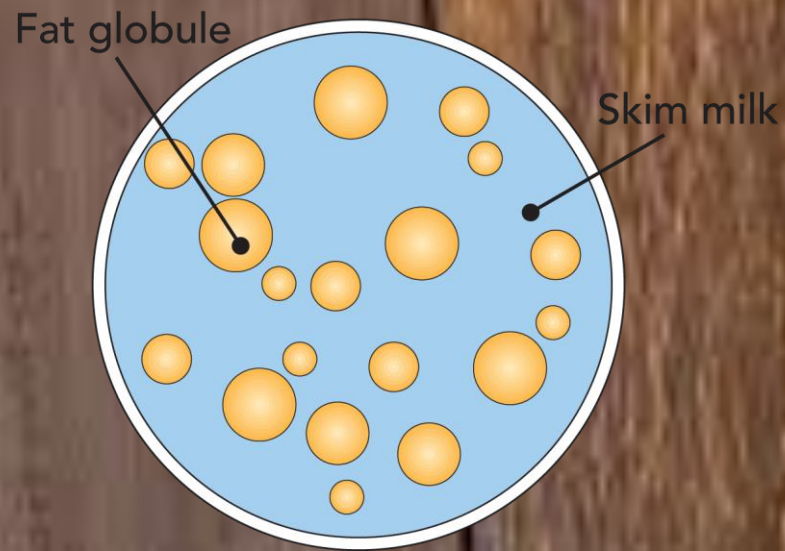


# PHYSICAL CHEMISTRY OF MILK



Soma Maji

# Definition of milk

Milk may be defined as the whole, fresh, clean, lacteal secretion obtained by the complete milking of one or more healthy milch animals, excluding that obtained within 15 days before and 5 days after calving to avoid colostrum milk and should contain minimum prescribed percentage of milk fat and milk Solid Not Fat.

(De, 1980)

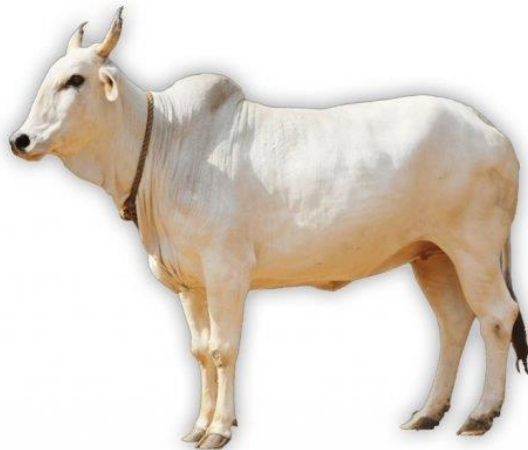
## Gross Composition of cow milk

Component	Average Content percentage (w/w)	Range Percentage (w/w)	Average % of Dry matter
Water	87.3	85.5 -88.7	
Solids not fat	8.8	7.9-10.0	69
Fat	3.9	2.4-5.5	31
Protein	3.25	2.3-4.4	26
Lactose	4.6	3.8-5.3	36
Casein	2.6	1.7-3.5	20
Mineral substances	0.65	0.53-0.80	5.1
Organic acids	0.18	--	1.4

Walstra and Jenness, 1984)

# Gross composition of milk from different species of mammals

Composition (g/100g)	Human	Cow	Buffalo	Goat	Sheep	Horse	Camel
Water	87.1	87.3	82.8	86.7	82.0	88.8	86.5
Fat	4.5	3.9	7.4	4.5	7.2	1.9	4.0
Casein	0.4	2.6	3.2	2.6	3.9	1.3	2.7
Whey Protein	0.5	0.6	0.6	0.6	0.7	1.2	0.9
Lactose	7.1	4.6	4.8	4.3	4.8	6.2	5.0
Ash	0.2	0.7	0.8	0.8	0.9	0.5	0.8



# Major constituents of milk

The major constituents of milk are, water, fat, proteins, lactose, minerals and miscellaneous compounds.

## **1. Water**

It is the medium in which all the milk constituents are dispersed. It is a universal vehicle and plays an important role in the physical properties exhibited by the milk. It also assists in maintaining the much desirable equilibrium and keeps the constituents of the milk in their native state. Water acts as a solvent in keeping the constituents in soluble, colloidal or emulsion form and influences the colligative properties of milk.

## **2. Fat**

Fat is the costliest component of milk. It is characterized by its presence as an emulsion. The unique feature of milk fat is its fatty acid composition. Milk fat is rich in saturated fatty acids and mono unsaturated fatty acids and also acts as a carrier for the fat soluble vitamins. The unique feature of the milk fat from ruminants is that they are having short chain saturated fatty acids in substantial quantities and imparts the unique flavour to the milk and milk products. Presence of long chain unsaturated fatty acids reduce the melting point of milk fat. In order to maintain the emulsion stability several surface active substance are also associated with the milk fat and present in higher proportion in fat globule membrane.

