.

Raoult, in 1886, established a relation between relative lowering in vapour pressure and mole fraction. The relationship is known as Raoult's law. It states that the relative lowering in vapour pressure of a dilute solution is equal to the mole fraction of the solute present in the solution

If n moles of solute is dissolved in N moles of the solvent, then according to Raoult's law

$$\frac{Po - Ps}{Po} = \frac{n}{n + N}$$

Vapour pressure and its application in distillation

Distillation is the process of separating the component or substances from a liquid mixture by selective evaporation and condensation.

By this method, Separation of the liquids of the mixture, having a few degrees different boiling points, Separation of a liquid from non-volatile components, Purification of the liquid, is carried out.

Distillation processes depends on the vapour pressure characteristics of liquid mixtures.

The vapour pressure of a liquid at a particular temperature is the equilibrium pressure exerted by molecules leaving and entering the liquid surface.

Here are some important points regarding vapour pressure:

➢ energy input raises vapour pressure
➢ a liquid is said to 'boil' when its vapour pressure equals the surrounding pressure
➢ the ease with which a liquid boils depends on its volatility
➢ liquids with high vapour pressures (volatile liquids) will boil at lower temperatures
➢ the vapour pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture
➢ distillation occurs because of the differences in the volatility of the components in the liquid mixture

Anomalous colligative properties of solutions

When the experimentally measured colligative property of a solution is different from that calculated theoretically by the van't Hoff equation or by the laws of osmosis, then the solution is said to have Anamalous colligative property.

The anamalous behaviour of colligative properties has been explained in terms of dissociation and association of solute molecules.

Dissociation of the solute molecules:

When a solute like an electrolyte is dissolved in a polar solvent like water, it undergoes dissociation, which results in the increase in the number of particles in the solution. Hence, the observed value of the colligative property becomes higher than the theoretical value, e.g., when one mole of KCl is dissolved in the solution then due to dissociation, $KCl \rightarrow K^+ + Cl^-$, the number of particles increases, hence, the colligative properties like osmotic pressure elevation in the boiling point, etc. increase.

Association of the solute molecules:

When a solute like a non-electrolyte is dissolved in a non-polar solvent like benzene, it undergoes association forming molecules of higher molecular mass. Hence, the number of the particles in the solution decreases. Therefore the colligative properties like osmotic pressure, elevation in the boiling point, etc., are lower than the theoretical value, e.g., $nA \rightarrow A_n$.

$2CH_3COOH \rightarrow (CH_3COOH)_2$

$2C_6H_5COOH \rightarrow (C_6H_5COOH)_2$
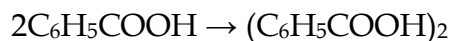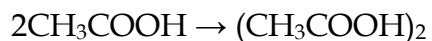
Roult`s law

Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is equal to the vapour pressure of the pure solvent multiplied by its mole fraction in the solution.

Mathematically, Raoult's law equation is written as;

Psolution = Xsolvent x P^0solvent

Where,

Psolution = Vapour pressure of the solution

Xsolvent = Mole fraction of the solvent

P^0solvent = Vapour pressure of the pure solvent

Osmosis

The phenomenon of the spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution is called osmosis.

The flow of solvent molecules through the semipermeable membrane can be stopped if some extra pressure is applied from the solution side. This pressure that just stops the flow of solvent is called osmotic pressure of the solution.

Osmotic pressure of biological fluids is frequently expressed as milli osmoles. The osmotic pressure of plasma is 280-300 milli osmoles.
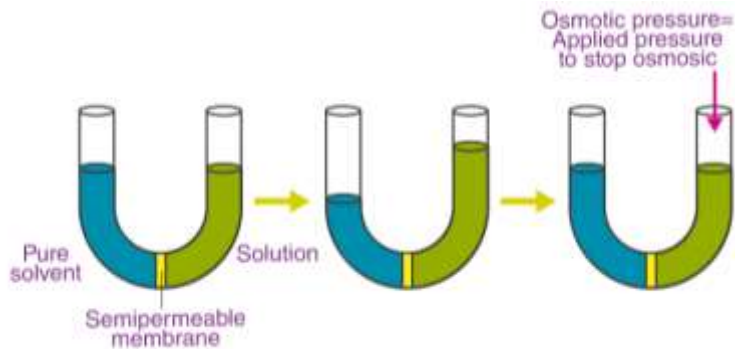
Vant Hoff law

Van't Hoff law states that for dilute solutions, the osmotic pressure is directly proportional to the molar concentration of the solute and the temperature of the solution.