### **3. Proteins**

Milk is rich in protein content and has a unique protein namely the casein. It is present in the form of colloidal dispersion in milk and is responsible for several physical properties of milk. It also supplies all the essential amino acids, hence a complete protein and is easily digestible. In addition to casein, milk also contains (other) proteins which are known as whey proteins. Milk is a biological secretion of living cells synthesized through several (enzyme mediated) biochemical reactions (which are often mediated through enzymes). It is a well known fact that these enzymes are basically protein in nature and act as biological catalysts. Milk is a good source for several enzymes which have both desirable and also undesirable effect on preservation and processing of milk.

### **4. Lactose**

Lactose is a major soluble component present in milk. Milk contains approximately 4.6% carbohydrate that is predominately lactose with trace amounts of monosaccharides and oligosaccharides. Lactose is a disaccharide of glucose and galactose. It is first carbon source for the microbes gaining entry into milk. It is a reducing sugar and is present in soluble state. It is a good source of energy for the young ones. In addition to lactose, milk also contain several other carbohydrates in trace levels (negligible).

## **5. Minerals**

Minerals in milk are mainly inorganic salts, partly ionized and partly present as complex salts. Some inorganic matter is bound covalently such as calcium phosphate groups in casein. They are responsible for the ionic balance of milk and helps in maintaining the equilibrium between the soluble and colloidal state.

## **6. Vitamins**

Milk contains almost all the essential vitamins which include fat soluble and water soluble vitamins. It is a very good source for the most essential fat soluble vitamin namely the Vitamin A. It is also interesting to observe that this vitamin is existing in the cow milk in its precursor form i.e. carotene a provitamin A imparts golden yellow colour to milk. Milk is not a good source of Vitamin K and Vitamin C.

## **7. Miscellaneous compounds**

Milk contains many components which are in low concentrations (less than 100 mg/liter) which do not fall into any of the above categories. These compounds may be considered as natural if they present in freshly drawn milk and have been detected in most samples tested for that component. The compounds considered in this category are gases, alcohols, carbonyl compounds, carboxylic acids, conjugated compounds, non protein nitrogenous compounds, phosphate esters, nucleotides, nucleic acids, sulfur containing compounds, hormones etc.

# Colloid

## Introduction:

- About 87% of milk is water, in which the other constituents are distributed in various forms.
- Milk has various components in the form of emulsions, colloids, molecular and ionic solutions.
- Lactose in milk is present in form of true solution and milk fat as an emulsion whereas milk proteins are dispersed as a colloid.

## Definition of colloid:

A colloid is a substance microscopically dispersed evenly throughout another substance or a colloid system is one in which a substance is distributed throughout another substance in the form of finely divided particles. These systems are known as disperse systems or dispersions. They usually consist of at least two phases; a dispersed phase (or internal phase) and a continuous phase (or dispersion medium).

## Definition of dispersed phase and dispersion medium:

The dispersed phase consists of the suspended particles and dispersion medium surrounding the suspended particles.

# Classification of colloid

Based on the affinity of dispersed molecules with dispersing media colloid can be classified into two groups.

1. Lyophilic colloid
2. Lyophobic colloid

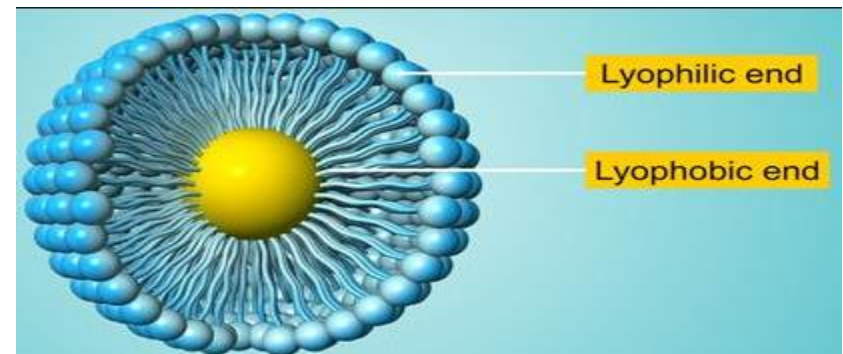
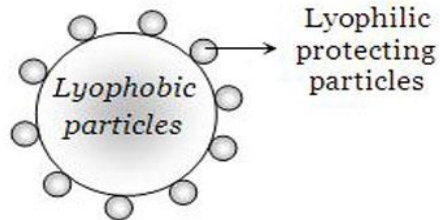
**Definition of Lyophilic colloid:** If the affinity on dispersion medium is more it is lyophilic or reversible sol. Lyophilic colloidal systems with aqueous continuous phase are known as hydrophilic.

**Definition of Lyophobic colloid:** If the affinity on dispersion medium is less it is lyophobic or irreversible sol. The lyophobic systems with aqueous dispersion medium are known as hydrophobic.



# Differences between the lyophobic and lyophilic colloids

Characteristics	LYOPHYLIC	LYOPHOBIC
Physical state	Reversible	Irreversible
Method of preparation	Can be prepared by simple methods of mixing	Needs special methods for preparation
Stability	More solvated because of which it is more stable	Not solvated hence less stable
Viscosity	Viscosity is more for sol than for dispersion medium	Viscosity of sol is similar to dispersion medium
Surface Tension	Surface tension is less than dispersion medium	Surface tension of colloid sol is same for dispersion medium
Tyndall effect	Exhibit weak tyndall effect	Exhibit strong tyndall effect



# Classification of colloids on the basis of the physical state of dispersed phase and dispersion medium

Dispersed phase	Dispersion medium	Name	Examples
Solid	Gas	Solid aerosol	Smoke dust, cloud
Solid	Liquid	Sol	Paints, blood
Solid	Solid	Solid sol	Coloured gem stones
Liquid	Solid	Gel	Jelly, Gelatin
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Liquid Aerosol	Fog, mist
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Whipped cream froth



# Difference between true solution and colloidal solution

Property	True solution	Colloidal solution
Particle size	Less than $10^{-7}$ cm	Between $10^{-5}$ and $10^{-7}$ cm
Visibility of particles	Invisible to naked eye and even not under powerful microscope	Invisible to naked eye. Visible under powerful microscope
Sedimentation of particles	Do not settle down	Settle down under high centrifugation
Filtration through filter paper	No residue is formed	Residue is formed

**True solution:** A true solution is a homogeneous solution in which the solute particles have diameters less than  $10^{-7}$  cm. i.e., the solute particles are of molecular dimensions. The particles are invisible even under powerful microscopes.

The **colloidal particles were observed to be in constant motion in a zig zag path** in all possible directions. This motion is known as **Brownian motion**. It arises because of the impact of solvent molecules on the colloidal particles. The forces are unequal from different directions.

# Properties of colloidal system

The colloidal system will have two phases one is a dispersed phase and a dispersion medium. The state of aggregation of the dispersed phase and the intensity of its interaction with the dispersion medium determines many fundamental characteristics of the colloid system.

- ✚ Lyophilic colloids have a strong attraction for the molecules of dispersion medium and thus binding large number of them into so called solvent shells.
- ✚ In lyophobic colloids the particles do not interact so strongly with the molecules of the surrounding medium
- ✚ Lyophobic colloids are heterogeneous and are highly disperse colloidal systems
- ✚ Lyophilic colloids are in fact true solutions which mean that molecular species disperse homogenous in the system and not colloids.
- ✚ The great difference in the size of the solvent and solute particles and to the structure of these particles However to the large size of the molecules solutions of such substances are in many respects similar to colloid system

# Milk as a colloidal solution

## **Chemical definition of milk:**

Milk is a chemical substance which consists milk protein in colloidal form, milk fat in emulsion form and lactose and some minerals in true solution.

## **Stability of the colloidal system in milk:**

The stability of a colloidal system is the capability of the system to remain as it. Stability is hindered by aggregation and by sedimentation phenomena that determine phase separation.

- If the hydrophobic colloid particles are fluid (fat globules at normal temp and air bubbles) which may coalesce with each other if the thin film of continuous phase between closely approaching globules or bubbles is ruptured.
- Two colloidal particles of equal composition always attract each other because of van der Waals forces. If the attraction energy is not too strong the Brownian motion will be sufficient to keep the particle apart and maintain the colloidal stability
- There will also be repulsion due to hydration on close contact of individual molecular chains when the protruding chains are hydrophilic. This is important for the stability of fat globules

## De- stabilization of the colloidal system in milk

Disintegration of the colloid system could be by two processes namely **sedimentation** and **coagulation**

- **Sedimentation:** The dispersed phase may either settle out or raise to the surface of the system depending upon the difference in densities between the dispersed particles and the dispersion medium and is known as sedimentation
- **Coagulation:** The dispersed particles adhere to one another or coalesce increase in size. This process is called coagulation. Under definite conditions coagulation can proceed spontaneously since it is accompanied by decrease in surface

The determination of kinetic stability and aggregate stability will help in characterizing the stability of colloidal system with respect to sedimentation process and to change in particle size (coagulation)

# Emulsion

## Definition:

An 'emulsion' is a system in which the dispersion medium and dispersed phase are liquids. For an emulsion to be stable, the two liquids must practically be insoluble in each other or only slightly soluble. One liquid (the dispersed phase) is dispersed in the other (the continuous phase). Example: butter and margarine, milk and cream

- **Water-in-oil emulsion (W/O)** : fat surrounds droplets of water. Example- butter and margarine.
- **Oil-in water emulsion (O/W)** : water surrounds droplets of fat. Example-milk, cream, mayonnaise, ice cream, salad dressing.