$\pi = CRT$

where,

π = Osmotic pressure
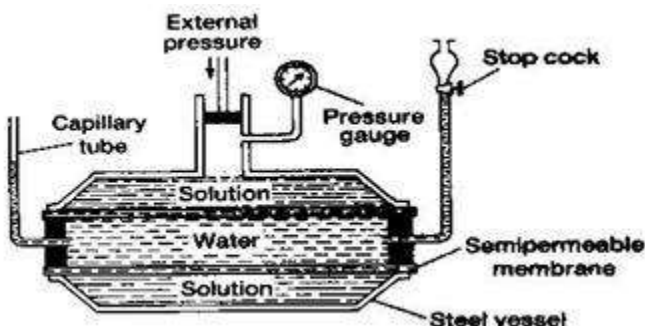
C = concentration

T = Temperature

R = gas constant

Osmotic pressure determination

The osmotic pressure of a solution can be conveniently measured by Berkley - Hartley method. The apparatus consists of two concentric tubes. The inner tube is made of semipermeable membrane with two side tubes. The outer tube is made of gun metal which contains the solution. The solvent is taken in the inner tube. As a result of

osmosis, there is fall of level in the capillary indicator attached to the inner tube. The external pressure is applied by means of a piston attached to the outer tube so that the level in the capillary indicator remains stationary. This pressure is equal to the osmotic pressure and the solvent flow from inner to outer tube is also stopped.


Advantages of this Method

> ➢ The osmotic pressure is recorded directly and the method is quick.
> ➢ There is no change in the concentration of the solution during the measurement of osmotic pressure.
> ➢ The osmotic pressure is balanced by the external pressure and there is minimum strain on the semipermeable membrane.

Reverse osmosis

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Figure. When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose. The pressure required for the reverse osmosis is quite

high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.
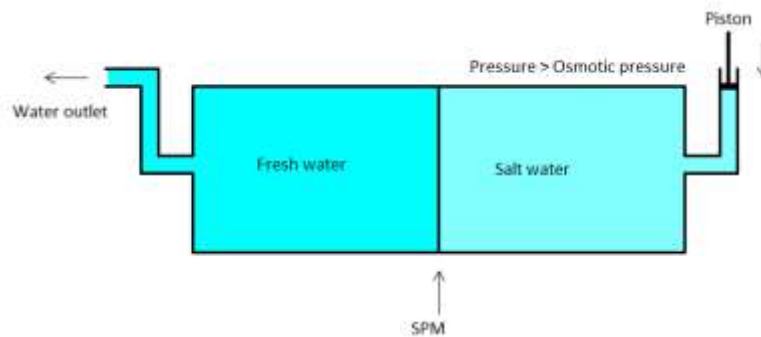
Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

De-icing

De-icing is the process of removing snow, ice or frost from a surface. Anti-icing is understood to be the application of chemicals that not only de-ice but also remain on a surface and continue to delay the reformation of ice for a certain period of time, or prevent adhesion of ice to make mechanical removal easier.

De-icing can be accomplished by mechanical methods (scraping, pushing); through the application of heat; by use of dry or liquid chemicals designed to lower the freezing point of water (various salts or brines, alcohols, glycols); or by a combination of these different techniques.

Application of De-icing:

- Deicing is needed for the operation and safety of aircraft.
- Deicing and antiicing of roads and driveways are particularly needed for enhancing traffic safety.

Surface tension

A molecule in the interior of a liquid is attracted by other molecules in all directions. In contrast, a molecule on the surface is attracted only downwards and sideways and not upwards. Due to this, the surface layer behaves like a stretched film.

Surface tension is the force with which the molecules on the surface are held together. It is expressed as dynes/cm. Surface tension decreases with increase in temperature. Due to the phenomenon of surface tension, any liquid occupies the minimum possible volume.

Applications of surface tension

1. Digestion and absorption of fat: Bile salts reduce the surface tension. They act as detergents and cause emulsification of fat, thereby allowing the formation of minute particles for effective digestion and absorption.

2. Hay's sulfur test: This is a common laboratory test employed for the detection of bile salts in urine of jaundice patients. Sulfur powder, when sprinkled on the surface of urine possessing bile salts, sinks. This is in contrast to normal urine where sulfur powder floats. Hay's test is based on the principle that bile salts in urine lower surface tension which is responsible for sulfur to sink.

3. Surface tension and adsorption: Adsorption, being a surface phenomenon, is closely related to surface tension. Due to the coupled action of these two processes, the formation of complexes of proteins and lipids occurs in the biological systems.

4. Lipoprotein complex membranes: The structure of plasma membrane is composed of surface tension reducing substances, namely lipids and proteins. This facilitates absorption of these compounds.