**Emulsification:** Emulsification is the process by which emulsions are prepared.

- Addition of emulsifying agents will reduce the inter facial tension by being adsorbed on the inter phase. Due to the stabilizing effect of these emulsifiers, substances with much larger size than that of ordinary colloids can also be stabilized.

- **Factors influencing the properties of emulsion:**
- The continuous phase
- Temperature
- Average droplet size
- Distribution of the droplets
- Volume fraction of the oil dispersed in water
- The oil that is dispersed
- Various additives which help in the stability of the emulsion



## **Definition**

Colligative properties are properties of solutions that depend on the number of molecules in a given amount of solvent and not on the properties/identity (e.g. size or mass) of the molecules or those properties of solutions that depend on the number of dissolved particles in solution, but not on the identities of the solutes.

**The four commonly studied colligative properties are**

1. Freezing point
2. Boiling point
3. Vapour pressure
4. Osmotic pressure.

Since these properties yield information on the number of solute particles in solution, one can use them to obtain the molecular weight of the solute.

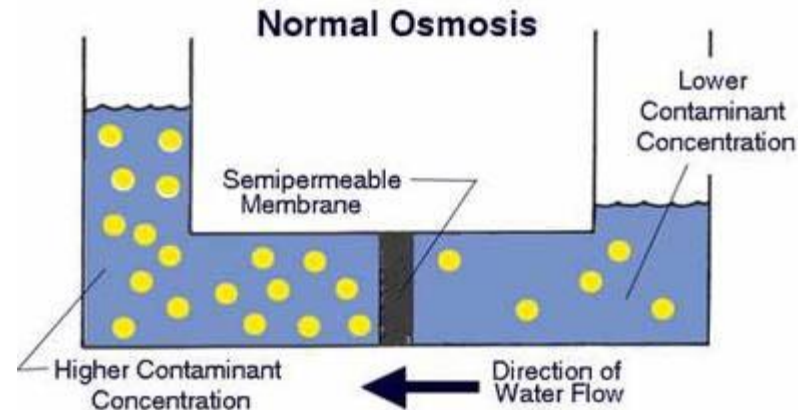
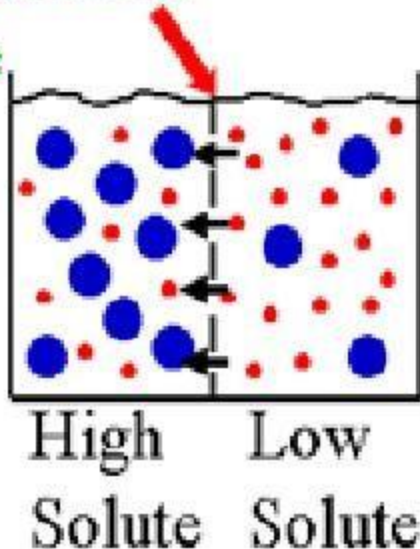
# Osmotic Pressure

Definition:

Osmosis is the movement of solvent molecules through a selectively permeable membrane into a region of higher solute concentration, aiming to equalize the solute concentrations on the two sides.

## Osmosis

•Semipermeable  
membrane



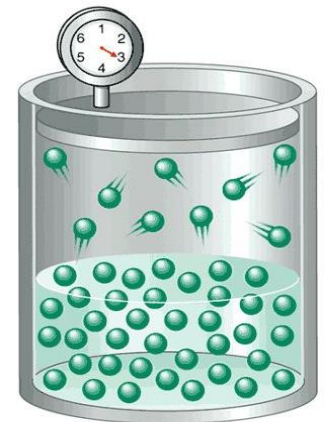
# Raoult's Law

The French chemist Francois Henricus Raoult discovered a law to determine the vapour pressure of a solution when a solute has been added to it. Raoult's law states that the vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component and the mole fraction of the component present in the solution.

## Vapour Pressure:

When a non-volatile solute is added to a liquid to form a solution, the vapour pressure above that solution decreases.

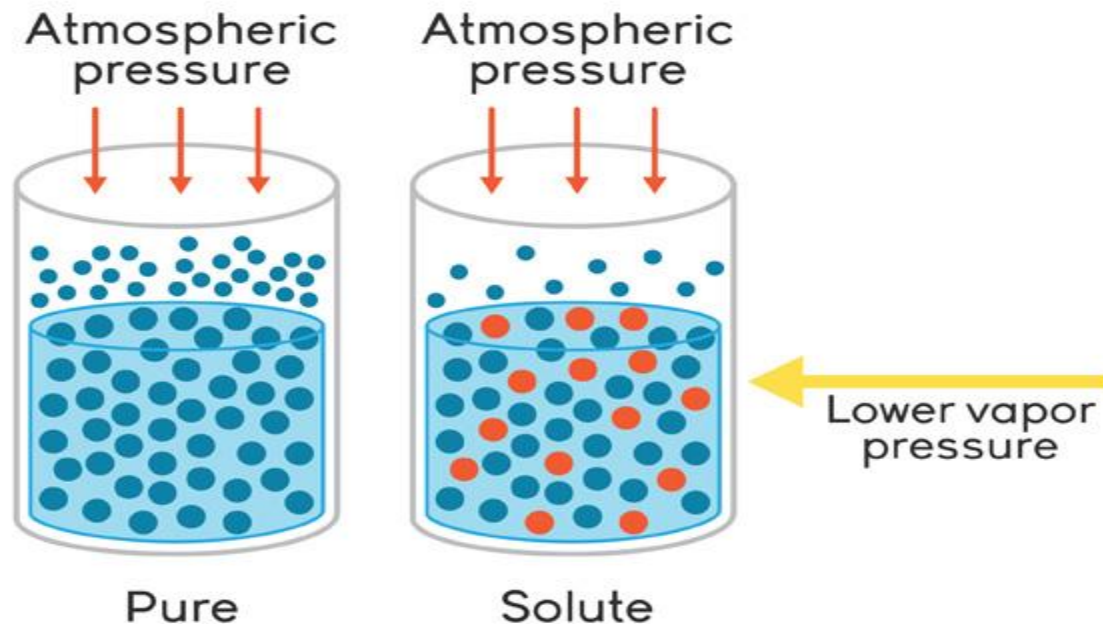
Liquid molecules at the surface of **a liquid can escape to the gas** phase when they have a sufficient amount of energy to break free of the liquid's intermolecular forces. That vaporization process is reversible. Gaseous molecules coming into contact with the surface of a liquid can be trapped by intermolecular forces in the liquid. Eventually the **rate of escape will equal the rate of capture** to establish a constant, **equilibrium vapour pressure** above the pure liquid.



Pure solvent

# Vapour pressure

If we add a non-volatile solute to that liquid, the amount of surface area available for the escaping solvent molecules is reduced because some of that area is occupied by solute particles. Therefore, the solvent molecules will have a lower probability to escape the solution than the pure solvent. That fact is reflected in the lower vapour pressure for a solution relative to the pure solvent. That statement is only true if the solvent is non-volatile. If the solute has its own vapour pressure, then the vapour pressure of the solution may be greater than the vapour pressure of the solvent.



## Raoult's law

The law that mathematically describes the vapour pressure lowering phenomenon. Raoult's law is given in:

$$P = C_{\text{solvent}} P_0$$

Where,  $P$  - vapour pressure of a solution

$C_{\text{solvent}}$  - Vapour pressure of the solvent above a solution

$P_0$  - vapour pressure of the pure solvent

Raoult's law states that the vapour pressure of a solution ( $P$ ), equals the mole fraction of the solvent ( $C_{\text{solvent}}$ ), multiplied by the vapour pressure of the pure solvent ( $P_0$ ). While that "law" is approximately obeyed by most solutions, some show deviations from the expected behaviour. Deviations from Raoult's law can either be positive or negative. A positive deviation means that there is a higher than expected vapour pressure above the solution. A negative deviation, conversely, means that we find a lower than expected vapour pressure for the solution.

Solutions that obey Raoult's law are called ideal solutions because they behave exactly as we would predict. Solutions that show **a deviation from Raoult's law** are called **non-ideal solutions** because they deviate from the expected behaviour. Very few solutions actually approach ideality, but Raoult's law for the ideal solution is a good enough approximation for the non-ideal solutions that we will continue to use Raoult's law.

### **Definition:**

Boiling point of a solution is the temperature at which the vapour pressure of the liquid equals to the external (Atmospheric) pressure.

1. The water content in fluid milk is highest and hence the boiling point of milk will be close to that of water. But being a colligative property it is influenced by the dissolved substances like lactose, minerals etc. and hence it is slightly higher than that of water.
2. Since the vapour pressure of a solution is always less than the vapour pressure of the pure solvent it follows that the boiling point of a solution will always be higher than that of the pure solvent.
3. Pure water boils at  $100^{\circ}\text{C}$ . Milk constituents are responsible for the elevation of the boiling point of milk.
4. Addition of water lowers the concentration of dissolved substances responsible for the elevating the boiling points. As such adulterated milk with water boils at a lower temperature than the normal milk. The boiling point of normal milk is  $100.15^{\circ}\text{C}$ .

# Freezing point

## Definition:

Freezing point of a substance is defined as the temperature at which its solid form and its liquid form can exist in equilibrium with each other. In other words it is the temperature in which they have the same vapour pressure.

The depression of freezing point of a solvent by a dissolved solute is proportional to the concentration of the dissolved substance.

## Roult's law:

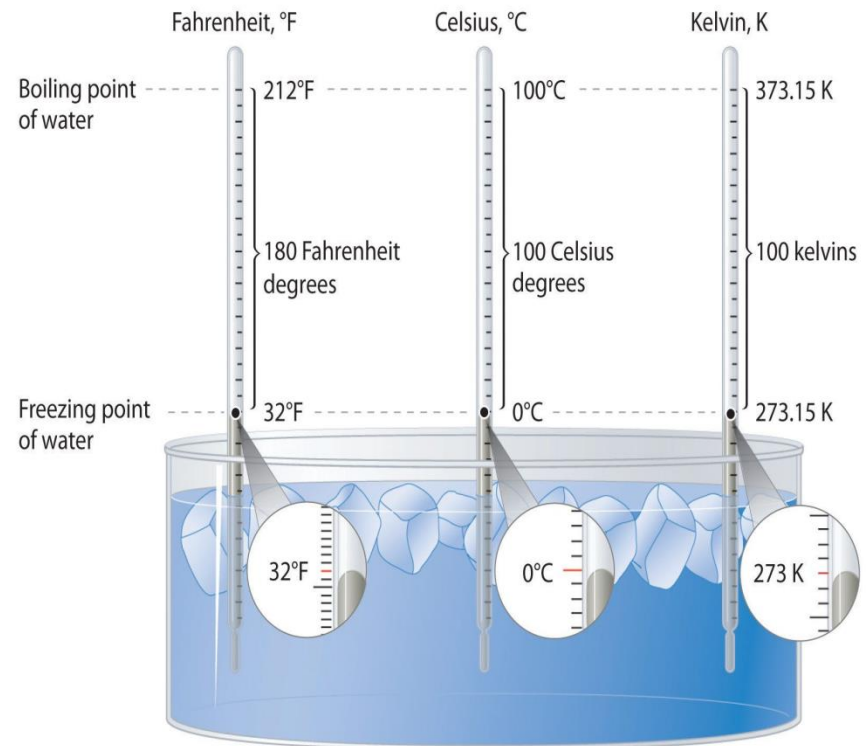
$$T_r = K_f C_m$$

Where,  $K_f$  = Molar depression constant

$T_r$  = depression of freezing point for solution

$C_m$  = molar concentration of solute.

The freezing point depression of milk is very constant. Since it is proportional to its osmotic pressure, which is essentially equal to the blood, which in turn is kept almost constant. Generally freezing point of milk ranges between  $-0.530$  to  $-0.570^\circ\text{C}$ .



## Factors affecting the freezing point

- Lactose and chloride are the principal components responsible for the freezing point depression of milk. The high molecular weight components such as fat, protein, CCP, fat globules have a negligible influence on freezing point depression because they contain few molecules per gram.
- Colostrum has a slightly lower freezing point than the normal milk.
- Chilling and heating of milk may raise freezing point slightly. These produces aggregation of dissolved salt or transfer of dissolved material to the colloidal caseinate micelles
- Souring which involves a net increase in the number of molecules in the solution due to degradation of lactose(sometimes citrate) results in lowering the freezing point
- The principal use of freezing point is to assess for watering of milk. The commonly used technique and apparatus are those of Horvet and it is used to record the freezing point at 0°C. Freezing point of milk is -0.550°C
- Thermistor type cyoscope is used for the determination of freezing point
- Percentage of added water= 
$$\frac{(0.550 - T) \times 100}{0.550}$$

Where, T= Freezing point depression of the sample

A tolerance of 3% added water is allowed by most regulatory agencies.



# ELECTROLYTES AND NON ELECTROLYTES, IONIC MOBILITY

## Electrolyte:

Substances which cause increase in electrical conductivity in solutions and which dissociate in the process of conducting the electric current are known as electrolytes. In other words, electrolyte is an electrical conductor in which current is carried by ions rather than by free electrons (as in a metal).

## Non electrolyte:

A non-electrolyte, however, is a compound composed of molecules that does not conduct electricity when molten or in aqueous solutions. If the substances which give the expected result to osmotic pressure, freezing point and boiling point but do not significantly increase the electrical conductivity such substances are known as non electrolytes.

## Main Electrolytes in the Body

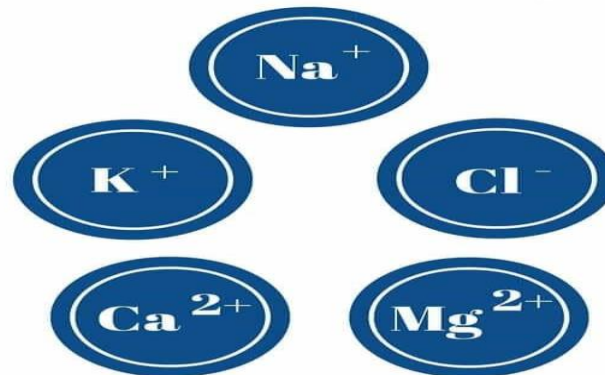
**Na<sup>+</sup> Sodium**

**Cl<sup>-</sup> Chloride**

**Mg<sup>2+</sup> Magnesium**

**Ca<sup>2+</sup> Calcium**

**K<sup>+</sup> Potassium**

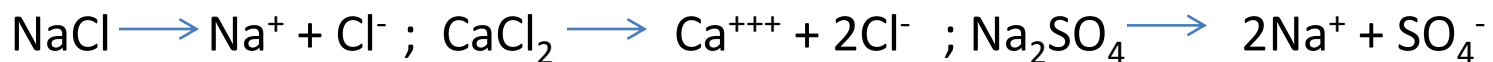


## Electrolytes Dissociation:

Non electrolytes behave in a definite manner with respect to osmotic pressure, freezing point and boiling point and this behaviour can be calculated and predicted with a fair degree of accuracy. But the electrolytes when subjected to similar calculations, the predicted results were always observed to be less than their effect as observed by actual trial. In case of very dilute solutions, their effect comes close to being even 2, 3, or 4 times greater than as predicted. As an explanation to such behaviour and to explain electrical conductivity of solutions and the facts of electrolysis, Arrhenius advanced the theory of electrolytic dissociation or ionization was proposed.

## Arrhenius Theory

According to this theory, molecules of an electrolyte on going into solution dissociate into ions. The ions are dissimilar as to the elements or elements represented in them and as to the electrical charge which they carry. In each case there are ions that carry positive charge and ions that carry negative charges in such numbers that the two types just compensate each other so that the solution is electrically neutral or balanced. This is illustrated by giving a few chemical dissociation equations



The above reactions are in equilibrium and the dissociation is more complete, the more dilute the solutions are made. At complete dissociation each molecule gives rise to 2, 3 or 4 ions as the case may be and this accounts for the fact that in very dilute solutions the effect on the osmotic pressure, freezing point and boiling point is nearly 2, 3 or 4 times as great as anticipated on the basis of calculations that holds for non electrolytes.

According to the modern views we consider the electric current to be a stream of electrons. The electron is the ultimate unit of electricity its charge is negative its mass is approximately 1/1000 the mass of the hydrogen atom. A positive ion has 1, 2 or 3 positive charges because it lacks 1, 2 or 3 electrons. A negative ion has 1, 2 or 3 negative charges because it contains an excess of 1, 2 or 3 electrons (A limited number of ions with a still larger number positive or negative charges are also there) to understand the difference between atoms and ions more fully e.g. Na (sodium atoms) as compared to Na<sup>+</sup> (sodium ion) it would be necessary to consider the structure of atoms. The atom consists of a positive nucleus surrounded by electrons in such number that the positive nucleus is just satisfied. The atoms of some elements have a strong tendency to lose electrons such elements yield positively charged ions. Other elements have a strong tendency to take on additional electrons such elements yield negatively charged ions.

When an electric current is passed through a solution it is conducted by the migration of ions. The positive ions migrate to the negative electrode and then take on the requisite number of electrons to neutralize the charge. The discharged ion is then an atom (if the ion contained only one element) and is deposited on the electrode (electro-plating) or it may escape as a gas (two atoms combining to form molecule) or it may react with water of the solution, depending upon the chemical nature of the element involved. Similarly negative ions migrate to the positive electrode and there give up the excess electrons.

# The Theory of Electrolytic Dissociation

The theory of electrolyte dissociation explains

1. The abnormal behaviours of electrolytes with respect to osmotic pressure, freezing point and boiling point.
2. The electrical conductivity of solutions
3. The facts of electrolysis.

Ions play an important role part in chemical behaviour. The degree of dissociation can be measured in various ways.

The extent, to which electrolytes deviate from the accepted rules for osmotic pressure, freezing point, and boiling point, can be a basis for computing the degree of dissociation.

Since electrical conductivity is dependent upon ions which can also be used to measure the dissociation.

The equilibrium conditions follow the law of mass action only in a qualitative sense in the case of electrolytes that dissociate very readily, but in strict mathematical sense in the case of electrolytes they dissociate only to a slight extent. Weak acids and bases fall under the latter class, and since we are dealing with such substances in milk it is necessary to consider the law of mass action if we are to develop a full understanding of milk acidity and buffering reaction.

## Ionic Mobility

In the absence of external electrical field, the ions of a solution are in random motion since all directions are equivalent. When an external electrical field is applied although the randomness of motion will basically remain, one of the directions becomes preferred, and more so the higher the potential gradient i.e. the greater drop of potential per cm. The velocity of an ion is the value of this preferential migration towards one of the electrode expressed in cm/s. The potential gradient for the purpose of comparing the ion velocity is 1 volt/cm and these mobilities are known as absolute mobilities. Since the mobilities are taken as proportional to the potential gradient, the absolute mobility is expressed in cm<sup>2</sup>/ volt. The mobilities are very low having values of only 0.0005 – 0.003 cm<sup>2</sup>/ volt. Ionic conductance is the contribution of a given type of ion to the total equivalent conductance in the limit of infinite dilution.

Ionic mobility = Ionic conductance/ 96500

# KOHLRAWSCH LAW AND OSTWALD'S DILUTION LAW AND ELECTRIC CONDUCTANCE OF MILK

It is now evident from the earlier studies that electrolytes dissociate into charged particles known as ions and they play an important role in various chemical reactions. Their behaviour at different dilutions needs to be assessed to understand the degree of ionization and their mobility. The Ostwald's dilution law and Kohlrausch's Law explain the behaviour of these ions and help in calculating their ionic mobility.

## Ostwald's Dilution Law

This law is concerned with the relationship between the dissociation constant and the degree of dissociation of a weak electrolyte (acids or bases). For any weak electrolyte Ostwald's dilution law states that the degree of dissociation is inversely proportional to square root of the molar concentration and is directly proportional to the square root of the volume containing one mole of electrolyte

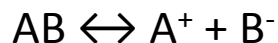
$$K_p = \frac{C(K^+) \cdot C(A^-)}{C(KA)} = \frac{\alpha^2}{(1-\alpha)} \times C_0$$

Where:

- $K_p$  = constant of proteolysis
- $\alpha$  = degree of dissociation (or degree of proteolysis)
- $C(A^-)$  = concentrations of anions
- $C(K^+)$  = concentration of cations
- $C_0$  = overall concentration
- $C(KA)$  = concentration of associated electrolyte

According to Arrhenius theory of electrolyte dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, law of mass action can be applied to such systems also.

Consider a binary electrolyte AB which dissociates into A<sup>+</sup> and B<sup>-</sup> ions and the equilibrium state is represented by the equation:



Initially $t=0$	C	0	0
At equilibrium	C	C $\alpha$	C $\alpha$

So, Dissociation constant may be given as

$$K = [A^+][B^-] = C(1-\alpha)^2 \dots\dots\dots (i)$$

For very weak electrolytes

$$\alpha \ll 1, (1-\alpha) = 1$$

$$\text{Therefore, } K = C\alpha^2 \dots\dots\dots (ii)$$

$$\alpha = \sqrt{K/C}$$

$$\text{Concentration of any ion} = C\alpha = \sqrt{CK}$$

From the equation (ii) it is clear that degree of ionization

### Increase with dilution

Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.



## Limitation of Ostwald's Dilution Law

The law holds good **only for weak electrolytes** and **fails completely** in case of **strong electrolytes**. The value of ' $\alpha$ ' is determined by conductivity measurements by applying the formula  $\Lambda/\Lambda^\infty$ . The value of ' $\alpha$ ' determined at various dilutions of an electrolyte when substituted in Eq. (i) gives a constant value of  $K$  only in the case of weak electrolytes like  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{OH}$ , etc.

the cause of failure of Ostwald's dilution law in case of strong electrolytes is due to the following factors“

- The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and  $\Lambda/\Lambda^\infty$  does not give accurate value of ' $\alpha$ '.
- When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, law of mass action its simple form cannot be strictly applied in case of strong electrolytes.